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**UNIVERSIDAD
DE GRANADA**

TESIS DOCTORAL / PhD. THESIS

Diseño y modelación mediante impresión 3D, de
sistemas híbridos foto-reactor/catalizador para
optimizar reacciones de interés medioambiental

Design and modeling by 3D printing of photo-
reactor/catalyst hybrid systems to optimize reactions
of environmental interest

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hybrid systems to optimize reactions of environmental interest**

por / by

JHON MAURICIO AGUIRRE CORTES

Memoria presentada para aspirar al grado de Doctor
por la Universidad de Granada

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*“I don’t want to believe.
I want to know.”*

Carl Sagan

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Resumen de la Tesis Doctoral

En esta Tesis Doctoral titulada: “Diseño y modelación mediante impresión 3D de sistemas híbridos foto-reactor/catalizador para optimizar reacciones de interés medioambiental” se presentan siete capítulos con la finalidad de mostrar cómo se logra el objetivo general planteado. En resumen, el [capítulo I](#) expone la peligrosidad del problema ambiental actual causado por fármacos presentes en el agua, considerados como contaminantes emergentes, los cuales pueden modificar las instrucciones genéticas en el ADN de animales y humanos debido a la ineficiencia de las tecnologías actuales para su eliminación. Además, se destaca que la implementación de la Industria 4.0, como una herramienta disruptiva en fotocatalisis, abre posibilidades sin precedentes para usar las tecnologías de manufacturación aditiva para imprimir en 3D reactores capaces de enfrentar estos desafíos. Así, el [capítulo II](#) describe los métodos de síntesis de fotocatalizadores efectivos en la degradación de este tipo de contaminantes emergentes y las técnicas de caracterización empleadas para su evaluación.

Los capítulos [III](#), [IV](#) y [V](#) presentan nuestros resultados para la aplicación de la tecnología de luces LED de color azul en la foto-degradación de sulfametoxazol, antibiótico seleccionado como molécula modelo difícil de eliminar mediante las tecnologías tradicionales de tratamiento de agua. Utilizando cantidades comparables y optimizadas de fotocatalizador, esta estrategia permite seleccionar el catalizador en fase polvo que, en dispersión acuosa, presenta el mejor rendimiento entre diferentes semiconductores formados por óxidos binarios de titanio, cerio, zirconio, zinc, así como vanadatos de bismuto, gracias a la obtención de las fases cristalinas deseadas mediante los métodos de síntesis empleados.

El [capítulo VI](#) muestra la optimización de la técnica de aerografía para depositar e inmovilizar la misma cantidad de fotocatalizador, optimizado previamente sobre los canales de microreactores de policarbonato transparente impreso en 3D a usando la técnica de modelado por deposición fundida (FMD, por su sigla en inglés). Posteriormente, utilizando la misma tecnología LED, el mismo volumen y concentración del contaminante, se describe cómo se selecciona la mejor configuración geométrica de canales en la estructura que, en combinación con el caudal de recirculación adecuado, maximiza la eficiencia del fotocatalizador más eficaz, obteniendo así un sistema híbrido e identificando la mejor combinación microreactor - fotocatalizador.

El [Capítulo VII](#) resume las conclusiones generales de las tesis obtenidas de cada uno de los capítulos anteriores:

Finalmente, se presenta a continuación la descripción detallada del contenido de cada capítulo:

[Capítulo I: Introducción y objetivos.](#) Este capítulo, basado en nuestro artículo publicado en “*Applied Materials Today*, [doi: 10.1016/j.apmt.2023.101831](https://doi.org/10.1016/j.apmt.2023.101831)”, revisa las tecnologías actuales de impresión 3D en la ingeniería de foto-reactores químicos, así como sus oportunidades y desafíos. Estas tecnologías posibilitan la creación de reactores y fotocatalizadores en una sola pieza, mejorando la eficiencia de las reacciones químicas al absorber más luz, aumentar la conversión química y optimizar el flujo. Estas innovaciones pueden aplicarse a la eliminación de contaminantes ambientales en general, así como a la purificación de agua potable y el tratamiento de aguas residuales en particular. Al

finalizar el capítulo, se recogen los objetivos de esta Tesis Doctoral, alineados con la revisión bibliográfica y añadiendo ideas originales para su desarrollo.

Capítulo II: Síntesis de materiales, métodos y técnicas de caracterización.

Este capítulo describe la metodología desarrollada para la preparación de fotocatalizadores utilizando semiconductores acoplados formados por óxidos puros y mixtos de titanio, cerio, zinc y zirconio mediante el método de microemulsión inversa, así como la síntesis solvotérmica para obtener fotocatalizadores de vanadato de bismuto. Se detallan los métodos empleados en el diseño e impresión 3D de microreactores. Además, se explican los procedimientos para la fabricación de reactores de foto-degradación destinados a reacciones en lotes y recirculación, utilizados para evaluar el desempeño de los fotocatalizadores en dispersión acuosa ([capítulos III a V](#)) y soportados mediante la técnica de aerografía ([capítulo VI](#)), respectivamente.

Asimismo, se describen los enfoques seguidos para realizar pruebas de foto-degradación utilizando la tecnología de luces LED de color azul con el objetivo de evaluar la eficiencia de los fotocatalizadores, empleando el sulfametoxazol, un antibiótico de alto consumo, como molécula modelo de un contaminante emergente. Finalmente, se explican las técnicas instrumentales utilizadas para la caracterización de los fotocatalizadores, junto con la metodología empleada en las evaluaciones de toxicidad para determinar su capacidad descontaminante en muestras simuladas de agua conteniendo el fármaco.

Capítulo III: Fotocatalizadores basados en BiVO_4 para la degradación de SMX de aguas residuales. Este capítulo analiza la síntesis y desempeño de fotocatalizadores de vanadato de bismuto sintetizados por el método solvotérmico

y calcinados a diferentes temperaturas. El objetivo principal es mostrar el efecto sinérgico entre la temperatura óptima de calcinación, y adicionalmente un dopaje con plata, sobre las propiedades fisicoquímicas del material durante la fotodegradación de un contaminante modelo. Estas pruebas se realizan utilizando nuestro reactor por lotes, adaptado con luces LED azules y el fotocatalizador disperso en soluciones acuosas de sulfametoxazol.

Los resultados muestran que el material dopado, calcinado a 300 °C, logra un 69.7 % de degradación después de 540 minutos bajo condiciones naturales de temperatura y presión a pH neutro. El modelo matemático LHHW, que mejor representa los resultados experimentales, indica que la reacción química superficial es el paso determinante en la velocidad de reacción. Estos resultados sugieren que el efecto combinado de la temperatura óptima de calcinación a 300 °C y el dopaje con 3.5 % de plata favorece la formación de la fase monoclinica de la sal, manteniendo su valor de energía de banda prohibida en 2.47 eV. Asimismo, la presencia de plata a escala nano, como se evidencia por microscopía electrónica, maximiza el transporte electrónico durante la degradación del contaminante y reduce los efectos adversos debidos a la recombinación electrón-hueco. Este fotocatalizador, siendo el más eficiente de este capítulo, se acopla, en el [Capítulo VI](#), a los dispositivos de policarbonato impresos en 3D con diferentes geometrías de canal e implementadas en el tratamiento de soluciones acuosas de SMX.

[Capítulo IV](#): TiX ($\text{X} = \text{Ce}, \text{Zr}, \text{Zn}$) Nanopartículas bimetálicas con actividad fotocatalítica sinérgica en la degradación de sulfametoxazol bajo irradiación de LED azul. Este capítulo describe la síntesis de nanopartículas formadas por óxidos mixtos con propiedades foto-catalíticas, utilizando un método

de microemulsión inversa. Así, nanopartículas binarias de semiconductores acoplados de óxidos de titanio, cerio, zinc y zirconio en proporción másica 1:1 fueron desarrollados con el objetivo de maximizar el rendimiento fotocatalítico en la durante la degradación de sulfametoxazol bajo radiación solar simulada, utilizando un diseño propio de reactor por lotes. Se consiguió la formación exitosa de fases mixtas en todos los casos que contienen titanio; entre ellas, las nanopartículas de titanio/zinc y titanio/zirconio muestran el mejor desempeño en la absorción de luz visible, logrando porcentajes de degradación de 86.6 % y 66 %, respectivamente.

En consecuencia, estos materiales se seleccionaron para estudios adicionales en el [Capítulo V](#), enfocados en la miniaturización del tamaño de partícula en diferentes relaciones másicas de titanio y zirconio. Las nanopartículas de titanio/zinc se utilizan para ser ancladas en los microreactores obtenidos mediante impresión 3D en el [Capítulo VI](#), al comportarse como el material fotoactivo más eficiente; así, estas fases se depositaron mediante aerografía en los microreactores 3D con configuración de canales previamente optimizada, y utilizandose otro fotoreactor LED de diseño propio.

[Capítulo V: Miniaturización de tamaño de semiconductores acoplados de \$\text{TiO}_2\text{-ZrO}_2\$ para desarrollar fotocatalizadores altamente eficientes impulsados por luz visible para la degradación de medicamentos en aguas residuales.](#) Este capítulo recoge los resultados publicados en la revista *Applied Surface Science*, dónde se sintetizaron nanopartículas de óxidos mixtos de titanio y zirconio con diferentes proporciones másicas, permitiendo controlar meticulosamente las dimensiones a nanoescala y sus fases cristalinas. Los resultados de caracterización

muestran que, a bajos contenidos de zirconio, se forman titanatos de zirconio, mientras que, a niveles altos, se desarrolla la fase cúbica de zirconia. Además, un mayor contenido de zirconio resulta en un menor tamaño de partícula y distribuciones de tamaño de poro más estrechas, lo que incrementa la superficie activa de los fotocatalizadores en términos de área superficial aparente.

Este enfoque innovador para preparar fotocatalizadores con 70 % de titanio y 30 % de zirconio activados por luz LED visible logra un rendimiento excepcional de hasta 80.1 % en la degradación de compuestos farmacéuticos presentes en aguas residuales, reduciendo proporcionalmente la toxicidad del agua tratada. Estos resultados se explican por la formación de una fase mixta que involucra titanato de zirconio y anatasa de titanio, observada por XRD y XPS, así como por la alta área de superficie activa, que podría ser responsable de la reducción en los valores de la banda prohibida hasta 2.8 eV.

Capítulo VI: Diseño por impresión 3D de microreactores fotocatalíticamente activos para la remoción de contaminantes emergentes.

Este capítulo describe el diseño y la fabricación de microreactores de policarbonato impresos en 3D en dos configuraciones: uno con múltiples canales rectos en paralelo, otro con los canales curvos o tortuosos, y ambas configuraciones se fabricaron con dos diferentes densidades de canal. Se detalla la metodología para recubrir la superficie interna de los microcanales con los fotocatalizadores más activos desarrollados en los capítulos anteriores, previa activación de sus superficies, y el empleo de una técnica de aerografía. Adicionalmente, siguiendo la misma metodología de las pruebas de fotodegradación anteriores se obtuvieron los resultados correspondientes a la degradación de la misma cantidad del

contaminante mediante sistemas de flujo continuo, usando la misma cantidad de fotocatalizador, pero con la novedad de estar soportado en los microreactores 3D. Se realizaron las pruebas de fotodegradación a dos condiciones de caudal de recirculación diferentes, manteniendo la misma concentración del contaminante, y en definitiva las mismas condiciones experimentales que en los foto-reactores por lotes con fotocatalizadores en dispersión acuosa usando luz LED azul. Tras la optimización del anclaje de las fases activas, siguiente objetivo de este capítulo fue seleccionar el microreactor con la configuración de canales más eficiente, y el caudal que maximiza la degradación del contaminante emergente. Los resultados muestran que los microreactores con menor densidad de canales tortuosos, recubiertos con las nanopartículas mixtas de titanio y zinc descritas en el [capítulo IV](#), logran exitosamente un 61.6 % de degradación de SMX tras 540 minutos de recirculación continua. Estos resultados se relacionan con la formación de un flujo laminar óptimo durante la degradación. Por tanto, nuestro dispositivo funciona como una unidad compacta y proporcionaría las bases tras el escalado correspondiente, de una tecnología alternativa para eliminar contaminantes emergentes de manera continua en plantas de tratamiento de aguas residuales, evitando las tediosas y costosas tareas de recuperación del catalizador cuando se utiliza en reactores por lotes con fotocatalizadores en dispersión acuosa.

La tesis finaliza con el Capítulo VII dónde se recogen, a modo de resumen, las conclusiones principales de este trabajo de investigación.

Some of the results of this work have been already published in the following Journal, and presented in several National Conferences:

List of papers

- Jhon Mauricio Aguirre-Cortés, Álvaro Munguía-Ubierna, Adriana Moral-Rodríguez, A.F. Pérez-Cadenas, F. Carrasco-Marín, E. Bailón-García., *Size-miniaturization of TiO₂-ZrO₂ coupled semiconductors to develop highly efficient visible- driven photocatalysts for the degradation of drugs in wastewater*, Applied Surface Science, 2024. (xx): p. xx.
- Jhon Mauricio Aguirre-Cortés, Adriana Isabel Moral-Rodríguez, Esther Bailón-García, Arantxa Davó-Quñonero, Agustín Francisco Pérez-Cadenas, Francisco Carrasco-Marín., *3D printing in photocatalysis: Methods and capabilities for the improved performance*, Applied Materials Today, 2023. **32**: p. 101831. <https://doi.org/10.1016/j.apmt.2023.101831>

List of conferences

- **Simposio anual de la Unidad de Excelencia de Química**, Granada, España, enero 20, 2023. Nanopartículas de Óxidos de Ce, Zr, Zn y Ti para la Degradación de Contaminantes Emergentes.
- **I Jornada Jóvenes Investigadores del Grupo Español del Carbón**, Baeza; España, noviembre 30 a diciembre 2, 2022. Fotodegradación de sulfametoxazol usando nanopartículas de semiconductores acoplados de ZnTi estimulados con luz azul.
- **I Jornada Jóvenes Investigadores del Grupo Español del Carbón**, Baeza; España, noviembre 30 a diciembre 2, 2022. Fotodegradación de Sulfametoxazol con nanoestructuras BiVO₄, Ag/BiVO₄ y G/BiVO₄ empleando luz visible LED.
- **42ª Reunión Ibérica de Adsorción (42RIA)**, Valencia; España, septiembre 13-16, 2022. Nanopartículas de Óxidos Metálicos como Fotocatalizadores Activos Bajo Luz Visible para la Eliminación de Contaminantes Emergentes de las Aguas.
- **XXXVIII Reunión Bienal de la Sociedad Española de Química**, Granada, España, junio 27-30, 2022. Metal Oxide M₁M₂.Np (M: Ce, Zr, Zn, Ti) Nanoparticles for the Photocatalytic Degradation of Organic Pollutants.
- **XV Reunión del Grupo Español del Carbón**, Granada, España, abril 24-27, 2022. Nanopartículas de Óxidos Metálicos M₁M₂.np (M: Ce, Zr, Zn, Ti) Para La Degradación Fotocatalítica De Contaminantes Orgánicos.

CHAPTER I: INTRODUCTION AND OBJECTIVES

1.1 ABSTRACT

The continuous miniaturization of technologies demands of high precision techniques in the microdevice manufacture, where 3D printing arises as a powerful tool. 3D printing technologies are attracting an uprising interest and their constant development is bringing tremendous advances in the micro- to nano-scale material fabrication. Though 3D printing is yet considered a novel technology, it is being consolidated in the fabrication of chemical reactors with application in the catalytic field. In this scenario, photocatalysis is a type of catalysis activated by light and additional challenges must be tackled for the efficient implementation of 3D printing in photoreactors.

This review article covers the state-of-the-art in the developments of 3D printing technologies in the photochemical reactor engineering and their downsizing opportunities. As reviewed, 3D printing enables to obtain new outperforming photocatalysts and photocatalytic supports of sophisticated configurations and geometries that were before unthinkable for traditional materials manufacture. The reactor and catalyst co-design has a tremendous impact on the photoreaction in terms of light harvesting efficiency, chemical conversion and flow regimes. In summary, the utilization of 3D printing in photocatalysis has a promising outlook given its freedom design in the macro but also in the low scale, the expansion of the family of printable materials and its integration with nanotechnology in the overall material design. Thus, through a precise control over the photocatalyst loading and its distribution, but also the substrates design in terms of volume, tortuosity and downsizing, 3D printing opens up a new horizon in the photocatalytic field.

1.2 INTRODUCTION

1.2.1 Photocatalysis

Photocatalysis consists in the acceleration of a chemical reaction driven by light irradiation to photoactive materials. Namely, semiconductors (SC) typically serve as photoactive materials. A semiconductor is a material with a moderate band gap ($E_g < 3.5$ eV), *i.e.*, the energy difference between the valence band (VB) and the conduction band (CB) in its electronic band structure. The SC exposure to light of sufficient energy leads to the promotion of electrons (e^-) from the valence band (VB) to the conduction band (CB), leaving positive holes (h^+) in the VB. For the photogeneration of the e^-/h^+ pairs, the incident light energy ($h\nu$) must overcome the band gap. Both, e^- and h^+ , can initiate redox processes on the substances present in the surrounding media [1]. For instance, the excited e^- in the CB can get involved in reduction processes, such as in the production of fuels; whilst the positive h^+ in oxidative processes such as in the degradation of pollutants [2].

In aqueous solution, for instance, the excited material particles after photon absorption split H_2O and O_2 molecules adsorbed on their surface forming the reactive hydroxyl ($\bullet OH$) and superoxide ($\bullet O_2^-$) radicals. These radical species initiate a cascade of chemical processes onto the interacting matter that end with the radical annihilation and the production of other stable molecules. As such, photocatalysis is widely used to degrade harmful chemicals, including emerging contaminants, such as cyanotoxins, pesticides, industrial synthetic compounds, pharmaceuticals, hormones, and personal care products, which have been found in drinking water sources and effluent of wastewater treatment plants [3]. Rokesh *et al.* reported an overview of the recent achievements that used solar-assisted

photocatalytic techniques for the complete degradation of antibiotics [1]. In comparison to other processes, photocatalysis outperforms in pollutant removal methods such as adsorption, microbial degradation, ozonolysis, and membrane filtration [4]. However, the photocatalytic efficiency is in general too low owing to the fast e^-/h^+ recombination (in ns) driven by the strong Coulomb effect, which ends up leading to useless heat.

In fact, the typical low efficiencies is the greatest drawback of photocatalysis and a research challenge pending to resolve yet. To achieve the successful outputs, it is necessary to judiciously select and optimize both the photocatalyst and process conditions carefully. The photocatalytic efficiency depends on several variables, such as band edge position, band-gap energy, charge recombination frequency, enhanced charge separation, transfer, and surface-active sites.

From the point of view of the catalytic systems design strategy, a quantitative assessment of the material performance is critical. This needs to be rationalized using standard photoactivity indicators such as the quantum yield (Φ) (**Equation 1-1**) [5,6]. This parameter corresponds to the ratio between the number of converted molecules (N_m) and the photons absorbed (N_{hv}) by the photocatalyst per unit of time, typically ranging between 0.01–0.1 mol Einstein⁻¹ [7].

$$\phi = \frac{dN_m/dt}{dN_{hv}/dt}$$

Equation 1-1. Photochemical quantum yield.

$$\Phi = \frac{k_{tr}S_o\chi\alpha L^2}{D\left(\tanh\left(\frac{d}{2L}\right) + \xi\right)(1-\alpha^2 L^2)}\left(\tanh\left(\frac{d}{2L}\right)\coth\left(\frac{\alpha d}{2}\right) - \alpha L\right)$$

Equation 1-2 Quantum yield applied an elementary process in one-dimensional model.

The photochemical quantum yield is function of time, concentration, light intensity and the energy of the actinic photons. The above involves that Φ is spectral-dependent, which means it is sensitive to the incident wavelength. **Equation 1-2** depicts a mathematical expression for Φ in a one-dimensional elementary process, where k_{tr} is the rate constant of charge carrier trapping; S_o the surface of the active center; D the diffusion coefficient of charge carrier migration; ξ the ratio between the surface and bulk recombination of the charge carriers; d is the size of the photocatalyst crystal (one-dimensional); L the diffusion length of the charge carrier; χ the quantum yield of the internal photoeffects and α the absorption coefficient of the photocatalyst [6,8]. The spectral-dependency of the latter two parameters are responsible for introducing the analogue dependency nature in Φ . Alternatively, the photonic efficiency (ζ) is other parameter typically used to characterize the photoactivity of a material, especially of interest when comparing a series of photocatalysts. It can be straightforwardly calculated as the ratio of the reaction rate (in mol L⁻¹ s⁻¹) and the incident photon flow (Einstein L⁻¹ s⁻¹), the latter being determined by actinometry [9,10].

From an environmental point of view, an ideal photocatalyst should present sufficient energy harvesting efficiency generating a generous carrier concentration to achieve high photoreaction rates with sunlight exposure. Thus, the band gap

should ideally fall within the visible range (380–700 nm), since it is the strongest emission of the solar irradiance spectrum. However, this does not present a trivial solution since a narrow band gap (E_g) benefits the absorption range of the material, but the thermodynamic drive of the redox ability is weakened. On the contrary, materials with large band gaps will be deemed as very active but will present high energy absorption thresholds. Because of that, most of the photoactive materials reported so far are UV-activated (<380 nm), owing to their larger E_g . Unfortunately, these two conditions: (i) wide absorption range and (ii) good redox ability, are incompatible in a single photocatalyst. In this context, material scientists have explored nano-engineered photocatalysts with a precise control of the spatial separation of the e^-/h^+ pairs that enable to maximize both targeted features. In the following Section we review the principal advances in this field of material design.

1.2.2 Environmental Challenge

Global overheating is a phenomenon that occurs when global warming, resulting from the escalation in greenhouse gas emissions, surpasses the natural variability range of the climate [11,12]. This escalation can give rise to diverse climate changes, encompassing temperature elevation, sea level rise, and the intensification of extreme weather events [13,14].

Addressing this issue comprehensively is imperative because of its multifaceted impacts on the environment and human societies. Implementation of mitigation strategies and promotion of international cooperation are pivotal steps toward alleviating the adverse effects of global overheating [15]. The repercussions of global warming extend beyond agriculture and the living environment; they also

affect the industrialization process, affecting the production process and the final output of the economic system [16].

Emerging pollutants can also contribute to global overheating [17], as some of them, such as greenhouse gasses and persistent organic compounds that re-enter ecosystems due to the incomplete effectiveness of current wastewater treatment operations [18], can amplify the warming effect by contributing to temperature rise [19–21]. This escalation may increase their toxicity and impact on human health and the environment. Addressing the management of emerging pollutants is crucial not only for mitigating climate change effects but also for safeguarding human health and ecological well-being [22].

1.3 EMERGING POLLUTANTS

Emerging pollutants are chemical and biological substances that have not traditionally been regarded as contaminants but have begun to appear in the environment, raising concerns because of their potential negative impact on human health and the environment [16–18]. Some examples of these pollutants include the following:

1.3.1 Heavy Metal

Prominent among these are lead, mercury, and arsenic, which act as neurotoxins and can adversely affect the central nervous system in humans [23–26]. For instance, lead can impact the way the brain processes information and may lead to learning and behavioral issues [25,26]. Mercury can cause coordination problems, muscle weakness, and changes in vision [24]. Arsenic may result in

memory and coordination issues [23]. Exposure to these heavy metals can occur through the inhalation of dust or vapors, ingestion of contaminated food or water, or absorption through the skin.

1.3.2 Cyanide

It inhibits the body's cells' ability to use oxygen, leading to cellular death and the failure of vital organs such as the brain and heart. When inhaled, it can quickly impact and cause symptoms such as dizziness, nausea, difficulty breathing, and headaches. Exposure to high doses of cyanide can also result in seizures, loss of consciousness, and cardiorespiratory arrest. If ingested, it can cause symptoms similar to those of inhalation, along with abdominal pain and vomiting. It is extremely toxic and can be hazardous even in small quantities [27,28].

1.3.3 Micro and Nanoplastic

They consist of micro- or nanoscopic particles of plastic, generally less than 5 mm in length, which, when released into the environment, can cause harm to aquatic life and humans if consumed. These particles can be ingested by animals and humans through water and food, and once inside the body, they can cause damage to tissues and organs, releasing toxic chemicals. For instance, small marine animals such as plankton may ingest these particles, which can then be transported through the food chain, reaching larger animals and eventually humans [29–31].

1.3.4 Endocrine Disruptor

These are chemicals that can interfere with the functioning of the endocrine system, which is responsible for producing, releasing, and regulating hormones in

the body. These substances can mimic, block, or modify the action of the body's natural hormones and can have negative health effects. They can be found in a variety of chemicals used in homes and workplaces, such as cleaning products, plastics, beauty products, and personal care items. They may also be in some consumer products, including food and beverages, and can be released into the environment through industry and wastewater treatment [32,33].

1.3.5 Pesticide

These are used to control pests and diseases in crops, gardens, and homes. While they can be beneficial in protecting crops and improving food production, they can also be emerging pollutants due to their potentially negative effects on the environment and human health. This is because they can be absorbed by plants and animals and transported through the food chain, leading to potential long-term health effects [34].

1.3.6 Antibiotics

Antibiotics are medications used to treat infections caused by bacteria [35]. While they can be highly beneficial in preventing and treating infections, they can also be emerging pollutants because of their potentially negative effects on the environment and human health [36]. One of the main concerns associated with antibiotic use is their contribution to antimicrobial resistance, in which bacteria can develop tolerance to these drugs, rendering them ineffective [37]. This can lead to infections that are more challenging to treat and increase the risk of severe complications and death [36]. Antibiotics can be released into the environment through human and animal excretion and may enter water bodies through

wastewater treatment systems [18,38]. Once in the environment, antibiotics can impact other organisms and contribute to antimicrobial resistance. Examples of antibiotics used to treat urinary tract infections include:

Ciprofloxacin: A broad-spectrum antibiotic used to treat urinary tract infections such as cystitis and urethritis [39].

Nitrofurantoin: An antibiotic used to treat urinary tract infections and may be effective against different types of bacteria [40].

Sulfamethoxazole–trimethoprim (SMX-TMP): This combination of two medications is used to treat urinary tract infections and can be effective against various bacteria. Sulfamethoxazole (SMX) is an antibiotic used to treat bacterial infections, particularly in the urinary system. It is a broad-spectrum drug that inhibits the synthesis of nucleic acids in bacteria, thereby preventing their growth and reproduction [41]. Conventional treatment for urinary tract infections in adults typically requires a dose of 40 to 80 mg per kilogram of body weight per day, divided into two or three doses. For the treatment of respiratory infections in adults, the dose is usually 800–1,600 mg per day, which can also be divided into two or three doses [42].

It is crucial to acknowledge that the proportion of an antibiotic metabolized by humans can fluctuate based on the substance and individual patient characteristics [43]. In the case of SMX, approximately 50 % of the dose is excreted unchanged in the urine, while the remainder undergoes hepatic metabolism and is subsequently excreted in the urine as metabolites [43,44].

Quantifying its concentration in the environment poses a challenge because of various influencing factors, including geographic location, usage patterns within the population, and the effectiveness of wastewater treatment systems [45].

It is improbable to detect significant levels of SMX in the air because this medication is predominantly eliminated through urine and feces, with minimal release into the atmosphere. However, measurable concentrations may be identified in soil and water because the substance is released through excretion [46].

Ultimately, the average concentration of SMX in water bodies is contingent on various factors, including the volume of waste discharged into the water, its capacity to dilute and dissolve the substance, and the presence of bacteria and other organisms capable of degradation. Generally, any concentration exceeding 0.1 mg/L is deemed harmful to aquatic life [47].

This antibiotic can undergo environmental degradation facilitated by sunlight and bacteria, leading to the formation of degradation products such as sodium SMX and sulfamethoxazolic acid [48]. Nevertheless, it is noteworthy that these degradation products may exhibit comparable toxicity to aquatic life. The process of environmental degradation is gradual, often taking weeks or months to complete, and involves various mechanisms such as oxidation and biodegradation [32,44,48].

One prevalent degradation pathway involves its reaction with atmospheric oxygen, which then transforms into more stable compounds. In addition, microbial processes contribute to degradation, with soil and water bacteria using antibiotics as sources of carbon and nitrogen [18,45,48,49].

1.3.6.1 *Strategies for Antibiotic Disposal*

For their removal and treatment, global powers have adopted various strategies to eliminate antibiotics from the environment. Some implemented measures include the following:

Regulation of antibiotic production and use: Many countries have adopted regulations to control the production and use of antibiotics, promoting responsible use of these medications. This may include restrictions on the use of certain types of antibiotics in animal production and the use of lower doses of these drugs [11,28].

Wastewater treatment: Many countries have implemented wastewater treatment systems to remove contaminants, including antibiotics, from water. This may involve chemical and biological treatments [16,38,46,50].

Research and development of new technologies: Many countries have funded research to develop new technologies that can enhance the removal of antibiotics from the environment. This may include the exploration and development of more efficient and cost-effective wastewater treatment systems and the adoption of new contaminant removal techniques, such as:

Chemical treatment: This involves adding specific chemicals to the water to oxidize or reduce the antibiotic concentration. However, this method can generate even more toxic residues and is not suitable for all contaminants [51].

Phytoremediation: This involves using plants and microorganisms to absorb and degrade emerging pollutants. It is a natural and ecological method, but it can be slow and not suitable for all contaminants [52,53].

Biological treatment: involves the use of bacteria and other microorganisms. Although it is an effective and ecological method, strict control may be required to avoid the generation of unpleasant odors and other issues [54].

Physical treatment: Physical methods such as filtration, sedimentation, and flocculation are used to separate emerging pollutants from water. It is a fast and effective method, but it can be expensive and may require a significant amount of energy [55].

Oxidation and photocatalysis: With this technology, semiconductors can be used to degrade these compounds, breaking their chemical bonds to convert them into less harmful substances. Photocatalysis, an advanced oxidation process, is an ecological and effective method for removing such contaminants. It enables the rapid and efficient degradation of these compounds without generating toxic residues. In addition, this process can be used continuously and does not require the use of chemicals, making it the most attractive option for treating water bodies [56–59].

1.4 3D PRINTING IN PHOTOCATALYSIS: METHODS AND CAPABILITIES FOR THE IMPROVED PERFORMANCE

The development of three-dimensional (3D) printing as a powerful tool to fabricate functional products with previously unthinkable features has thrived a momentous revolution in materials science. The integration of computer-aided design (CAD) has provided 3D-printing of a versatile nature, which makes it not only appealing in the manufacture industry but also attainable to individual users for household applications, too. Although it has been in the last decade where the

3D-printing potential has been extensively spurred, the first patent dates back to the 1980s [60]. Currently, 3D-printing is a solid technology under unstoppable development with a raising number of emerging application niches and promising outlook in different markets. In fact, in the so-called fourth industrial revolution (4IR or Industry 4.0), 3D printing is an embedded reality and a key structural element in the materials chain manufacture in multiple sectors [60,61]. Namely, some of these include: the automotive [62,63] and aerospace [64] industries, electronic devices fabrication [65], acoustic absorption [66] and thermal insulation [67] elements, key components for the internet of things (IoT) [68,69], as well as educational [70,71], medical [72], robotics [73], biotechnology [74], construction and architecture [75,76], pharmaceutical [77], materials science [78], but also in chemical synthesis [79], electrochemical devices [80] and catalysis [73,79,81,82]. Figure 1.1 illustrates the creative process of custom design and product fabrication in different stages highlighting the opportunities of 3D printing in a variety of fields.

Among other features, 3D printing is a material efficient fabrication technique. Thus, it is also appealing in the road toward the circular economy (CE), concept that refers to an ensemble of principles aiming to the closure of raw materials use and energy loops [83] in pursuit of the environmental well-being along with societal progress [84,85]. The CE premises advocate against traditional linear production methods known as “rapid manufacturing” where a product becomes waste after its usefulness life span. Instead, it is proposed to reduce the volume of material utilization and complexity for the sake of a complete recovery, redesign and remanufacture. 3D printing is attractive since it has almost negligible design constrains and its characteristic layer-by-layer growth to build up functional materials is efficient in terms of waste. This freedom of design permits the

construction of devices with complex architectures and tunable surfaces. Thus, altogether, 3D printing is claimed to be a promising tool in catalysis, with a robust potential in the fabrication of structured catalysts and reactor engineering [86,87].

The current state-of-the-art of 3D printing in catalysis has been recently reviewed by Zhu *et al.* and Lawson *et al.* in [90] and [91], respectively. In this short review, it is our aim to cover the recent achievements of 3D printing-based methods in reactor and catalysis design with emphasis on the opportunities in photocatalysis attaining to flow dynamics. Photocatalysis is a special type of catalysis driven by light activation, which can be ideally accomplished through solar irradiation into active materials. Besides, it involves another loop in the material design since the assemblies should accommodate a light source inside the reaction-ware or enable homogeneous and efficient light irradiation from the outside. Thus, since the photocatalytic approach is more sustainable and cost-effective [92,93] compared to thermally-activated catalysis, photocatalysis is encouraged for the seek of the achievement of CE goals. In photocatalysis, 3D-printing is gaining relevance, though breakthroughs come out slower when compared to conventional catalysts since additional challenges must be tackled. Herein, we briefly present the fundamentals of photocatalytic processes and report the current state, principal achievements, and future perspectives of 3D-printing with application in photocatalysis covering its main principles and challenges. Very recently, Li and co-workers [94] reviewed the 3D printing progresses in photocatalysis, addressing the integral catalyst printing and post modification techniques. It is our aim to compile the main discoveries in this field with special emphasis the effect of the in-printed photocatalytic substrates in the flow dynamics, too, aspect not covered before for these systems.

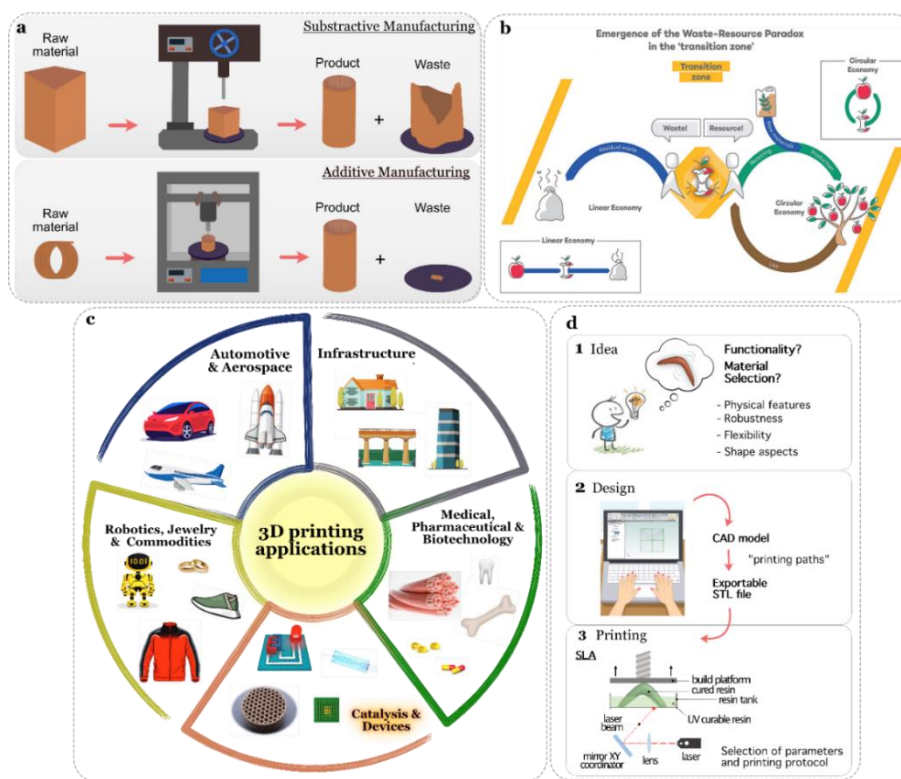


Figure 1.1. (a) Substrate manufacturing (top) vs. additive manufacturing (below) where the amount of residual material left over after the process is significantly lower. Adapted from [88] with permission. (b) Waste-resource paradox in the transition zone from linear to circular economy. Reprinted with permission from [89]. (c) Uses of 3D printing technologies in different fields. (d) Example of idea-to-object process through 3D printing.

1.4.1 Photocatalyst design

Typically, photocatalysts are heterogeneous systems composed of two phases: a finely dispersed active material in the form of nanoparticles and a structural

porous support (or carrier) that provides the mechanical robustness and stability. The support not only has a structural role but also may tune the electronic behavior of the photoactive particles and *vice versa*. The activity, selectivity and the type of residual products to be obtained largely depend on the physicochemical features of photocatalytic material: crystal size, surface area, electronic features and last but not least, the chemical composition [95]. A significant advantage of leaning toward heterogeneous catalysts is the facile catalyst recovery after the reaction cycles. Alternatively, homogeneous photocatalysts such as supramolecular complexes or dissolved light-absorbing photoactive phases in the reactant media have been extensively exploited in this field, too, in photodegradation reactions (solar-photo Fenton) and CO₂ reduction [96–98]. Nonetheless, it is our aim to focus our discussion on the heterogeneous systems, which are economically preferred and present more implementation opportunities in 3D-printing.

Metal oxides [99,100], polymeric carbon nitrides (CNs) [93,101,102], metal-organic frameworks (MOFs) [103,104], and metal sulfides [105] among others are well reported heterogeneous photocatalysts. From the above battery of photoactive materials TiO₂ is by large the most studied semiconductor in photocatalysis owing to its practical convenience in terms of its non-toxicity, remarkable chemical and thermal stability, low cost and high electron transfer capacity [106,107]. Nevertheless, TiO₂ inherently presents limitations, such as high e^-/h^+ recombination rate, moderate visible-range energy harvesting efficiency and low quantum yield so different modification strategies have been developed to achieve an improved performance [3,108,109] (see **Table 1.2**). On the one hand, doping leads to the formation of new energy levels near the CB, which consequently reduces E_g . Broadly speaking, doping is a powerful route to tune the solid-state

properties by introducing small amounts of heterogeneous nuclei in the material lattice structure either by substitution, interstitial accommodation or incorporation [110]. Despite doping is at impurity level (low concentration), it can thrive effects of orders of magnitude in the material conductivity, as well as improve significantly the photocatalytic performance [109,111,112]. Doping induces, among other effects, a crystal lattice distortion and the formation of defects such as oxygen vacancies, which not only affect to the electronic and redox features of the material [113,114] but also serve as strong adsorption sites [114,115] and suppress the recombination of e^-/h^+ pairs.

Alternatively, the deposition of metal nanoparticles opens up more possibilities [116,117]. When nanoparticles are loaded, new active adsorption sites and reactive electronic centers are generated, the redox properties of the semiconductor substrate (or carrier) are tuned and plasmon assistance can be provided [118]. Nanoparticles intrinsically present a high surface-to-volume ratio, which is a property of special interest in catalysis owing to the surface nature of this process. By definition, a nanoparticle refers to a particulate material with at least one dimension in the range between 1 to 100 nm.

The downscaling at such low dimensions confers to matter unique electronic, optical and physicochemical features differing from characteristic ones of the bulk state [119]. The raise of nanotechnology has provided the possibility of manipulating matter at nanometric scales (i.e. < 100 nm) aiming to achieve extraordinary properties [120]. The surge of nanotechnology has additionally brought the discovery of new materials able to acquire other chemical nature by changing the position of atoms or the relationship between them [121]. Ever since

we coined the term “nanotechnology”, a momentous advance in materials science spurred owing to the increased attention for this emerging and fascinating field [120].

In this regard, it should be highlighted the contribution of Norio Taniguchi, who used for the first time the term “nanotechnology” at referring to his work in semiconductors (1974). In 1986, Erick Drexler published a pioneer book relating the surprising capabilities of nanotechnology and forecasted its promising outlook. However, it was Richard Feynman (1965 Physics Nobel awardee), who, for the first time, demonstrated to the scientific community the atomic and molecular scale manipulation of matter [122,123].

A landmark in the consolidation of nanotechnology dates to 1992, when Al Harrington and Tom Maganas synthesized carbon nanotubes by means of chemical vapor deposition process. Today, the role and importance of nanoparticles is well established in photocatalysis, merit of the in-depth fundamental and applied research studies conducted so far. On the nanoparticle surface, oxidative species are generated by the stimulation of incident radiation, which effectively conduct the pollutant elimination.

Additionally, new promising future opportunities are forecasted with the continuous development of nanotechnology and the assessment of the specific surface activity descriptors. As such, it is worth to highlight the unique case of Janus-type nanoparticles, which are bi-faced species either composed of two different materials or the area-selective group functionalization leading to a two-fold chemical nature in one standalone nanoparticle assembly. This confers

extraordinary properties such as self-assembly capacity, multifunctional performance as catalysts and photocatalysts and a precise control in the interface chemistry and defects [56,124].

A different strategy that has attracted much attention in the last decade consists in the fabrication of the so-called heterojunctions. A heterojunction is the result of the juxtaposition of two SCs with different band structures, which confers to the global arrangement unique optoelectronic properties compared from the separate constituents.

There are different types, as summarized in **Figure 1.2**, depending on edge band alignment of the SC pair in contact. The relative band bending and positioning, as well as the resulting interfacial carrier flow is largely affected by the interfacial properties, strongly reliant on the grain sizes, particulate shaping, exposed facets, surface terminations and defects. As depicted from **Figure 1.2a**, heterojunctions trigger the spatial separation of the charge carriers, preventing the e^-/h^+ recombination for the seek of a photoefficiency gain.

Novel nanostructures based on efficient solid solutions of binary or ternary SC combinations of wide and narrow band gaps such as ZnS–CdS, TiO₂–SnO₂ or perovskite-based structures have been proposed [129–131]. These systems can either be used as photocatalysts themselves or participate in conjunction with other SC or solid solution to form complex heterojunctions [132–134]. Therefore, given the remarkable structure-activity relationship and the numerous possibilities yet to unravel, surface nanoengineering in this field is a hot research topic with a promising outlook.

A first classification of heterojunctions distinguishes between type I, type II and type III, referring to the nanocomposite assemblies with straddling gap, staggered gap or broken gap, respectively [134–138]. The resultant optoelectronic properties depend on the relative electron affinities (bottom edge CB) and work functions (top edge VB). Among the above cited heterojunctions, it is the type II (staggered gap), the one that presents a beneficial effect in the photocatalytic activity by suppressing the e^-/h^+ recombination.

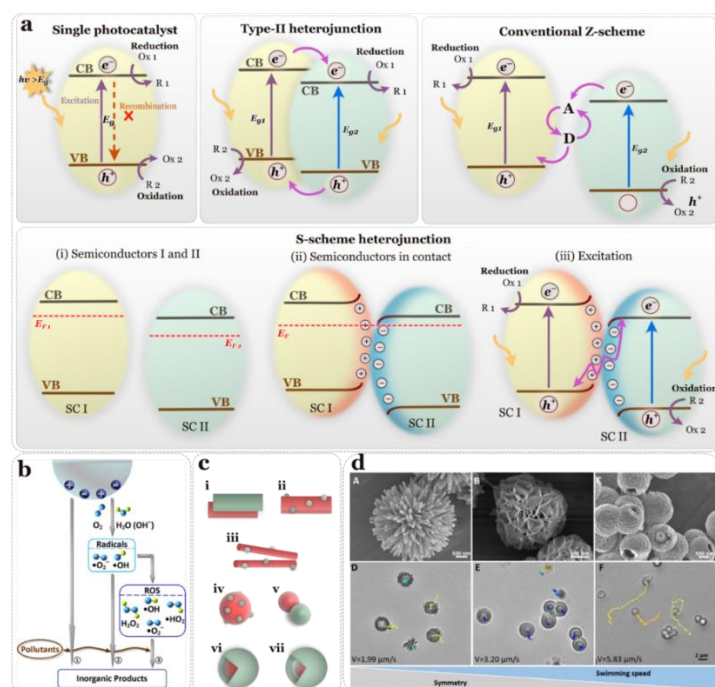


Figure 1.2. (a) Schematic illustration of the electron–hole pairs separation in the case of a single photocatalyst and in different light-responsive heterojunctions. (b) Schematics of 3 plausible mechanisms for the photodegradation of pollutants. Reproduced with permission from [127]. (c) Bi-phase material configurations from left to right: 2D-layered (i); dispersed nanoparticles on surfaces (ii), rods (iii) and

spheres (iv); Janus-type particles (v); core-shell (vi) and yolk-shell (vii) nanoparticles. (d) SEM images of (A) urchin, (B) flower and (C) yolk-shell structured ZnO particles with “swimming” properties. Reprinted with permission from [128].

As such, electrons diffuse through the interface to the SC of lower CB edge (SC1), which is deemed as the reduction photocatalyst. On the contrary, the positive holes will flow to the SC with an upper VB edge (SC2), where the oxidation will take place. $\text{TiO}_2/\text{g-C}_3\text{N}_4$, $\text{BiVO}_4/\text{WO}_3$, $\text{g-C}_3\text{N}_4\text{-WO}_3$ are examples of reported type II heterojunctions, but also in TiO_2 particles composed of anatase/brookite phases in certain ratios this characteristic staggered band bending is expected.

It is important to notice that the improved charge separation occurs at expenses of the reduction of the thermodynamic drive (i.e., redox ability) of the photocatalytic reaction, which penalizes the photoactivity. On the other hand, the asserted model on the charge-transfer of photoelectrons and holes is hard to occur in practice, given the repulsion between transferred charges from one SC to the inherently accumulated in the other. An improvement of type II heterojunction photocatalysts proposed later by Bard in 1979 is the Z-scheme [139].

These systems have the particularity that are constituted by two SC: SC1 and SC2 which are not in physical contact. Instead, SC1 and SC2 are electronically interacting by means of mediator species with redox capacity to act as donor (D) and acceptor (A) of e^- providing a pathway for the charge transfer as the excitation takes place in SC1 and SC2 in a two-step process. Unfortunately, there are application limitations since the conventional Z-scheme is only practicable in liquid phase reactions, where the photocatalysts are immersed in the reactant media with

the A/D pairs. Later, all-solid Z-scheme systems were proposed, attaining the second generation of this type of photocatalysts [140–143] with a higher versatility than conventional Z-scheme counterparts. These systems combine two SCs and an e^- mediator on surface, namely metal nanoparticles such as Au, Ag, Pt, Cu or Bi; or conductive carbon materials such as reduced graphene oxide (RGO). However, the fabrication cost of these materials is high and it is yet hard to control the precise location of the conductor particles, which sometimes function as co-catalysts instead of carrier-transfer shuttles. One of the main drawbacks of these Z-scheme systems, though, is their lower light efficiency since the light absorption by the conductor particles competes with the light harvesting of the photocatalysts [144].

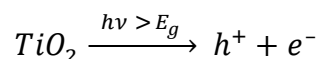
More recently, S-scheme heterojunctions were suggested as a solution to the high recombination rates of the photogenerated e^-/h^+ pairs without losing redox ability [145]. These systems are composed of two SCs with staggered band alignments as in type II heterojunction, but are ruled by a different charge-transfer route. In this case, the different work functions of the SCs leads to an opposite shift in their energy Fermi levels until their alignment upon their contact, which generates an internal electric field. This electric field leads the charge-transfer flow of the photogenerated species the other way around than that of type II, which boosts the photocatalysts redox potential. In some cases, too, the incorporation of cocatalyst in the assembly increases the charge separation and the photoactivity rates. To date, S-scheme photocatalysts have been employed in H_2 production [146], CO_2 reduction [147], bacteria disinfection [148] and pollutant degradation [149], but these systems are still in a very incipient degree of development. Further exploration by means of in situ experiments will disentangle the yet unresolved charge transfer rules and enable to achieve outperforming photocatalyst designs.

1.4.2 Advanced oxidation processes (AOP) and advanced reduction processes (ARP)

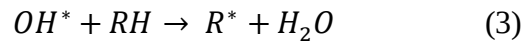
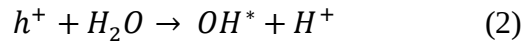
As mentioned above, the most extended heterogeneous photocatalyst in the daily basis is TiO_2 . Despite the availability of other more active materials, titania is by large the most extensively studied photocatalyst in advanced oxidation processes (AOPs) and advanced reduction processes (ARPs) [3]. When e^- and h^+ reach the material surface, they can either initiate direct redox reactions with pollutants, or react with oxygen or water, respectively, forming their corresponding surface radicals.

These surface radicals can initiate redox processes on the pollutants or be detached from the surface as they form the mobile reactive oxygen species (ROS), which also react with the contaminants [127]. On the one hand, AOPs are based on the in-situ production of highly reactive oxidizers such as the superoxide anion radical ($\text{O}_2^{\bullet-}$), the hydroxyl radical ($\text{OH}^{\bullet}$), hydrogen peroxide (H_2O_2), oxygen (O_2), and ozone (O_3).

In contrast, counterpart ARPs aim at the in-situ production of reactive reducers, to reform highly harmful contaminants to less toxic or even chemically simple molecules. The ideal photoreaction process corresponds with the promotion of an electron to the conduction band of the semiconductor, leaving a hole in the valence band [150], according to **Equation 1-3**:

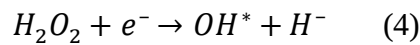
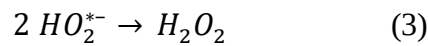
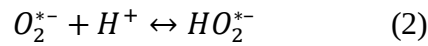
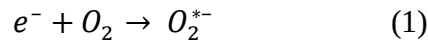


Equation 1-3. Ideal photoreaction process TiO_2 .



Equation 1-4. Hole reaction process.

On the one hand, the hole (h^+) represents a strong oxidant. It can oxidize an organic contaminant (R) or participate in the production of hydroxyl radical (OH^*) by reaction with water (see **Equation 1-4**). On the other hand, the electron (e^-) can act to forming a superoxide radical anion, according to **Equation 1-5**.



Equation 1-5. Potential photoactivated electron reaction process.

Photocatalysis is thus, a powerful tool in water disinfection and air purification and also holds a promising outlook in energy and storage technologies. Namely, photoactive materials with quantum confinement effects, plasmonic materials or the design of 2D photocatalysts has enabled to reach extraordinary optoelectronic properties with relevance in photocatalytic materials [151–155].

Nonetheless, there are yet extensive efforts to be made in terms of material design. Altogether, we have compiled a summary of achievements in photocatalysts design, and a brief description of the physicochemical principles occurring. In the following Sections we review the recent advances in material design by means of 3D-printing.

1.4.3 3D-printing and Additive Manufacturing

The International Organization for Standardization (ISO) and the American Society for Testing and Materials (ASTM) 52900:2015 define additive manufacturing (AM) as “a process of joining materials to make objects from three-dimensional (3D) model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies” [156]. Other authors refer to additive manufacturing as a technology that builds up physical 3D geometries by successive addition of material [157]. In general, the term AM involves a wide variety of manufacturing technologies used in several industries and is classified into seven different groups [158], as shown in **Table 1.1**. Herein we only aim to provide general overview of the current AM processes, since it tangentially overlaps with our review scope. The reader will find further details and deeper explanations of these methods in the literature [5,15,39,44,50]. As depicted, the additive methods can be categorized depending on the type and the physicochemical properties of the material loaded on the cartridges, besides the curation process to obtain the final product. Additionally, new materials are continuously being added to the list as result of the ongoing research and development, expanding the possibilities of 3D printing devices [159,160]. Broadly speaking, a 3D printer consists of a computer numerical control (CNC) instrument capable of moving in the three spatial axes (x, y, z), utilizing an adapted electronic control [161,162]. Due to the high technological interest, cutting-

edge companies and research laboratories have investigated advanced material formulations for light-sensitive 3D printing filaments that use synthetic resins, aiming to achieve a precise curation in pursuit of an eventual high quality [163].

Table 1.1. Classification of additive manufacturing processes and reported catalytic applications (when applicable).

AM Method/Technology	Raw Material	Description	Ref.
Directed energy deposition/ Laser metal deposition (LMD)	Metal wires or powder	A laser or electron beam is used to melt the material as it is being deposited. Complex method that typically requires of a vacuum system and a sealed chamber	[169]
Material jetting/ modeling (MJM)	Multijet Thermoplastic polymers wires or powder	The heated resins are sprayed as tiny drops where desired and instantly cured with UV light. Precise and fast method that enables multi material dispensing through a single print	[170,171]
Sheet lamination/ Laminated object manufacturing (LOM)	Paper, metals, ceramic- based materials	The material is deposited layer by layer and bound together using an adhesive. Low temperature process not suitable for structural applications when mechanical robustness is required	[172–174]
Binder jetting / Binder jetting (BJ)	Alloys, polymers, silica and graphite	This technology uses a binder substance that is alternately injected to put together the powdered material on a dynamic platform	[64,175]
Material extrusion / Fused deposition modeling (FMD) or Fused filament fabrication (FFF)	Thermoplastic polymers (eg.: PLA, ABS, PVA, PET, PETG, PP)	Melt polymers are extruded through a mobile heated nozzle building up the materials layer by layer. Simple set-up with high versatility	[176,177]

Table 1.1 (*Continued*)

Vat Photopolymerization / Stereolithography (SLA), Direct light processing (DLP) or Continuous direct light processing (CDLP)	UV-curable Photopolymer	UV-activated polymerization curates a light-sensitive resin placed in a vat. A light source selectively irradiates the liquid photopolymer and the objects are constructed layer by layer	[178,179]
Powder bed fusion / Electron beam melting (EBM), Selective laser melting (SLM), Selective heat sintering (SHS), and Selective laser sintering (SLS)	Metals, alloys, polymers	Method based on the application of a focused heat source to melt and fuse with high precision the material contained in a powdered bed. This technique does not need structural supports and the possibility to design complex material architectures with outstanding versatility	[180]

One representative method of the above mentioned is the so-called direct-ink-writing (DIW) or robocasting, able to fabricate complex and precise architecture structures in the micron scale. This technique operates like an extrusion-based printing where a liquid-phase, the “ink”, is sprayed out of small nozzles to fabricate layer-by-layer 3D structures. It is also adaptable to obtain desired characteristics as surface area, porosity and tortuosity in specific flow directions [164]. The last step is the ink solidification through gelation, evaporation, or phase change induced by temperature [165].

The fused deposition modeling (FMD) is the simplest and most inexpensive 3D printing technique. This approach takes a filament of a thermoplastic material and gets it extruded through a heated nozzle to build the desired 3D structures.

The 2D cross-sections grow in the perpendicular direction assembling layer by layer the tridimensional object.

In these 3D printers, the extruders comprise a fan, a heat sink and a nozzle where the filament of solid polymer passes through, being liquified at ca. 200 °C and rapidly solidified when deposited [166].

Among these parts, the nozzle is the key component since the quality of the final object is intimately related to its features. Namely, the nozzle inner section determines the diameter of the extruded fiber, and its type can confer the fiber different shapes.

Table 1.2. Highlighted examples of second generation of photocatalysts following different rational approaches.

Photocatalyst/ crystal phase	Modification	Absorption Range	Dopant Effect	Application [Ref.]
TiO ₂ / anatase	N-doping	Visible Spectral Region	Stabilization of intrinsic defects in TiO ₂	Adsorption of O ₂ and H ₂ [8]
CaTiO ₃ Orthorhombic	/ Cu-doping	Visible Light	Charge transfer from the donor levels formed by copper(II)	Water splitting [125]
TiO ₂ 3DOM Anatase (>98 %)	/ Colloidal crystal templating	UV	Improved surface accessibility, diffusion and light penetration	Photodegradation of methylene blue [126]

In the resultant material, the porosity is determined by the interstices left upon between fibers and stacking sheets within the structure [167]. On the other hand, the printing speed affects to the final object quality [166]. It is possible to find

plastic filaments in a rich palette of colors and some of the commercial ones can additionally acquire luminescent properties that glow in the dark.

Today, approximately an 80 % of the printed objects are made of plastic and, regrettably, only a small fraction of it corresponds to recycled plastics [168]. In terms of sustainability, renewable resources such as corn starch, a natural biodegradable polymer, can be used as a feedstock for the synthesis plastic 3D-printing filaments, though this route is yet minor in the market share [83,168].

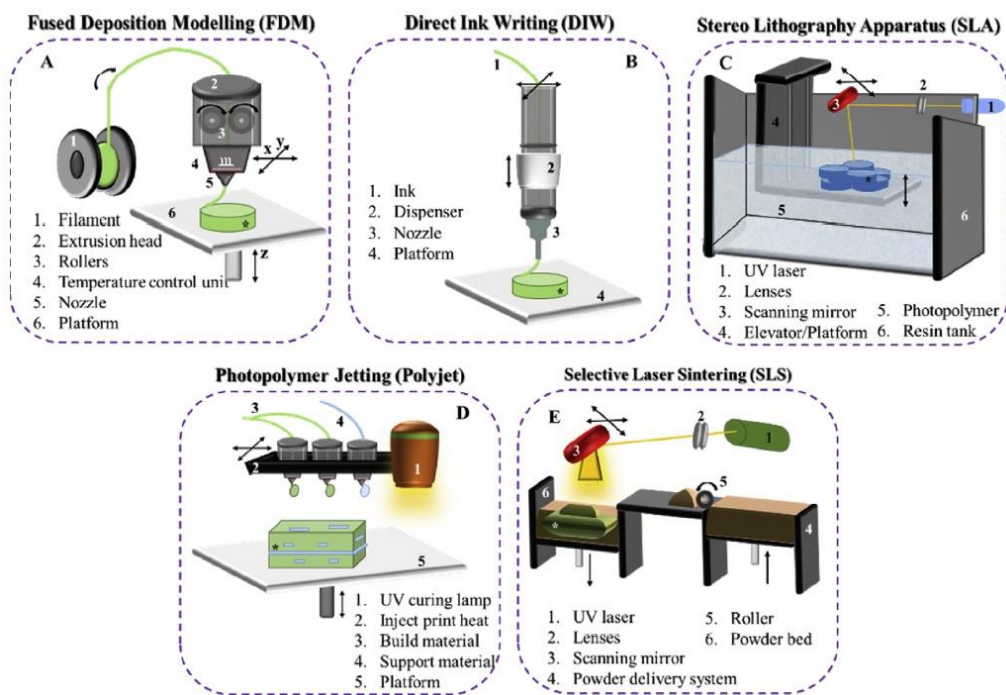


Figure 1.3. 3D Printing techniques most frequently used in device fabrication. Extrusion processes employing (a) FDM and (b) DIW. Photopolymerization methods using (c) SLA and (d) Polyjet. (e) Representative powder bed fusion technology by means of SLS. Reprinted from [88] with publisher permission.

As a complement to **Table 1.1**, **Figure 1.3** shows the Schematic representation of various 3D printing techniques for general uses [88].

1.4.4 3D Printing in Catalysis

The fabrication of catalysts through 3D printing is deemed a revolutionary process with numerous unique possibilities. It allows to build bespoke architectures with beneficial catalytic surface features with improved interaction with the reactant media, based on theoretical models according to specific needs such as size, geometry, and cross-sections type, if applied to reactor design. In terms of catalyst fabrication, 3D printing allows to control wall thicknesses, pore sizes and shapes. The goal usually consists in the increase of surface areas to maximize the access of the active sites involved in the reaction to the reactant molecules [181]. The literature in the design and application of microreactors using 3D printing technologies is yet limited but it is attracting much attention and becoming a research hot topic. Its recentness condition lets us imagine that there is much to discover, and important developments to come as alternative to the currently mature design and application of conventional reactor systems [182–184]. Thus, the outlook of 3D printing is promising for example, in the fabrication of microreactors. Microreactors have tremendous potential in the miniaturization of devices owing to their capacity to operate safely in continuous mode [183] provided their custom-built porous framework and periodic channel array [185].

In relation to the active phases and supports in catalysis and photocatalysis, special attention to the integrity, availability and restitution ability of the active centers throughout the catalytic bed must be paid. Through AM, these crucial aspects can be tackled. Nonetheless, other relevant properties such as the porous

network, mechanical properties, thermal conductivity, dielectric constant, specific surface area, chemical resistance, hardness, and channel tortuosity can additionally be precisely tuned. For instance, focusing on porosity, the International Union of Pure and Applied Chemistry (IUPAC) classified the prefixes *micro*, *meso*, and *macro* to pores sizing less than 2 nm, between 2 and 50 nm, and larger than 50 nm in diameter, respectively. As it is well established, porous materials can be effective at solving environmental, energy, health, and transport problems [158].

The successful porous materials fabrication aiming to obtain functional components may also require of efficient coating techniques to ensure the desired material properties. Namely, mechanical strength, specific surface area, thermal shock resistance, corrosion resistance, pore size, distribution, and shape (open or closed; spherical, elongated, or random), and their interconnectivity.

Recent studies have pinpointed that the deployment of catalytic systems fabricated by means of 3D printing technology is an emerging field with huge potential. As such, AM is deemed to play a relevant role in the miniaturization of reactor sizes besides offering the possibility of generating specific surface species claimed to be active [72].

To date, studies reporting improvements in catalysts and catalytic supports with the target of pollutant removal can be found in literature [161,186,187]. It is now possible to imagine new alternatives that combine the design and application of reaction systems aiming a faster prototyping and testing cycle [82,188]. With these considerations in mind, a yet missing piece is the elucidation of the reaction mechanisms occurring in these catalytic processes, since this information is the pillar knowledge to conceptualize into adapted designs.

From the point of view of the chemical reactor design, AM offers many opportunities with polymeric materials, metals, or metallic alloys [162,185,188,189]. This straightforward strategy for constructing advanced chemical reactors differs from the typical and consolidated processes in the reactor manufacture. Inherently, the idealization of the design and assembly in the conventional manufacture can be complex steps, while on the contrary, the construction stage in AM may only require the fabrication of a single piece to be joint to other components and accessories for its start-up [82,182,190]. On the other hand, the set of unit operations involved in the reaction stage and reagents mixing are pivotal for the optimal evolution of the reaction rate. These aspects are also of particular relevance in the conventional design rules [191]. Currently, different options for the scientific and engineering design besides start-up of reactors are being reported, some of them are of as small as the size of a mobile phone or even on a micro-scale [75,192,193]. Combining knowledge of CAD and AM, geometries can be tailored to the physicochemical needs of each specific process, reaching high conversions and selectivities adapted to on-demand [194]. These advantages arise from the reduced dependence on conventional structures with 3D printing able to make almost any idea real. Through 3D printing it is possible to obtain complex structures capable of combining process operations in an indivisible joint-less piece, thus, intrinsically free of leak risks, which is high demanded feature for a chemical reactor in terms of safety [191].

An additional substantial benefit is that the scaling of the process in AM is rationally simple, which minimizes the process costs while keeping the same basic design rules in the production at both the small and industrial sizes. An encouraging note to add is that AM production volumes could be increased ever since it has been

possible to joint multiple batch reaction units in one only system running in parallel, which needs reduced space in their installation [188].

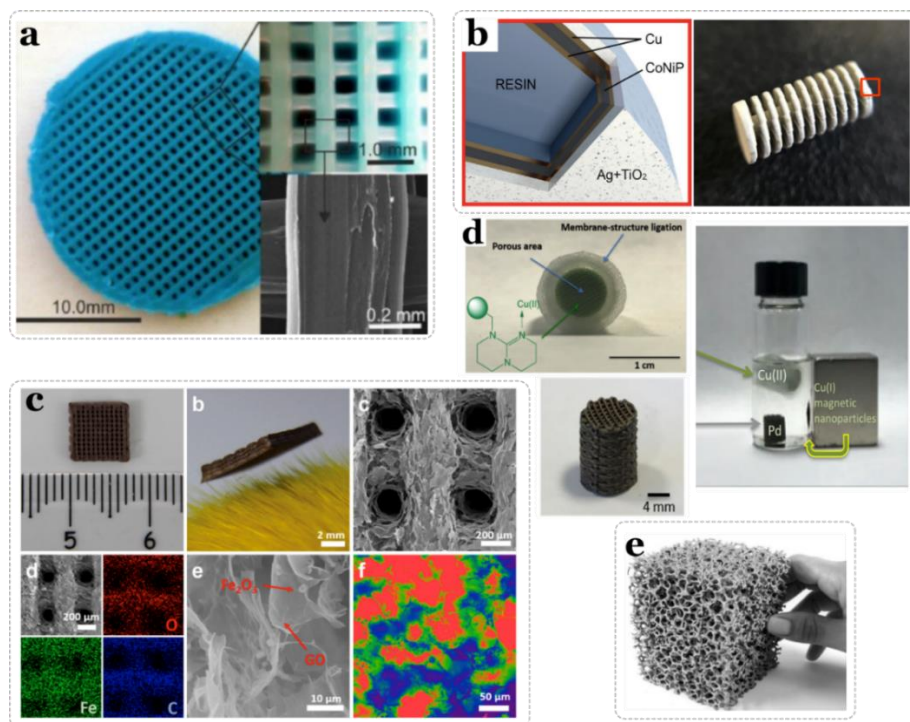


Figure 1.4. (a) 3D printed ABS filter reprinted from [198]. (b) Internal structure (top) and final appearance (below) of a 3D printed photoactive/antimicrobial microdevice. Reprinted from [199]. (c) 3D printed photoactive composite aerogel of extraordinary lightness and SEM/EDX/ confocal laser microscope images corresponding to its inner structure. Reprinted from [200]. (d) Three-fold catalyst (Cu^{2+} , Cu^+ , Pd^0) composed of a porous capsule with immobilized $\text{Cu}(\text{II})$ species and a Pd^0 -functionalized SiO_2 monolith. Adapted with permission from [201] (e) Ti-6Al-4V open cellular foam 3D-printed prototype. Reprinted with permission from [197].

On the other hand, AM may enhance to reach optimal values in the reactant mixture flow and reaction rate. The possibility of printing in 3D enables to modulate the turbulence and intensity of agitation of the chemical reaction to be complete with the design of channels based on complex internal geometries and surface roughness elements adjusted to the desired conversion needs. In conventional continuous flow reactors, the acquisition of these characteristics is highly complex or even impossible [195,196].

As another example, Murr and co-workers demonstrated the possibility of creating an unprecedented structure with special chemical feature [197]. The authors successfully fabricated complex, multifunctional Ti-6Al-4V and other alloy foams through the electron beam melting (EBM) process. Finally, as a proof of concept, Kitson and co-workers [188] provided a protocol to target design strategies for the fabrication of a 3D-printed sealed reactor versatile to catalyze a multistep organic synthesis where the reagents, catalysts, and purification units are integrated in one device (see **Figure 1.4**).

Summarizing, 3D printing coupled with CAD for the manufacture of catalytic materials at a miniature scale presents a challenge worth to address. It brings new ways in the full picture of all chemistry areas and enables to tailor reaction systems to the user demands with increasingly smaller dimensions [1,73,161,202].

Materials science plays an important role in this new approach, for instance, in the catalysis area and the catalytic supports, while the nanometric scale definition opens-up an horizon of new opportunities. In the field of photocatalysis, semiconductor materials with photoactivity have been obtained with digitally adjustable architectures through 3D printing [1,2,93]. It is our aim to compile and

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1.4.5 Reactor design

1.4.5.1 General Considerations

A chemical reactor is the physical container of a chemical process and should host the catalyst in a convenient configuration. Its design has a pivotal effect in the

operation of the reaction unit, where the costs minimization aiming the highest yields while meeting the most stringent safety requirements is prioritized. The mass balance in a chemical reactor follows the **Equation 1-6** [203], which serves as a descriptor to carry out the reactor design:

$$\text{In} + \text{Made} = \text{Accumulation} + \text{Out}$$

Equation 1-6. Mass balance in chemical reactor.

For instance, for a simple reaction such, as $A \rightarrow B$, the reaction rate is defined by the speed that B species is created, equal to the A consumption velocity (r_A). The term ‘Made’, is defined by the product $r_A V$, where V is the volume of the reactor.

Among different reactor designs, the most popular are those known as “plug flow” reactors, continuously stirred tank reactors (CSTR), or batch-type reactors. From the technical point of view, the judicious selection of the reactor technology for a particular process chemistry should be based upon theoretical-empirical knowledge at different levels (molecular, particulate, reactor and process scale). However, it is yet challenging to predict the energy and mass efficiency of the overall process, as well as its eventual environmental impacts [182].

For instance, problems on transport phenomena may arise when using monolithic catalysts in discontinuous liquid-phase processes, which tend to yield limited reaction rates. Nonetheless, monolithic substrates present other significant advantages when compared to fixed-bed reactors such as high heat and mass transport rates, low pressure drop and temperature gradients besides facile scale up. In monolith fabrication, 3D printing has meant a revolution that opened up new

possibilities in the control of micro and macroscopic features of the heterogeneous catalysts, enabling to improve their performance in a wider range of applications [81].

Over the last 40 years, research focused on photocatalytic technology has received attention and significant advances have been presented, extending the limits of its potential uses. As a result, a broad battery of photoactive catalysts have been reported with a demonstrated improved photocatalytic efficiency, stability, visible light activation, and selectivity. A more active surface improves the performance in terms of both the quality of the product and the critical environmental footprint derived [190,204].

However, despite the large advances in material design and surface modification, the counterpart reactor engineering has not progressed as fast, so that the challenge of adapting new designs in both the photocatalyst and the photoreactor remain yet unresolved. Namely, some reactor-design features sought to improve the overall performance are the effective irradiation, efficient catalyst exposure, and the minimization of mass transfer in novel structures, respectively [205]. In many cases, the design of catalytic systems converges on the design of the photoactive material, where nanoparticles show huge opportunities [206,207].

In a photocatalyst/reactor system, it is essential to consider the intrinsic parameters of the reactor. For instance, geometry, capacity, radiation source location, and the way the light is distributed across the reaction zone [10,191,208]. All these aspects are determining to approve or disapprove of a specific reactionware design.

Table 1.3. Conventional configuration in photoreaction systems.

Reactor Type/Basic Features	Pros	Cons	3D Printing Improvement [Ref.]
Slurry / Catalyst in suspension, intense mixing needed	High surface exposure; limited mass transfer if efficient mixing is achieved	Scale-up issues; inefficient light penetration due to scattering or opaque solutions; recovery of catalyst powder	3D printable photon concentrator designed to operate under visible light (LED) for the determination of the photocatalytic and photo-Fenton activity [211]
Fixed bed / Catalyst immobilized over beads	Immobilized catalyst; no recovery issues	Inefficient light penetration	3D printed photoreactors to understand the robustness, scalability, and practicality of immobilized g-C ₃ N ₄ for solar water treatment [92]
Microreactors, capillary reactors / Catalyst immobilized in microchannels exposed to light	Good catalyst exposure to light and reactants; limited size of the channels and so limited mass transfer issues	Needed high surface to volume ratio	PDMS photocatalytic microreactors with the photocatalyst homogeneously distributed and firmly adhered at the silicone channel walls during curing step [211]
Monoliths / Catalyst immobilized in microchannels of a monolith exposed to light	Good surface to volume ratio; effective irradiation with LED or optical fibers in each channel	Need of complex arrangement for irradiation; complex coating procedures	Successful fabrication through 3D-printed Au/TiO ₂ monoliths with enhanced performance in the photoproduction of hydrogen [212]
Twin reactor / Separate compartments for different reactions	Separate production of different products	Applications limited by needs of transport through a membrane; rates possibly limited for the same reason	

Table 1.3 (Continued)

Single or multitubular with parabolic (CPC) / collection concentration of radiation on the tubes	Enhanced irradiation; relatively compact and simple design for multitubular systems	Sizing dependent on reaction rate	Rapid and accurate for the combination of 3D printing and fractal photobioreactor. Opens new routes for the process intensification in the photosynthetic cultivation process [213]
Spinning disc / Solution/suspension spread in thin film irradiated on top	Short optical path; limited mass transfer	Possible irregular flow shape; mechanically more complex due to moving parts	
Stacked frame, rotating impeller / Catalyst immobilized over rotating blades	Improved mass transfer	Mechanically more complex due to moving parts; irradiation spreading and averaging over the surface	
Water bell, falling Film / Solution/suspension recirculated in thin layers flowing	Improved mass transfer; effective irradiation	Need of high recirculation; intrinsic unsteady operation	

Compared with conventional technologies for the construction of chemical reactors, based on the transformation of large material pieces and welded joints, 3D printing technology has already demonstrated the potential to obtain successful results in reactor fabrication while gaining large process simplicity. The addition of different materials follows a layer by layer growth until the desired structure is built in the size, and shape with the physical, chemical and mechanical characteristics requested in the final simple or intricate configuration [7].

Thus, a promising alternative to traditional methodologies for the design and construction of chemical reactors relies on the process intensification due to the possibility to achieve advanced and complex structures integrating conventional and 3D-printed designs through additive manufacturing. The traditional methods for designing both catalysts and reactors have advantages compared to 3D printing technology. For instance, with regard to catalysts conformation, pelletization and granulation are the fastest methods. However, they confer poor dynamic properties, which deems their use unattractive industrially. From the point of view of the reactor, traditional manufacturing, such as extrusion, limits the fabrication possibilities to simple structures. In contrast, 3D printing enables the design of catalysts and reactors with novel attributes that facilitate mass transfer, reduce pressure drops, and increase reactivity among these physicochemical parameters such as channel size, cell density, wall thickness, active site density, hierarchical porosity and mechanical strength [7]. A summary of the different possible configurations for conventional photoreactors is reported in **Table 1.3** where some examples and improvements when is used for 3D printing are cited [150,209].

1.4.6 Photoreactor Considerations

The ‘slurry’-type is the most extended photoreactor configuration, where both catalyst and the reactant mixture containing the pollutants are co-suspended in the reaction medium. In this reactor arrangement, the light irradiation is either supplied from the outer reactor surface or sourced inside with immersed lamps. This reactor type has the advantage of exploiting the intrinsic activity of the catalytic material and maximizing the site exposure to light and the contaminants. However, a portion of the photocatalyst is shadowed by the absorption and light scattering by the

suspended solid itself as consequence of the particle concentration. To solve this drawback, the use of photomicroreactors arises as an alternative, where the catalyst is coherently immobilized on a structured substrate. This strategy not only facilitates the catalyst recovery after the reaction is but also enables a more efficient light irradiation through the clear particulate-free solution. However, these advances are achieved at expenses of reducing active site exposure when compared to the conventional ‘slurry’ reactor [150]. **Table 1.4** compiles the main reactor features to be considered throughout the design step of a photoreactor and some updated examples with the use of 3D printing are depicted.

Table 1.4. Prominent features on photoreactor.

No.	Feature	3D Printing application [Ref.]
1	High surface exposure of the photocatalyst per unit volume	Fractal-like photobioreactors designed and manufactured via 3D printing technology to determine the effect of the cultivation process of chlorella [213]
2	Mixing and turbulence regime to ensure fast mass transfer of the reactants and efficient suspension of the catalyst	Modular, scalable and versatile honeycomb-type polyamide photo(electro)chemical reactor [214]
3	Transparency of the solution/suspension to radiation	Fabrication of custom-built architectures with improved optical properties [208,215]
4	Effective and continuous oxygen supply for oxidation reactions	Online measurement of the oxygen concentration in the reactor to monitor the progress of reactions in real-time [216].

In complement, **Table 1.5** present some application examples of 3D printing technology in catalysis.

1.4.7 Microreactors

The forecasted continuous downscaling of technology requires of the gradual miniaturization of devices, which is a major material science challenge. In this context, a microreactor comprises all the functional elements of conventional counterparts but with reduced physical dimensions to yet carry out the precise operation units. Such downsizing approach may include several assemblies using separators and reactors modularized toward the process intensification [217]. Small-scale reactors –microreactors– open-up opportunities for the chemical processes design. The system confinement into the milli, micro, and nano-scale, leads to modifications of the reaction conditions and output product distribution as result of the increased heat and mass transfer rates per volume unit when compared to conventional chemical reactors [218]. Additionally, microreactors increase residence time and mixing in the case of continuous flow configurations, besides functioning in safer operation conditions [219] and reducing the overall plant capital cost significantly [217].

The term "microreactor" was initially coined to refer to a small tubular device with application in catalytic reactions [220] assembled with conventional techniques in milli-micro–nanotechnology of precision engineering [217]. The internal structure of microreactors consists of single or multiple sub-millimeter channels where the reactant fluid is continuously flowing and the chemical transformations occur [220]. The small-scale reactors traditionally consist of a parallelly arranged system of channels connected with an inlet and an outlet. The channels (catalytic zone) are aligned in vertical arrays and packed or coated with the catalytically active phase. This assembly reduces the reactor volume without

modifying the overall productivity, and it is thereby, a simplified scale-down prototype [217,221]. Miniaturization is a crucial aspect for many technological applications in chemical areas. The use of microreactors is a potential solution for the intensification processes and this small-scale technology has several advantages when applied to conventional continuous chemical processes.

A more precise control of the process is possible in microreactors owing to their larger portability and manageability, diminished and simpler design considerations, and reduced working volume. Furthermore, it is possible to modulate other characteristics, such as the surface-to-volume ratio, which is paramount, since it determines the effectiveness of the heat and mass transfer throughout the system [195,222]. Typically, microreactors present channel sections ranging from 10 to 500 μm . In this micro-region, diffusion limitations are lowered while heat transfer coefficients are enhanced up to $25 \text{ kW m}^{-2} \text{ K}^{-1}$ [217,222].

Additive manufacturing brings numerous opportunities for the creation of microreactors with original and novel alternative channel configurations, thus a disruptive technology compared to conventional fabricating techniques [223] (see **Figure 1.5**). To date, several prototypes of multichannel microreactors fabricated by additive manufacturing have been reported. We tentatively may highlight the work of Anderson and co-workers [224], who successfully fabricated microreactors structured by a different number of channels: from single channel to 8 channels of $3 \times 1.5 \text{ mm}$ by 3D printing.

Their methodology comprised the use of inkjet deposition technique with a photopolymerizable material, reproducing the designs created with McNeel Rhinoceros or PTC Creo software [224]. This simple design enabled the efficient

and homogeneous spread of the inlet stream in each well/insert. In the use of 3D-printing for the fabrication of microreactors, we should differentiate two approaches: (i) light-induced process and photo-curable materials, and (ii) heat-induced process and thermo-softening resins and metals [223], with especial mention to SLA, DLP, and MJM techniques. The rational choice within the latter group of techniques is rather based on the desired resolution of the final product also owing to differences in the laser beam spot sizes and the employed resin absorption spectra [225].

Cabrera and co-authors [195] investigated the photocatalytic performance of microreactors fabricated by 3D printing for different applications (please see **Table 1.6**). In their pioneer work, the authors used a twofold system that combined a filament with the photoactive material through an economical and rapid process of printing the reactor microchannels while the design was devised by means of SolidWorks software [195].

The full microreactor assembly was made of ABS polymer and consisted of three main parts: (i) the main body frame; (ii) a serpentine-shaped channel with a trapezoidal section ($1.5 \times 1 \times 0.5$ mm) of ca. 0.3 cm^3 volume, (ii) a top cover with a transparent PDMS window. The serpentine channel located in the main body was homogeneously coated with the Cu–TiO₂ photocatalyst by means of drop-casting to achieve a sufficient coating density of ca. $0.85 \text{ mg} \cdot \text{cm}^{-2}$.

Finally, the 3D-printed reactionware was tested in the photooxidation and photoreduction of the probe molecules: methylene blue (MB) and 4-nitrophenol (4NP), respectively, under LED irradiation. In the next Section, we review more examples in detail.

1.4.8 3D Printing applied to Reactor and Microreactor Engineering

1.4.8.1 General Considerations

In the last recent years, 3D-printed catalysts have been prepared combining additive manufacturing to achieve specific structures with the suitable chemical modifications to acquire the desired surface features. For instance, Wang *et al.* [76] prepared nickel and copper coated microlattices, hollow balls, and even metallic Eiffel towers for the first time in a programmable way without any specialized, expensive processes nor instruments. These authors integrated an initiator into the 3D acrylate-based ink, which was followed by surface modification and subsequent coating to generate the complex metallic architectures.

On the contrary, AM applied for catalysts fabrication based on ceramic materials suppose a greater challenge to tackle that some groups have addressed. Díaz-Marta *et al.* [81] prepared heterogeneous palladium and copper-based catalysts upon functionalized 3D-printed monolithic silica supports. The catalytic activity of the hybrid material was successfully tested in the Suzuki, Stille, and Sonogashira-type reactions. Li and co-workers [93] fabricated active catalysts based on iron-based metal-organic frameworks (Fe-MOF) grafted to 3D-printed polymeric surfaces for the photodegradation of ciprofloxacin, a common antibiotic. In a different study, Qiao *et al.* [79] fabricated a microreactor of reduced graphene oxide by means of the 3D-printing of a graphene oxide (GO) slurry. This device was used as a synthesis microreactor to prepare Ru nanoparticles embedded in the mesoporous carbon material CMK-3. The resulting product of synthesis Ru@CMK-3 was tested and confirmed as an active cathode in Li-CO₂ batteries. The bespoke shaping of the 3D-printed reactor provides the platform for the

synthesis of this type of nanocatalysts inducing a heat shock over Ru nanoparticles. Thus, the obtained Ru nanoparticles presented uniform sizes of 2 nm in average and remained bound to the carbonaceous substrate after a transient heating at ca. 1500K for 500 ms. This study presented a proof-of-concept where a 3D-printed microreactor was capable to synthesize with reproducibility nanomaterials with potential application in energy storage and catalysis. Furthermore, this work demonstrated the possibility of realizing a trans-scale modulation through AM, involving a micro- but also a macroscale control, concept introduced by Gu [226].

In this context, Wei *et al.* [82] pointed that the chemical properties and catalytic behavior of 3D-printed nanomaterials are too few times considered in a technical discussion. Instead, these discussions center in the investigation the use of metal-3D printing to fabricate materials with a twofold potential as chemical reactors and catalysts (a self-catalytic reactor, SCR) with the aim to enable integration in the design of chemical synthesis and 3D printing methodologies. However, to date, the research of chemical catalysts and reactors is still in two divergent directions, being necessary to develop methods that unify these two areas where 3D printing simultaneously with the catalyst material is expected to reduce technical inconvenience. To test this hypothesis, authors used CAD, (Rhinoceros 5.0), to create the virtual models and then realized them via SLS technology. Three metal-based reactor systems (Fe-SCR, Co-SCR, and Ni-SCR) were fabricated and proven to be effective in the direct conversion of CO, CO₂, and CH₄ molecules even in hindered temperature and pressure conditions. Thus, this original work demonstrated that the facile integration of reactors and catalysts is possible, whilst opened the horizon for new designs in future catalytic systems.

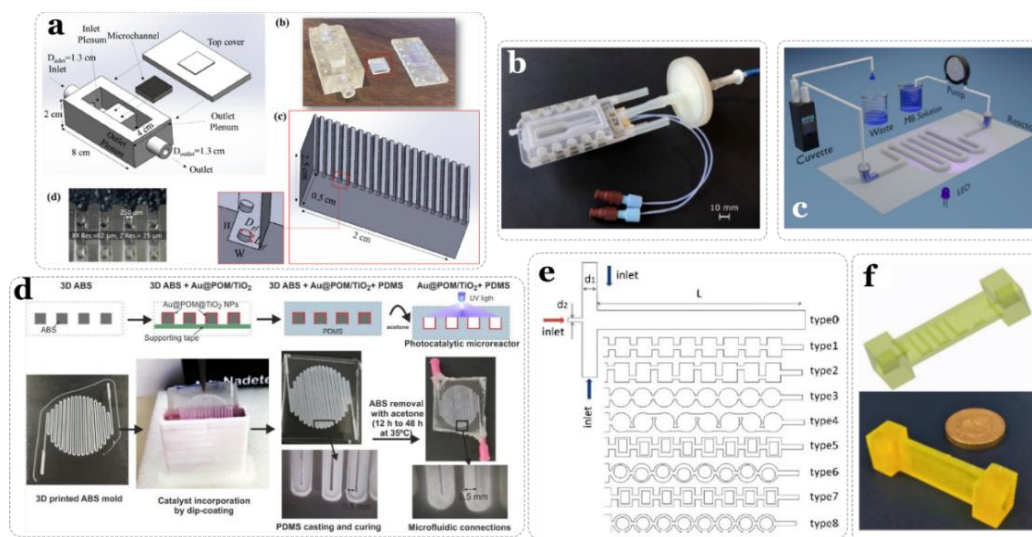


Figure 1.5. (a) 3D-printed microreactor assembly with tunable heat and mass transfer properties built upon a microchannel block with micro-pin fins of different geometrical specifications. Reprinted from [227]. (b) Image of fully assembled 3D- μ BCR with fluid connectors, tubing, and inlet filter [191]. (c) Illustration of a single pass flow reactor comprised of a 1 mm thick PLA gutter lined with a 0.5 mm thick coating of 5 wt.% TiO_2/PLA , sealed onto PLA film; the 'PLA window'. Reprinted from [228]. (d) Fabrication protocol of silicone microreactors with integrated photocatalysts by means of the so-called "scaffold-removal" method. Reprinted from [211]. (e) Schematic of various novel semi-T-shaped microreactors configurations. Adapted with permission from [196]. (f) 3D printed photoreactor (01 cm³) built upon St-BTZ incorporated polypropylene. CAD image of design (top) and real image of the 3D-printed object. Reprinted with permission [229].

Symes and colleagues [184] reported 3D-printed systems with application as chemical reactors but also as spectroelectrochemistry devices for in situ analyses.

Digital technology used in this coupled system enables to design and manufacture efficient reaction vessels, exploring the configurations and relationships between the design of the device and the chemical reaction yields. Eventually, these authors could develop architectures to form and crystallize two previously unreported crystals inorganic nanoclusters. Namely, the new route synthesis for phenanthridine, an organic heterocyclic compound, and spectroscopy measurements in-situ could demonstrate the relationship between the potential for ‘printing-in’ catalysts into the structure of the reaction system. This test could further prove the ease and relationship of reactor design and production of new and conventional chemical products over traditional techniques. As repeatedly stated in above, 3D-printed reaction systems give almost limitless control opening the scope for creativity than traditional reaction systems and this technology is deemed to be one of the pillars of the 4IR [116].

In a different work, Parra-Cabrera and co-workers [190], illustrated the potential of 3D printing technology aided by computational modeling as digital tools in the design of all-purpose reactors and also structured functional catalysts. These authors reported a novel in-print fabrication procedure with technological interest and their discussion additionally brought up the point of the knowledge gap that yet exists in terms of chemical functionalities and catalytic activity in chemical engineering tackled through AM.

Machado and co-workers [230] used for the first time a mixture of poly(butylene adipate-co-terephthalate) and LPA as printing substrate for FDM, being the latter a biodegradable polyester regularly used in desktop 3D printers. In the output product, the porosity referred to spaces between adjacent in-printed

threads and the authors observe microstructural anisotropy within the same layer. The apparent porosity of the printed components was roughly determined by Archimedes' method [231]. To do so, it is necessary to determine the actual mass (dry mass: W_d), followed by the mass when the material is in ethanol (wet mass: W_w). Thus, the apparent fraction porosity (P_a) of the material was determined by **Equation 1-7** to **Equation 1-9**.

$$\rho_s = \frac{W_d \rho_e}{(W_d - W_w)}$$

Equation 1-7. The density of the sample.

$$V_p = V_f - \frac{W_d}{\rho_e}$$

Equation 1-8. The volume of pores.

Where ρ_s , is the density of the sample, ρ_e , corresponds to the ethanol density, V_p , V_t and V_f , are volume of pores, total and final volume, respectively. Besides, Young's modulus, maximum strength and elongation, and other flexural properties of the printed parts were assessed following ASTM D 790 (2016) standards using a universal testing machine [230].

$$P_a = V_t - \frac{V_p}{V_t}$$

Equation 1-9. Fraction Apparent Porosity.

Another contribution worth to highlight was authored by Aubert *et al.* in [232], who pondered the high potential and open possibilities of converging 3D printing

techniques and nanomaterials. The authors managed to implement precise characteristics in 3D printed objects with a localized deposition of a guest material within a host matrix, generating a complex 3D-printed composite. Nonetheless, another twist in 3D-printing technology is 4D printing, standing for height, width, thickness and, additionally, time. The difference between 3D and 4D printing is the added forth dimension, that corresponds to the dynamic material response upon an external stimulus. This concept has been explored in literature [176,233,234], where geometrical or optical changes are observed in the material when subjected to temperature or pH variations in the surrounding media. When it comes to 4D printing, a representative example of material design was reported by Carbonell and co-workers, [235] who through surface reactions activated 4D polymeric nano-printed platforms. The authors constructed adaptable micropatterns in a microfluidic photoreactor in a new concept disruptive with the research of materials assembly able to create ordered and sub-micron polymer patterns.

In a different study, Mie *et al.* [178] studied by means of UV–Vis DRS the photocatalytic performance of MoS₂ on 3D-printed supports with square array patterns for the photodegradation of Rhodamine B. The MoS₂ catalyst was loaded on the surface of in-printed support by means of a hydrothermal method while the ceramic support material was fabricated by means of SLA method using a UV-curable resin. Finally, the authors conclude that 3D printing effectively yields a catalytic outperformance owing to the support enhanced porosity and this greater surface exposure maximizes the active site availability. Thus, this is another example where 3D printing technology enabled to prepare a complicated but precise structure, adapted with efficiency to control the catalyst dispersion.

Scotti *et al.* [192] described for the first time the fabrication of reusable polypropylene miniature reactor through FDM. The system incorporated a magnetic stir bar for the homogenous mixing and a capillary coupled to a nano-ESI mass spectrometer for the real-time reaction monitorization. The designed reactor was successfully applied to carry out and analyze the Diels–Alder process but also the derived retro Diels-Alder. Miniaturized integration allowed minimal distance and volume between the reactor chamber and ESI capillary to reduce dead reaction volumes. Through this assembly, direct and fast MS analysis was possible without external pumps.

As such, 3D-printing was proved to enable to obtain a custom-built photocatalytic reactor for specific conditions with the need of lesser fabrication resources. As intrinsically for microreactors with high surface-to-volume ratios, the system offered an enhanced mass and heat transfer coefficients besides a low-pressure drop [182,236].

Since photocatalysis is highly structure-sensitive, different material layouts have been proposed, designed and studied [112,125,237]. For instance, the three dimensionally ordered macroporous (3DOM) materials have been synthesized, characterized, and tested in a wide range of catalytic applications. An encouraging feature of these materials is that their pore size in the macro range (> 50 nm) permits a facile surface access to bigger molecules in its high surface and open framework among other benefits. To date, metal oxides such as TiO_2 , CeO_2 or PrO_x with 3DOM structure have been achieved through polymer assisted templating using colloidal crystals such as sphere-packed PS or PMMA. Srinivasan *et al.* [126] depicted that quantum yield depends on crystal size, surface morphology and

composition when used a 3DOM TiO₂ catalyst with pore sizes ranging from 0.5 to 1.0 μm for the photodegradation of methylene blue (MB). In this study, the authors demonstrated that the 3DOM structure led to a band-gap narrowing down to 2.87 eV when gold nanoparticles were loaded, making this material photocatalytically active with visible light. This work is just an example that confirms the tight correlation of photocatalytic performance to surface characteristics.

The impact of 3D printing on the catalytic properties was investigated by Lefeverrea *et al.* [238] using different binders and geometries in 3D-printed ZSM-5 structures. The authors evaluated the effect of each binder on the catalytic activity, stability and selectivity in olefin production from methanol. The best outcome was achieved by a combination of aluminophosphate and silica as binders, while the catalytic performance of the catalyst improved with decreasing fiber diameter. This study demonstrates that slight changes in the type of binder or architecture of the material has a major impact on its catalytic properties [193,238,239].

In this context, many examples found in literature demonstrate it is possible to manufacture customized experimental devices or even full bioreactors of high complexity within few hours starting from scratch. As such, Frey *et al.* [191] presents a bespoke 3D-printed microbubble column reactor (3D- μBCR), which could cultivate microorganisms with online monitoring through an integrated microsensor. These authors designed and investigated three different reactor geometries investigating the structure effect on the hydrodynamics in the reaction chamber. In their design, the momentum of the ascendent gas bubbles is transferred to the fluid, which prevents concentration and temperature gradients throughout the

reactor. The enlarged interface area of the flowing gas in the fluid medium also enhances mass transfer from the gas to the liquid phase.

In a different study, Onisuru *et al.* [240] designed a continuous-flow PLA U-shaped reactor device for the catalytic conversion of Fe(III) into Fe(II). These authors conducted the catalytic degradation of $[\text{K}_3\text{Fe}(\text{CN})_6]$ into $[\text{K}_4\text{Fe}(\text{CN})_6]$ in a 3D-printed syringe pump using sodium borohydride. The system used a mesoporous manganese oxide catalyst and yielded an outstanding 94.1 % conversion of hexacyanoferrate ion at 55 °C in a 6-minute reaction. The convenience of using continuous-flow reactors is that they offer excellent performance compared to batch reactions [241] such as better homogeneity and heat transfer, reduced scale-up problems, and the possibility of performing multi-step reactions using numerous reactors in a single flow [242]. These attributes make the reaction is faster, safer and cleaner than other traditional reaction methods.

Similarly, Alimi *et al.* [220] focused their study on the design and optimization of a low cost 3D printed continuous flow microreactor. They examined different approaches where 3D printing technology serves for liquid phase catalytic applications such as the oxidation of Morin dye. Counterpart batch reactors require longer reaction times and complicated methodologies for the eventual catalyst separation and recovery. This work shows the implementation of a novel continuous reaction system achieved by means of 3D technology [243]. The aforementioned catalytic system, which integrates palladium nanoparticles embedded on mesoporous cobalt oxide attached to a cheap, easy to operate, and time-efficient 3D printed fixed bed reactor (see **Table 1.6**). This continuous flow microreactor system exhibits unique characteristics beneficial for the reaction, such

as stability, environmentally safety and fast operation. Furthermore, the authors report for this novel system, a maximum conversion of 98 % in 8 min, which saves 36 min compared to a batch reactor.

The authors used a sealed ATR-IR reaction cell with gas control to assess in real time the catalyst surface during the reaction progress. The presence of unstable compounds or hazardous species was monitored using on line IR spectroscopy, which was optimized on-site and with a short residence time. Mohammad and co-workers [217] confirmed the key importance of design in microchanneled reactors made from 3D-printed silicon and 316 stainless steel. These authors target four main objectives in their study: (1) elimination dead flow zones; (2) enhancement of mixing throughout the reactor; (3) enhancement of heat dissipation; and (4) maximization of reactor yield. To achieve such goals, different channel designs were proposed, realized and successfully used in Fischer-Tropsch (FT) synthesis [196], as presented in **Figure 1.6**. The 3D-printed microreactors offered an outstanding yield in terms of carbon monoxide (CO) conversion and hydrocarbon selectivity. Thus, furthermore the authors claimed that the utilization of microreactors with a precise microstructure eases the understanding of metal-metal-support interaction for the effective catalyst development in FT synthesis.

Other uses in which 3D printing has been successfully applied is the production of biofuels from waste. Borges *et al.* [244] improved biodiesel production by deploying a 3D-printed microstructured catalytic material to tune the transesterification reaction using a stirred system. The heterogeneous catalyst was constituted by potassium loaded on an amorphous aluminum silicate, as an alternative to homogeneous catalysts. A 3D negative mold was printed using a

MakerBot® model with PLA filaments, which was later coated with the active catalyst. Then, the template was removed by thermal treatment resulting in the microstructured catalytic material defined by the original 3D design. The potassium-based catalyst was loaded on the reactor and it showed good activity despite the abundant presence of free fatty acids and water accumulated on the catalytic surface owing to the balanced basic-acid sites generated upon this methodology. This approach allowed the design of a suitable catalyst used for a stirred-reactor system, with high mechanical resistance, efficiency and reusability.

Another significant contribution was presented by Viskadourakis *et al.* [108], who described a novel methodology for the quick and reproducible production of nanocomposites. Authors made use of a commercial FDM-type 3D printer with homemade polystyrene filaments enriched with 20 % w/w of ZnO and TiO₂ nanoparticles. The photoactivity of the 3D-printed materials was tested under UV-A light irradiation for the removal of methylene blue (MB) dye in aqueous solutions, yielding efficiencies near a 70 % following a first-order kinetics decomposition reaction. With this immobilized methodology, MB adsorption on the catalyst is reduced, which enables to skip the additional catalyst-adsorbate separation step to recover the photocatalytic material. **Table 1.6** depicts a summary of the technical aspects of the 3D printer model/trademark.

1.4.9 Reaction Kinetics and Reynolds Number in a Microreactors

The Reynolds number (N_{Re}) (see **Equation 1-10**) is a dimensionless parameter of relevance in fluid dynamics that is used as descriptor of the predominant transport phenomena occurring in a flowing stream. The Reynolds number

correlates inertial forces to viscous forces and its ratio enables to evaluate whether the liquid flow in a pipeline follows a laminar or turbulent regime.

The N_{Re} is minimal for the case of incompressible fluids in microchannels [246]. As such, the Reynolds number can be as small as 0.1 in a typical water-based microfluidic system. Therefore, in milli and microreactors, the laminar flow is the dominant regime. This condition is unfavorable for the chemical reaction because at such regimes, turbulent mixing or reactant convection in the cross section toward the catalytic phase does not occur. Therefore, the mixing of reactive species in the radial direction depends on the diffusion in this type of small reactors. A solution to improve the conversion and selectivity of the reaction is to extend the contact area between the reaction species, creating long and tortuous channels (see **Figure 1.6**) that tune mixing according to the needs of the desired products [87].

The estimation of the N_{Re} parameter (see **Equation 1-10**) and the microfluidic dynamic pre-assessment is essential in the design of channeled reactors by the revolutionary 3D printing.

$$N_{Re} = \frac{\rho \vec{V} D}{\mu}$$

Equation 1-10. Reynolds number.

Equation 1-10 is the conventional equation to calculate the Reynolds number (N_{Re}). In this formula, D is the conduct diameter, ρ is the fluid density, μ and $\vec{V}$ are the dynamic viscosity and media velocity of the fluid, respectively. The Reynolds number enables to characterize the primary conditions of speed and

residence time (τ) (see **Equation 1-11**), which intervene in the design of a microreactor.

$$\tau = \frac{L}{\vec{V}} \frac{A}{A} = \frac{L}{\vec{V}}$$

Equation 1-11. Residence time.

Equation 1-11, corresponds to residence time, where τ is the residence time, A and L are transversal section and the longitude of the microchannel, respectively. The above calculations correspond to straight pipes, but the N_{Re} can be substantially increased (i.e., the turbulent nature) when disruptors of the laminar flow such as channel tortuosity items such as periodic constrictions, protuberances and or unparallel channels that force the flow to bend along the stream direction are placed [228,247–249]. In this context, 3D printing has permitted the realization of prototypes with turbulence promoters conferring an improved mass transfer whilst minimal pressure drop [250].

It should be highlighted the work presented by Zhakeyev and co-workers [86], who reported the fabrication of intricate photoactive monoliths made of di(4-vinyl)phenylbenzo-2,1,3-thiadiazole incorporated bespoke resins (**Figure 1.6d**).

However, in their study, the flowing gas disruptions along the complex geometries lead to maldistributions in the reagent paths, resulting in an activity loss with regards to simpler designs. Regardless, it can be concluded that 3D-printing offers the unique possibility to precisely tune the channel inner sections in order to achieve an optimal flow regimes.

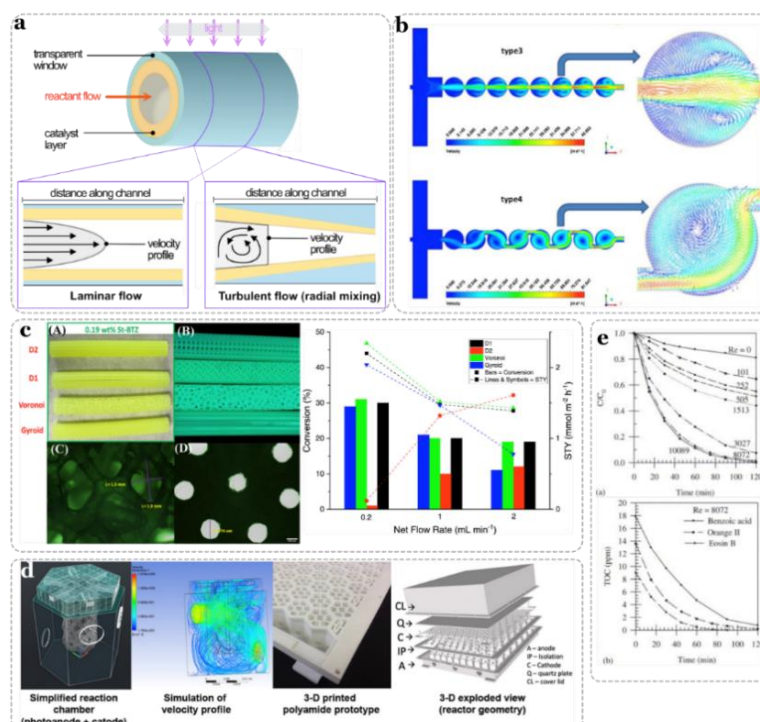


Figure 1.6. (a) Section of a microreactor with different channel configurations acquiring laminar and turbulent flow, respectively (b) Velocity profiles along microreactors channel with a common shape design and different flow redirection. Reproduced with permission from [196]. (c) 3D printed photoactive monoliths of intricate geometries with even distribution of incorporated fluorescent material (left). Influence of the flowrate on the 2-furoic acid conversion in 3D printed monoliths and the space-time yield (STY) (right). Reprinted with permission from [86]. (d) Modular and flexible photoelectrocatalytic reactor composed of honeycomb-type anode and prismatic mesh cathode. Reproduced with permission from [211]. (e) Comparison of photocatalytic degradation rates of different organic compounds at two different Reynolds number. Reprinted with permission from [245].

1.4.10 LED Irradiation and application in 3D printing

Light-emitting diodes (LED) are secure, efficient, inexpensive, and present long emission wavelength irradiation sources. These versatile characteristics are useful in the area of photocatalysis. Liu *et al.* [251] worked with seven chalcone-anthracene derivatives designed for near-UV and visible light absorption. These photoactive systems were tested in 3D printed reaction wares with excellent spatial resolution by means of direct laser writing (DLW) methodology. This technique used a laser diode of 405 nm and allowed the authors to achieve with precision the miniaturized shapes and architectures with a resolution of $\sim 50 \mu\text{m}$.

Rossi *et al.* [252] used an inexpensive and non-toxic PLA (polylactic acid) polymer for the 3D printing process, coupled with decorative ultraviolet LED (UV-A) as a light source. This polymeric device was used to perform photochemical reactions in a high school laboratory. The target reaction was the reductive homocoupling of benzophenone to benzopinacol, leading to the formation of the desired product with an 81 % yield. These authors make the point that this combined technology could facilitate the introduction of photochemistry experiments in high school laboratories with small budgets.

In study of Sharma *et al.* [253], the authors developed a p-n heterojunction of binary and ternary combinations of semiconductors TiO_2 , Bi_2O_3 , and CuO . This combined material was activated by visible light-LED and enabled the photo removal and complete mineralization of RhB.

The photodegradation of RhB showed a pseudo-first-order kinetics process and the % of photodegradation was determined by means of **Equation 1-12**:

$$\text{Photodegradation (\%)} = 100 \left[\frac{C_o - C}{C_o} \right]$$

Equation 1-12. % of photodegradation.

C_o is the concentration of RhB after attaining equilibrium, and C is the concentration at a specific time x .

The photocatalytic activity of a Fe-doped C_3N_4 in the presence of H_2O_2 for the degradation of dicamba, a persistent water pollutant that is used as herbicide, was studied by Desipio and co-workers [254]. AM technology (Ultimaker 2 instrument with black PLA) enabled the construction of a 3D-printed photon concentrator with complex parabolic mirrors. This assembled device was efficient to maximize the incident light sourced by 100 W LEDs, which led to an increased decomposition rate when compared to the photocatalyst with hydrogen peroxide alone. Thus, 3D-printing improved the photocatalytic response.

1.4.11 VOC's Elimination and 3D Printing Devices

Medina *et al.* [255] showed the potential of the mix of SLA 3D printing and HCP-carbon nanoparticles to obtain advanced supports for water disinfection. The developed coating procedure begins with the binding of 10 mg of HCP to the SLA 3D printed device by means of an Eppendorf tube. The carbon-coated device was cured with UV for 4 h until for a complete crosslinking of the active phase with the in-printed polymeric substrate

Table 1.5. Applications 3D printing technology.

3D printing technology		Support		Coating	Deposition Method	Application [Ref.]	
Stereo Lithography Apparatus		Carbon and support	ceramic ceramic	Molybdenum disulfide (MoS ₂)	Hydrothermal	Degradation of Rhodamine B	[178]
Stereo Lithography Apparatus		Acrylate-based liquid resin		Cu- and Ni-coated structure	Immersion	Fabrication of metallic architectures with complex geometries [76]	
Direct Writing	Ink	Silica		APTS-Cu and APTS-Pd	Immersion	Sonogashira, Stille, and Suzuki reactions [81]	
Extrusion		Zeolite/inorganic binder		Self-supporting catalysts	--	Converted methanol to olefins [193,238,239]	
SLA printing	3D	Clear resin	Photoactive (Formlabs).	hyperporous carbons (HCP-carbons)	vigorously shaken for 1 min and UV cured	Extraction of rhodamine B from water [255]	

The resulting device was employed to extract RhB from water over 12 h experiments, obtaining a yield of 74 %. Comparatively, just 4 % of the RhB with the unmodified 3D printed device under similar experimental conditions could be extract. Therefore, the synergistic addition of carbon onto the printed polymer was proven.

In another example, Lagalante et al. [256] prepared 3D-printed sorbents from an unmodified, commercially available carbon black conductive PLA filament. The instrument used is a Monoprice Mini Pro controlled by Ultimaker Cura (v15.04.6) at a layer resolution of 0.15 mm through a 0.4 mm nozzle heated to 215 °C.

Table 1.6. Relationship between additive method and reaction characteristics.

3D Additive Method	Filament material	Nozzle size	Design Parameters/ Reactor Features	Application	3D printer model/ [Ref.]
FDM	PP	0.4 mm	Integrated stirring system and nano-ESI capillary	Diels-Alder reactions	MiniFactory 3; Minifactory Oy Ltd. [192]
SLA	Photo sensitive resin	---	Cold plasma activated 3D fractal support	Photodegradation of RhB	AnyCubic Photon-s LCD-based SLA printer [93]
DIW	SiO ₂ colloidal ink	410 μ m	Functionalized cylinder structures	Sonogashira, Stille, and Suzuki reactions	Aerotech Inc., USA model A3200 [81]
Extrusion3 DFD	zeolite/binder paste	0.9 mm	Fixed bed alumina reactor with an inner diameter of 22 mm	Converted methanol to olefins	In-house built [193,238,239]
SLA	Clear Photoactive resin (Formlabs)	---	---	Extraction of rhodamine B from water	Form + 1 3D Printer (Formlabs Inc., Somerville, USA) [255]
FMD	PLA	1.75 mm	U-shaped cylindrical device	Catalytic degradation of [K ₃ Fe(CN) ₆]	Prusa i3 MK3S [240]
FMD	PLA	1.75 mm		Catalytic oxidation of morin dye	Prusa i3 MK3S [220]

Table 1.6 (Continued)

FMD	PP	~ mm	Two reactors connected in series. Two inputs and one output.	Synthesis of organic compounds	3DTouch™ printer [242]
FMD	PLA	100 μ m	3D microstructured catalytic material	Biofuel production	MakerBot® Replicator® Desktop 3D Printer (5th Gen) [244]
FDM	PS enriched with ZnO and TiO ₂	1.75 +/- 0.15 mm	Simple rectangular shaped and rectangular with cylinders	Removal of MB in aqueous solution	Makerbot Replicator 2X [108]
FDM	ABS	400 μ m	The serpentine shape channel was coated with Cu–TiO ₂ photocatalysts	Photooxidation of MB and photoreduction of 4-nitrophenol (4NP) in water	Creality Ender-3 3D Printer [195]

The adsorbents were tested for the adsorption of benzene, toluene, and ethylbenzene in aqueous solution. This study concluded that increased surface areas at the higher fill densities are advantageous for removing VOC's from water faster. 3D-printed Acrylonitrile Butadiene Styrene (ABS) polymer was used by Pellejero et al. [256] for VOC's removal in air. In particular, a series of adsorption experiments were conducted taking as probe gas molecule dimethyl methylphosphonate (DMMP) tests. These authors proved ABS/ZIF-8 systems as

efficient for this target, reaching a total adsorption capacity of 0.14 mg of DMMP per g of the filter. This system is represented in **Figure 1.6**.

1.4.12 Concluding Remarks

1.4.12.1 Advantages of 3D printing in photocatalysis

3D printing promises to change the conventional way of obtaining objects permitting the switch from manufactured by modeling material blocks to become directly constructed. Consequently, it requires less raw material, fabrication time and less energy consumption in a process that adapts out to be environmentally friendly because it proportionally reduces CO₂ emissions to the atmosphere during these production stages. On the other hand, it is more independent of supply transport chains because it is no longer necessary to move from one place to another or store objects since virtually created designs can be fabricated in-place wherever the printing device is settled. When applied to catalysis, monolithic catalysts also have numerous advantages over packed-bed reactors, and it is where AM has huge outperformance potential. Key aspects to consider when designing a reactor include heat and mass transport rates per unit pressure drop, transversal temperature gradients, and scale-up facility. Shape and size are pivotal features in the design of heterogeneous catalysts, and 3D printing offers the large versatility of modulating these macroscopic aspects.

A 3D printed reactor is not only smaller and cheaper, it can also be more efficient compared to those made by conventional methods, with the additional feature of flexibility.

As it has been reviewed herein, they can be manufactured in a laboratory without an advanced synthesis equipment. Additionally, high precisions are possible even downscaling to the μm range. At such low scales, the printed microreactors offer improved heat transfer, efficient mixing, and lower reagent consumption.

In chemical reactor engineering, the preferred 3D printing technology is SLA, especially when the goal is to fabricate a continuous flow reactor or when pressure drop is a crucial parameter. As an advantage over other AM methods, the individual layers are covalently crosslinked, providing isotropy in the three dimensions of space, with no macroscopic grain structure or voids. Thus, the SLA-printed structures possess the sufficient mechanical robustness [86].

When it comes to photocatalysis, the interest relies in developing efficient visible-light activated photocatalysis owing to sustainable reasons [215]. 3D printing also has potential to facilitate the design and preparation of photocatalytic systems including the reactionware with the demanded optical properties and the photoactive material.

We have reviewed how in the very recent years, the field of in-printed structured materials for uses as photoactivated (micro)reactor systems is exponentially growing with innovative designs with integrated devices for the real-time process monitoring [90]. Additionally, computational simulation studies have enabled a further understanding of the transport properties of the reactant media in the reactor volume and thus, implement further optimizations in the design only achievable by 3D printing.

1.4.13 Current disadvantages and pending challenges

Despite that AM technologies open great opportunities for the design and construction of photochemical reactors, it is yet necessary to make a life-cycle assessment of the processes since some of the filaments used in 3D printers are of expensive and/or non-renewable. These disadvantages combine with the need of the use of software packages for using CAD tools to convert architectures digitally adjustable from the 3D theoretical model into a series of 2D layers after the print. Moreover, layer-by-layer printing with lower-boiling metal alloys is only possible in specific cases [76]. For circumstances when the final object is metallic, the suspensions or nanoparticles used must be distinctive for each type of metal. This fact makes that printing with these substrates is expensive both in terms of time and funds [169]. Additionally, the production of large metal structures with high-quality details is still under study. Since a comparison of the AM technologies with traditional methods show low-resolution accuracy and produces surfaces with higher macro roughness. The used polymer materials for construction 3D are challenging because they exhibit low resistance for organic substances dissolvent type aromatics, ethers, and chloroform. Another disadvantage of coated structured catalysts is the limited catalyst loading per reactor volume [238].

3D printing techniques, SLA and DLP, give higher resolution, smoother surfaces, greater z-axis force, and faster manufacturing than the FDM technique. However, its use is limited because the UV stimulation requires expensive resins to form 3D objects. An alternative to solve this problem is to continue developing studies to explore the possibility of synthesizing resins from low-cost materials [257]. In the FDM context, this has remarkable limitations for the fabrication of

flow reactor because the nature of printing layer by layer creates anisotropy in the final structure and voids between the individual layers. These defects affect the mechanical properties of the product because the reaction mix could percolate through the voids and present leaks [86].

1.4.14 Future Perspectives and Conclusions

To date, many studies have focused on printed catalysts supported on different surfaces are millimeter to micrometer-sized materials. Nevertheless, the synthesis of nano or atomic scale catalysts is still challenging to 3D printing technology. Therefore, it is necessary to continue researching to unify even more 3D printing techniques and nanomaterials with multiple functionalities and unconventional structures. Despite the research shown in this review, few studies discuss integrating the reaction system and the catalytic activity of the catalyst using 3D printing, both for the manufacture of the structure and the deposition of the active phase. Thus, this type of research gives new alternatives to the intensification of the process in the future.

It is still necessary to investigate the development of materials and inks for injection from 3D printer filaments that demand less cost and time. It is essential to implement that new methodology without forgetting. The 3D printing technology in reactions systems that require high strength and high impact resistance should also find new alternatives for the catalyst supporting external stimulus while realizing the catalytic function. In addition, it is interesting that the new materials and the evolution in additive manufacturing will allow finding new possibilities of self-organization of materials that will enable going from 3D to 4D technology in chemical reactions of experimental or industrial interest.

The ultimate implementation of additive technologies will make possible to obtain other added values through the printing process, the possibility of combining several objects in one, or increasing the printing speed, improving the quality of the final product. Despite significant advances, the speed of 3D printers is still moderately slow to fabricate big structures, inaccurate to certain levels, and more expensive than traditional methods. Additionally, it will be necessary to promote recycled plastics since they can implement value-added chains in other vital areas for society. The ease of creating complex structures through the 3D printing opens the possibility of developing research focused on eliminating atmospheric gases responsible for global warming and emerging pollutants. As we have reviewed, it is possible to build adapted novel reaction systems capable of achieving the necessary selectivities and conversions to attain industrial relevance.

Concerning the previous context, the research community, including our group, is currently developing 3D-printed monoliths with bespoke channel configuration to outperform in environmental protection reactions such as the degradation of contaminating molecules in gas but also liquid media. These systems are efficient supports for photoactive phases based on semiconductor materials. Finally, the combination between synthesis of nanomaterials and 3D printing has enabled to design different alternatives to model and realize the best reaction conditions for a greener societal progress.

1.5 CATALYTIC PHASE TREND

Titanium [57], cerium [237], zirconium [258], and zinc oxides [259] possess photocatalytic properties and can initiate chemical reactions. Each of these materials exhibits unique characteristics that differentiate them in terms of

efficiency and activity. However, their characteristic bandwidth and functionality at wavelengths closer to ultraviolet light limit their applications.

For example, titanium oxide is acknowledged as one of the most efficient materials for photocatalytic activity, rendering it ideal for applications requiring a high reaction rate [260]. Common applications include water disinfection and the removal of air contaminants. Cerium oxide, conversely, distinguishes itself by its ability to oxidize and reduce various compounds, proving valuable in water and air purification because of its effectiveness in eliminating organic contaminants. In addition, it is recognized for its high stability in acidic environments and its ability to produce hydroxyl radicals [261].

Zirconium oxide is known for its elevated corrosion resistance and light absorption capacity at different wavelengths, making it suitable for use in photovoltaic cells. It is also renowned for its low toxicity and ease of synthesis [262]. Finally, zinc oxide is noteworthy for its capacity to absorb light at narrower wavelengths than titanium oxide, making it suitable for water disinfection applications [259]. It is recognized for its affordability and high stability in alkaline environments, although it may experience a reduction in activity due to hydration phenomena. Bismuth vanadate exhibits greater sensitivity to visible light than the oxides.

This characteristic allows its use in photocatalytic applications under natural light conditions, potentially offering a more efficient and cost-effective alternative to ultraviolet light [263,264]. Despite this advantage, a drawback is that bismuth vanadate is more challenging and expensive to synthesize than titanium oxide.

Considering the previously outlined characteristics of metal oxides, we propose the feasibility of narrowing the bandwidth of these materials by concurrently reducing their crystal size using a selected synthesis method. This approach yields nanometric mixed phases of semiconductors, fostering interaction between them and resulting in a synergistic effect attributed to the controlled crystalline phases. Consequently, the specific surface area (BET) can be increased and the electron–hole effect mitigated, thereby extending the activity of these materials to wavelengths within the visible spectrum. Moreover, in the case of bismuth vanadate salt, renowned for its capacity to absorb visible light, we posit that doping it with carbon and silver-materials contributing electrons can enhance its optical sensitivity. Thus, we deem it plausible to establish objectives related to the degradation of emerging pollutants by leveraging visible light simulated with LED lamps.

1.6 OBJECTIVES OF THE THESIS

The general objective of this thesis is the design and model hybrid reactor/photocatalyst systems by 3D printing potentially implementable in environmentally significant pollutant degradation reactions using solar light. To achieve this proposal the following specific objectives have been proposed:

- 1.- Synthesize and characterize new photocatalytic phases capable of degrading pollutants.
- 2.- Design and model, polycarbonate reactors with optimal geometry using additive technologies such as 3D printing to maximize the efficiency of the previous synthesized photocatalytic phases.

3.- Study and optimize the deposition or anchoring techniques of the photocatalysts on the microchannels of the 3D-printed reactor.

4.- Optimize the reaction conditions of the reactor/photocatalyst system to remove pollutants.

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CHAPTER II: SYNTHESIS OF MATERIALS, METHODS, AND CHARACTERIZATION TECHNIQUES

2.1 EXPERIMENTAL

2.1.1 Synthesis of Coupled Nanoparticles as Photocatalysts

The inverse microemulsion method for synthesizing coupled nanoparticles with different mass ratios is detailed below in six steps.

The Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$; Octylphenoxypolyethanol; CAS number: 9002-93-1), 98 % purity reactive-grade 1-Hexanol ($C_6H_{14}O$; CAS number: 111-27-3), greater than 97 % purity Tetramethylammonium pentahydrate (CAS number: 10424-65-4), 99 % purity Zirconium nitrate ($ZrO(NO_3)_2$; CAS number: 14985-18-3), 98 % purity Zinc nitrate hexahydrate ($(Zn(NO_3)_2 \cdot 6H_2O)$; CAS number: 10196-18-6), and 99.5 % purity Cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$; CAS number: 10294-41-4) were purchased from Sigma-Aldrich. Heptane (C_7H_{16}), a mixture of isomers, was obtained from VWR-Chemicals, while Titanium tetrachloride ($TiCl_4$) with a purity greater than 98 % (CAS number: 7550-45-0) was purchased from Fluka-Chemika. The experimental method chosen for the preparation of monometallic and mixed cerium, zinc, zirconium, and titanium oxide nanoparticles consisted of six synthesis steps following the inverse two-emulsion technique [1,2]. This methodology, illustrated in **Figure 2.1**, is based on the *in-situ* reaction of two microemulsions, one with alkaline characteristics and the other with acidic characteristics.

As **step 1**, microemulsion one (μ emulsion 1) was prepared, containing 74 g of Triton X-100 (as a surfactant), 58 g of 1-hexanol (as a co-surfactant), and 228 g of heptane (as a continuous oily phase). In each case, and according to the oxide intended to be prepared, the necessary amounts of metal salts were added to obtain

4.0 g of nanoparticles. In **step 2**, simultaneously, a second microemulsion (µemulsion 2) was prepared. This had the same amounts of surfactant, co-surfactant, and oily phase as µemulsion 1, in addition to 13.6 g of tetramethylammonium hydroxide pentahydrate, which acts as a precipitating agent for the corresponding metal hydroxide.

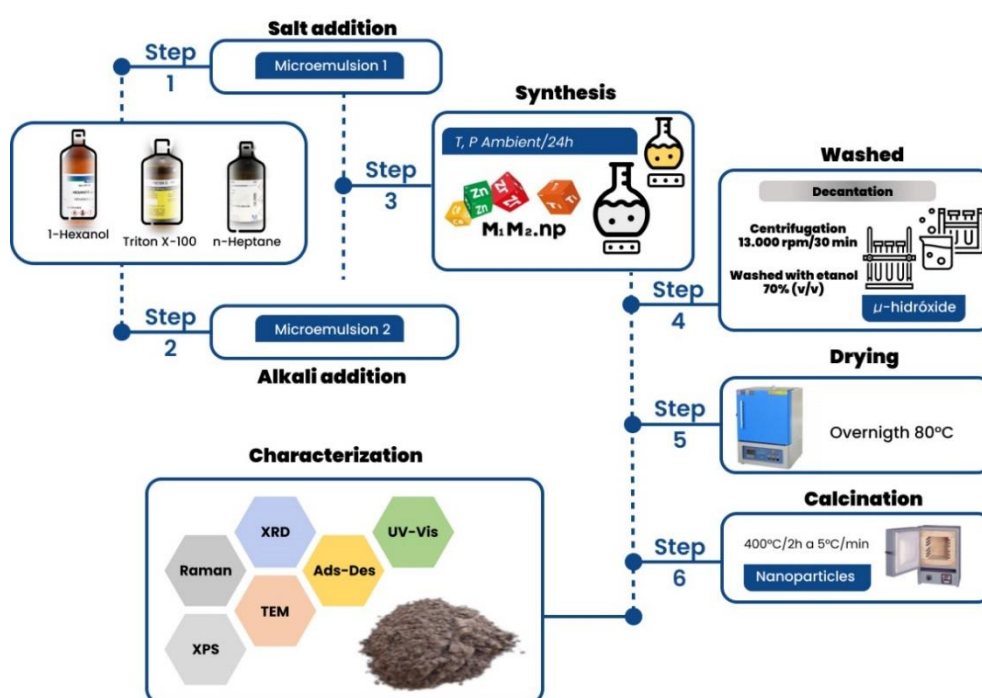


Figure 2.1. Schematic representation of steps for inverse two-emulsion synthesis of semiconductor nanoparticles.

Before initiating the synthesis reaction, it was necessary to make some key modifications to the methodology to prevent the hydrolysis of the titanium salt into TiO_2 . To achieve this, the presence of water during the reaction was excluded. Therefore, our modified protocol allowed the synthesis of metal oxides to be

discriminated into two distinct cases, A and B, depending on the presence or absence of titanium, as described below.

2.1.2 Synthesis of Cerium, Zirconia or Zinc containing nanoparticles free of Titanium, Case A

Case A involves the synthesis of nanoparticles containing monometallic or binary mixture of cerium, zirconia or zinc oxides but without the presence of titanium. For this purpose, 40 mL of distilled and deionized water (DDW) were added to each of the previously prepared microemulsions. In the first microemulsion, the salt or mixture of salts was dissolved in 40 mL of DDW, whereas in the second microemulsion, DDW was used to dissolve the tetramethylammonium hydroxide. Following this procedure, three oxide materials in monometallic phase and three in the mixed phase were prepared. The samples were labeled with the notation M-NPs, where M represents the metal of the oxide and NPs, nanoparticles. For example, Ce-NPs indicate that the nanoparticles contain 100 % of CeO₂. Meanwhile, mixed-phase materials are denoted as M₁M₂-NPs, where M₁ and M₂ represent the metals. For instance, CeZn-NPs denotes that the nanoparticles contain 50 % CeO₂ and 50 % ZnO.

2.1.3 Synthesis of titanium containing nanoparticles, Case B

Case B involved titanium tetrachloride as precursor. Because of the chemical characteristics of this compound, it was necessary to avoid the presence of water during the preparation of the two microemulsions. However, to maintain material balance, after mixing the two microemulsions (**step 3**), 80 mL of DDW was slowly added. Following this procedure, monometallic titanium oxide was prepared, which

is denoted as Ti-NPs. The remaining three materials in the mixed phase were named TiZr-NPs, TiCe-NPs, and TiZn-NPs, according to the notation described earlier.

Continuing with the synthesis procedure, in **step 3**, the reaction was initiated by mixing the two microemulsions and slowly adding microemulsion 1 onto microemulsion 2 while maintaining magnetic stirring at 2000 rpm under standard atmospheric pressure and temperature conditions. The reaction proceeded for 24 h with constant magnetic stirring. In **step 4**, on the following day, once the synthesis process was completed, the separation and washing of the materials began. The final dispersion was allowed to stand for 6 h, and the solid slurry was immediately recovered by decantation. Once the material was recovered, it was washed three times with 70 % ethanol and separated by centrifugation at 13000 rpm for 30 min. In **step 5**, the recovered solid was stored in a glass beaker and allowed to dry overnight in an oven at 80 °C. As in **step 6**, on the following day, the dried material was calcined in a muffle furnace at 400 °C for 2 h, following a temperature ramp of 5 °C min⁻¹ starting from room temperature; this temperature was selected based on thermogravimetric analysis. Finally, the so prepared materials were recovered and stored in plastic containers for further characterization analysis and photodegradation studies.

2.1.4 Synthesis of TiO₂-ZrO₂ and TiO₂-ZnO based Nanoparticles

TiO₂-ZrO₂ and TiO₂-ZnO nanoparticles were obtained using the inverse two-emulsion method [1,2] with zirconium(IV) oxynitrate hydrate, zinc nitrate hexahydrate, and titanium tetrachloride serving as precursors for ZrO₂, ZnO, and TiO₂, respectively. Briefly, two emulsions were prepared using 228 g of n-heptane, 74 g of Triton X-100, and 58 g of hexanol. In the first microemulsion, appropriate

amounts of zirconium, zinc, and titanium precursors were dissolved, whereas the second microemulsion substituted the metal precursors with tetramethylammonium hydroxide dissolved in 80 mL of water. Both microemulsions were mixed and vigorously stirred for 24 h. The resulting solids were recovered through centrifugation at 13000 rpm for 30 min, washed multiple times with ethanol, and finally dried at 80 °C before being calcined at 400 °C for 2 h. The samples were labeled with the notation Ti_xZr_y or Ti_xZn_y , where X and Y represent the weight percentages of TiO_2 , ZrO_2 , and ZnO , respectively. For instance, $Ti_{10}Zr_{90}$ signifies that the nanoparticles contain 10 wt.% of TiO_2 and 90 % of ZrO_2 . For this case exceptionally $Ti_{50}Zn_{50}$ signifies that the nanoparticles contain 50 wt.% of TiO_2 and 50 % of ZnO .

2.1.5 Synthesis of $BiVO_4$ based Photocatalysts

The $BiVO_4$ based photocatalyst were synthesized using solvothermal method in six steps, as illustrated in **Figure 2.2**. All the reagents were of analytical grade and were used without any further purification. In a typical synthesis, 4 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ (0.9739 g) was dissolved in 20 mL of Ethylene Glycol (EG) and 4 mmol of NH_4VO_3 (0.2347 g) in 20 mL of DDW [3,4]. The NH_4VO_3 solution was added dropwise to the $Bi(NO_3)_3$ solution with magnetic stirring at 100 rpm until a yellowish dispersion with a pH between 0.50 and 1.10 was obtained (**step 1**). Subsequently, the pH was adjusted to 7.0 using ammonium hydroxide NH_4OH (**step 2**). The dispersions were then transferred to a stainless-steel autoclave with a teflon coating, sealed tightly, and subjected to heat treatment at 140 °C for 3 h (**step 3**). The obtained materials were washed twice with DDW as well as with 70 % (v/v) ethanol (step 4), and finally dried at 80 °C for 12 h (step 5). After that, each material

was calcined at a selected temperature of 300, 450, or 600 °C using a heating rate of 5 °C min⁻¹ in air atmosphere (step 6). The so prepared bismuth vanadate based samples are denoted as BiV/T, whereas those obtained by a modify route with silver doping are denoted as Ag/BiV/T.

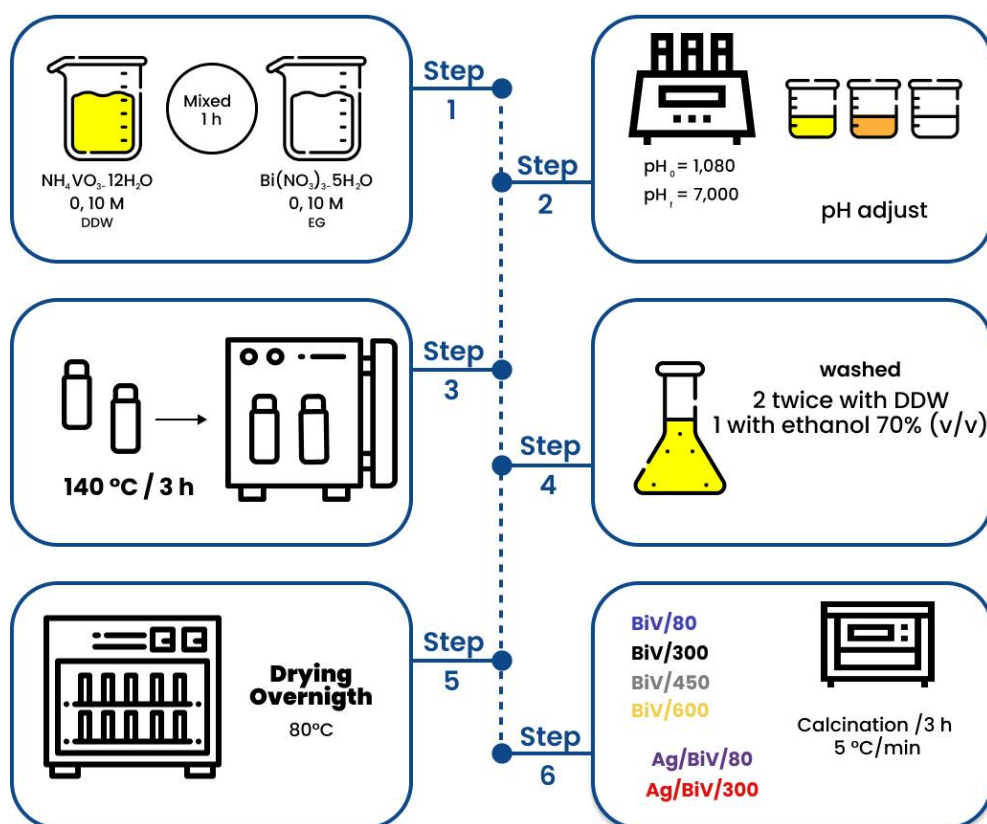


Figure 2.2. Schematic representation of steps for solvothermal synthesis of BiVO₄ photocatalysts.

Here T represents the temperature in Celsius degrees: 80, 300, 450, and 600 °C for the undoped photocatalysts, and 80 and 300 °C for the doped photocatalysts, respectively. For instance, BiV/300 indicates that the undoped BiVO₄ based

photocatalyst was treated at 300 °C, and Ag/BiV/300 indicates that the BiVO₄ based sample was doped with silver and calcined at 300 °C.

For the doping procedure, AgNO₃ was added and mixed immediately after the introduction of the BiVO₄ precursor to reach a silver content of 3.5 wt.% in the final material and being the rest of experimental conditions similar to those above mentioned. This percentage of silver doping was chosen on the basis of previous published works [5].

2.2 HOMEMADE LED PHOTOREACTOR DEVICES

To optimize the reaction conditions in photoreactor/photocatalyst systems for the removal of emerging pollutants (EPs), we devised a strategy that involved the design and construction of two laboratory-scale photoreaction setups. To facilitate the selection of the most efficient photocatalysts, the first design was focused on the batch LED-photoreaction mode using the photocatalyst as slurry dispersion phase (namely as slurry batch LED-reactor).

The second design is a hybrid system consisting of photo-catalytically phases coating 3D designed and printed microreactors. These microreactors were developed as compact devices suitable for implementation in a reactor system operating in continuous-flow recirculation mode, where the photocatalytic phases were anchored on the printed channels (namely as 3D-Printed LED-microreactor).

2.2.1 Slurry Batch LED-reactor

The batch LED-reactor system designed for slurry photocatalysts is depicted in **Figure 2.3**. A cubic stainless steel container measuring of 16 x 16 x 20 cm in width,

thickness, and height, respectively, was built for this purpose (see **Figure 2.3a**). Inside the container, two 50 W LED lamps were installed to simulate sunlight, emitting blue light at a wavelength of 465 nm.

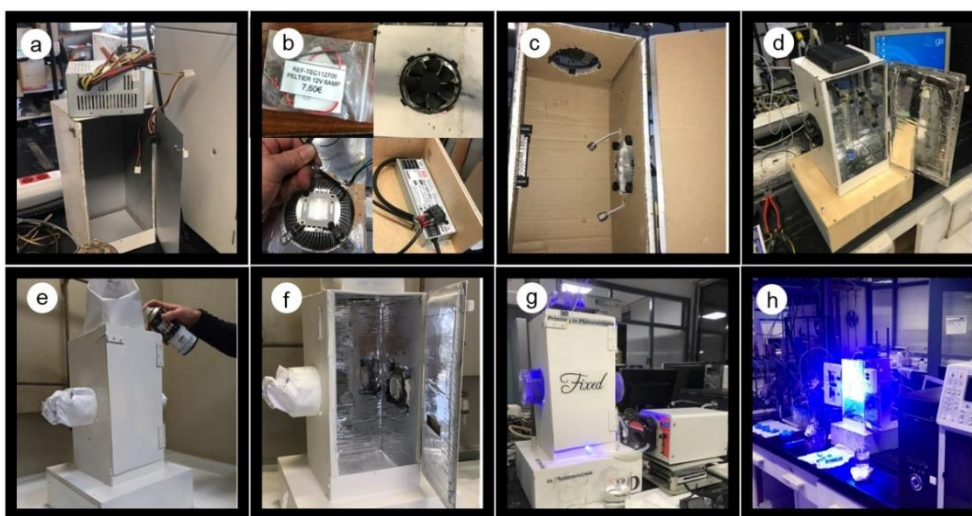


Figure 2.3. Homemade slurry batch LED-reactor, components, and construction process. (a) Initial construction phase involved a cubic stainless steel container, (b) Key components: thermoelectric plate (Peltier) in the upper left corner, a fan for extracting hot air in the upper right corner, a 50-bulb blue-LED lamp in the lower left corner, and the LED light power supply in the lower right corner, (c) Internal section of the reactor before covering it with reflective mirror-type adhesive paper, (d) Photoreactor after construction, prior to esthetic adjustments, (e) Beginning of the painting stage, (f) Internal cleaning of the mirror-type surface, (g) Front view of the finished reactor and (h) Final operation tests.

This setup generated a total power of 100 W and a luminous efficacy of 4080 $\text{lm}\cdot\text{W}^{-1}$. Each lamp comprised 5x10 LED bulbs, spaced 0.22 mm apart, as depicted

in the lower left image of **Figure 2.3b**. The power supply for the lamps, shown in the lower right image of the same figure, operated at 35 V DC. To maintain optimal operating temperatures, each LED lamp was fixed on an aluminum base, as shown in **Figure 2.3c**. A thermoelectric plate (Peltier) was placed between the LED lamp and the aluminum base to facilitate heat exchange between the cold and hot sides, operating with a 12 V DC current (see **Figure 2.3b**, top left).

In addition, a fan operating at 12 V DC was mounted on the outer side of each aluminum base to facilitate the intake of cold air from the surroundings. Another fan was positioned at the top to enable the expulsion of hot air from the interior. With this homemade design, the internal temperature was kept constant at 30 °C.

The geometric arrangement enabled the LED lamps to be placed perpendicular to the center of the reaction, positioned 5 cm away from the vertical plane intersecting the center of the stainless-steel cubic container. To ensure uniform illumination within the reaction vessel, which was a borosilicate glass flask, and to enhance light absorption, the entire internal surface was coated with reflective mirror-type adhesive paper. This modification resulted in an irradiance coefficient of 0.8 mW cm^{-2} for the equipment, as depicted in **Figure 2.3d** and **f**. Finally, **Figure 2.3e-h** depict the technical and esthetic adaptation of the batch LED-reactor for the slurry photocatalyst, showcasing its full functionality.

2.2.2 Recirculation 3D-Printed LED-Microreactor

The recirculation 3D-Printed LED-microreactor designed and constructed for continuous-flow recirculation reactor system for coated 3D-microreactor is depicted in **Figure 2.4**.

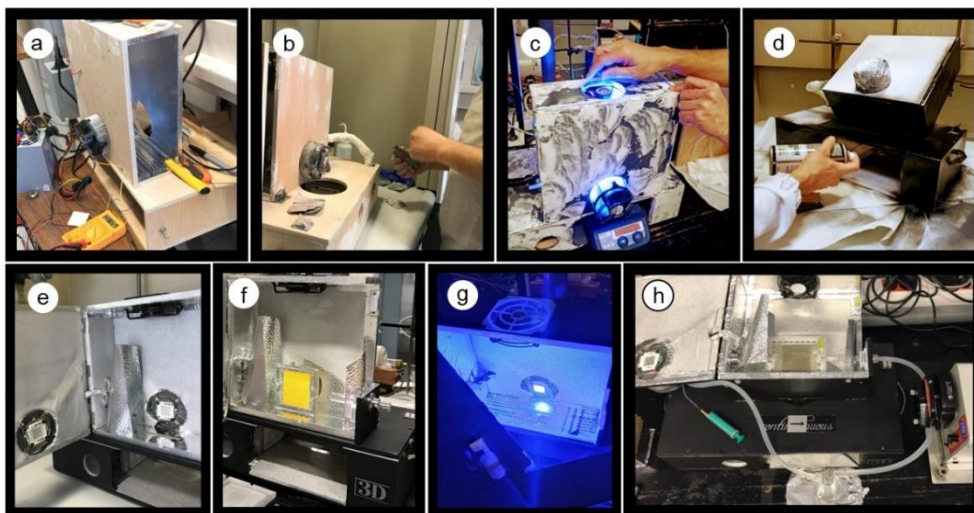


Figure 2.4. Homemade recirculation 3D-Printed LED-microreactor, components, and construction process. (a) Initial construction phase involved a wooden box and electric components, (b) Operation testing of the cooling system, (c) Functionality testing of all components, (d) Beginning of the esthetic painting stage, (e) Front internal view with LED lamps turned off, (f) Front internal view with a 3D microreactor between the LED lamps, (g) Front view of the reactor showing the intensity of the LED light on and (h) Top view of the continuous-flow recirculation reactor with an open door showing the microreactor with immobilized photocatalyst, with the peristaltic pump on the right, the mixing tank below, and the LED lamp on the left.

Following the design of the batch LED-reactor, the same technical configuration of the LED lights was maintained, as well as the distance between the lamps and the center of the reaction, ensuring the same irradiance coefficient. The design and purpose of the cooling and heat exchange elements were also preserved to maintain the internal temperature at 30 °C. The innovative design of our

photoreactor aims to increase its versatility, as its structure can be folded to allow reactions to be carried out both horizontally and vertically. For its construction, two wooden structures were used, with the one located at the bottom housing the electrical power supplies and facilitating the insertion of a magnetic stirring device when necessary.

2.3 PHOTODEGRADATION STUDY

Sulfamethoxazole, a pharmaceutical contaminant considered an emerging pollutant [9], commonly found in wastewater was chosen as a model molecule due to its relatively easy degradation and its environmental importance [10] as it is commonly used for treating urinary diseases [11]. For this purpose, both nanoparticle photocatalysts and reactor systems were utilized, including slurry batch LED-reactor or active 3D microreactors, serving as compact devices for implementation in a continuous-flow recirculation reactor system developed in our laboratory.

2.3.1 Photolysis and Catalysis

To evaluate the influence of the photocatalysts on drug degradation, two preliminary tests were conducted before starting the formal degradation experiments, maintaining the same reaction conditions. A photolysis test examined the effect of LED light on the pollutant in the absence of a photocatalyst, whereas the other explored the impact of the photocatalyst on the pollutant in the absence of light (LED-off). In both cases, no significant changes in the pollutant concentration were observed.

2.3.2 Photodegradation conditions

The photoactive properties of the synthesized powered photocatalysts were assessed in the photodegradation of SMX as probe molecule, under blue-LED light irradiation using two 50 W LED chips (465 nm main emission, total electric power~100 W and 4080 lm W⁻¹). A borosilicate glass reactor (as a homemade slurry batch LED-reactor) was placed between both LED chips (**Figure 2.5** and **Figure 2.3b**).

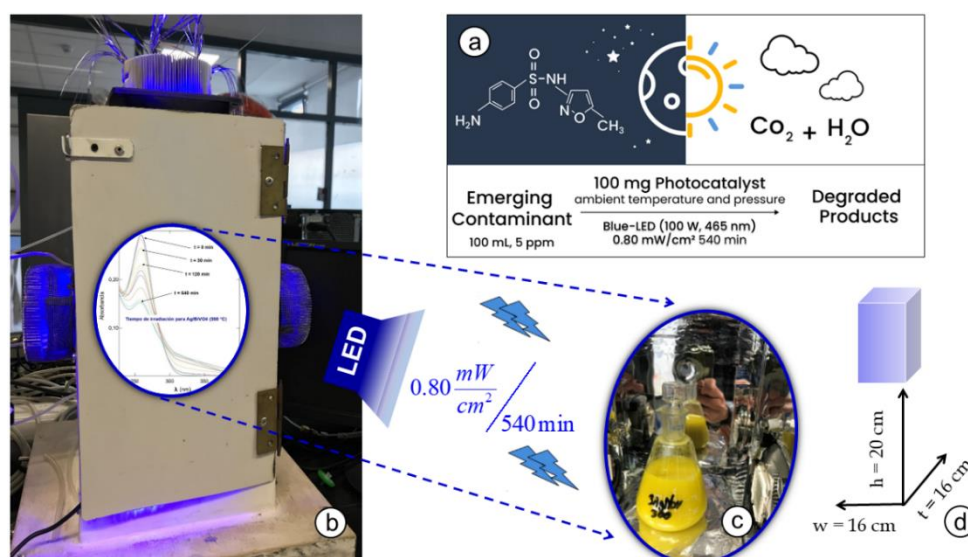


Figure 2.5. Schematic photodegradation experiment using the homemade slurry batch LED-reactor. (a) Schematic representation of the reaction, (b) Box batch reactor containing 5x10 blue-LED bulbs and fans to promote cooling, (c) 250 cm³ borosilicate glass reactor containing slurry photocatalyst and (d) Batch reactor dimensions.

The pH of the experiments was adjusted to 7 with different solutions of NaCl and HCl (0.01 N), and during the photodegradation experiments, the temperature was maintained at 30 °C.

Before exposure to light, the catalysts (100 mg) were immersed in a pollutant solution (100 mL) and allowed to reach adsorption-desorption equilibrium under stirring in the dark. The initial concentration of the pollutant in the solution was adjusted to achieve a final concentration of 5 mg L⁻¹, a value determined on the basis of the SMX adsorption isotherms on the materials. To assure the adsorption-desorption equilibrium, the suspensions were stirred at 220 rpm for 12 h in the dark before exposure to irradiation. Similar experimental conditions were used in the case of 3D-Printed LED-Microreactors.

2.3.3 Sulfamethoxazole Determination

Before the photocatalytic experiment, 100 cm³ of SMX pollutant solution at a concentration of 5 mg L⁻¹ was prepared, as determined from the SMX adsorption isotherms on the materials. The pH was adjusted to 7.0 using NaCl and HCl solutions (0.01 N).

The photodegradation experiment in both homemade LED reactors was initiated by switching to LED-on mode and continued for 540 min at 30 °C. Aliquots of 1.5 cm³ were extracted to control the reaction. These aliquots were then filtered using a 0.45 µm pore size filter. The SMX concentration was determined using a UV-Vis 6505 JENWAY spectrophotometer by measuring the maximum absorption of SMX at 264 nm. The % of SMX photodegradation (% SMX) was calculate according to **Equation 1-12**.

2.4 CHARACTERIZATION TECHNIQUES

2.4.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns were recorded using a BRUKER D8 ADVANCE diffractometer with Cu K α radiation (BRUKER, Rivas-Vaciamadrid, Spain). JCPDS files were consulted to assign the different diffraction lines observed. The diffraction patterns were recorded in the range of 5° to 75° (2 θ) with a step size of 0.05° at a rate of 1° m⁻¹. The average crystal size (dp) of the metal was determined using the Debye-Scherrer equation shown in **Equation 2-1**, where k is a constant (0.9 for powder samples), β_T is the full width at half maximum (FWHM), and λ is the wavelength of radiation (1.5406 nm for copper anode) [15].

$$dp = \kappa \lambda (B_T \cos \theta)$$

Equation 2-1. Debye-Scherrer equation.

2.4.2 Nitrogen Adsorption-Desorption Isotherms at 77 K

The textural properties of the photocatalysts were determined using a Quantachrome Autosorb-6B analyzer. Prior to measuring the adsorption isotherms, the samples were outgassed overnight at 110 °C under high vacuum (10⁻⁶ mbar). The BET equation was applied to the N₂ adsorption data from which the apparent surface area, S_{BET} , was obtained. The Dubinin-Radushkevich equation was applied to the N₂ adsorption data in order to obtain the corresponding micropore volume (W_0) and micropore mean width (L_0). Total pore volumes ($V_{0.95}$) were calculated from N₂ adsorption isotherms at -196 °C and at 0.95 relative pressures. The BJH method [14] was applied to the desorption branch of the N₂ adsorption isotherms to

obtain the pore size distribution (PSD) curves and mesopore volume (V_{BJH}). Finally, the mesopore volume (V_{MESO}) was determined using the Gurvich rule, with a minimum $V_{0.95}$ and $W_0(\text{N}_2)$.

2.4.3 UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS)

The optical absorption spectra of the samples were acquired using a VARIAN CARY 5E double-beam UV-vis spectrophotometer, which was outfitted with a Praying Mantis diffuse reflectance accessory (DRS). The reflectance spectra were then analyzed using the Kubelka–Munk (KM) method to determine the band gap (E_g) of the samples.

2.4.4 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was conducted using a Zeiss SUPRA40VP microscope, equipped with a secondary electron detector, back-scatter electron detector, and an X-Max 50 mm energy dispersive X-ray microanalysis system. Prior to analysis, all samples were triturated using an agate mortar to minimize its size.

2.4.5 Transmission Electron Microscopy (TEM)

The texture and morphology of the samples were analyzed through TEM imaging, using a LIBRA 120 PLUS microscope (Carl Zeiss). For high-resolution analysis (HRTEM), a Thermo Fisher Scientific model Talos F200X microscope was employed. For that the samples were ground finely and dispersed, with the aid of ultrasound, in an ethanol suspension and then depositing droplets of the suspension on a Cu grid coated with a holey amorphous carbon film.

2.4.6 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos Axis Ultra-DLD spectrometer equipped with a hemispherical electron analyzer connected to a DLD (delay-line detector) and an Al-K α monochromator with a power rating of 600 W. The X-ray source employed was a Mg/Al double anode with a power output of 450 W. For these measurements, the binding energy (BE) values were referred to the C_{1s} peak at 284.6 eV. A base pressure of 10^{-9} mbar was maintained during data acquisition. Survey and multi-region spectra were recorded.

Each spectral region of interest was scanned several times to obtain good signal-to-noise ratios. The spectra obtained after background signal correction were fitted to Lorentzian and Gaussian curves in order to obtain the number of components, the position of each peak and the peak areas.

The analyzer operated in constant pass energy mode at 29.35 eV, employing a 720 μ m diameter aperture. Throughout spectrum acquisition, the residual pressure in the analysis chamber remained below 1.33×10^{-7} Pa. Samples were affixed to a holder using a carbon conductive tape and subjected to overnight vacuum in the preparation chamber before transferring to the spectrometer's analysis chamber.

Each spectral region underwent scanning in two separate areas, employing multiple sweeps until a satisfactory signal-to-noise ratio was achieved. The spectra obtained after background signal correction (Shirley-type background) were fitted to Lorentzian and Gaussian curves in order to obtain the number of components, the position of each peak, and the peak areas.

2.4.7 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was conducted utilizing a METTLER-TOLEDO TGA/DSC1 Thermogravimetric Analyzer, while an Optima 8300 ICP-OES system from Perkin-Elmer was employed for elemental analysis.

2.4.8 Ultraviolet-Visible Spectroscopy (UV-Vis)

The pollutant concentration was determined in a UV-Vis 6505 JENWAY Spectrophotometer by registering the SMX maximum absorption at the wavelength of 264 nm.

2.4.9 Raman Spectroscopy

Raman spectra were acquired using a JASCO NRS-5100 dispersive spectrophotometer with a 532 nm laser line. Each spectra was obtained as an average of 64 scans obtained with 85 mW laser power.

2.4.10 Toxicity Assessments

Toxicity assessments were carried out on solutions both before and after catalytic degradation. These tests were conducted using the normalized biotest (UNE/EN/ISO 11345-2), which measures luminescent inhibition in *Vibrio Fischeri* bacteria. The assessments were performed with the LUMIStox 300 system from Dr. LangeGmbH, coupled with a LUMIStherm incubator. Toxicity levels were quantified as inhibition percentages at a 30 min exposure duration (I30), with a reference to a control solution consisting of a stock saline solution.

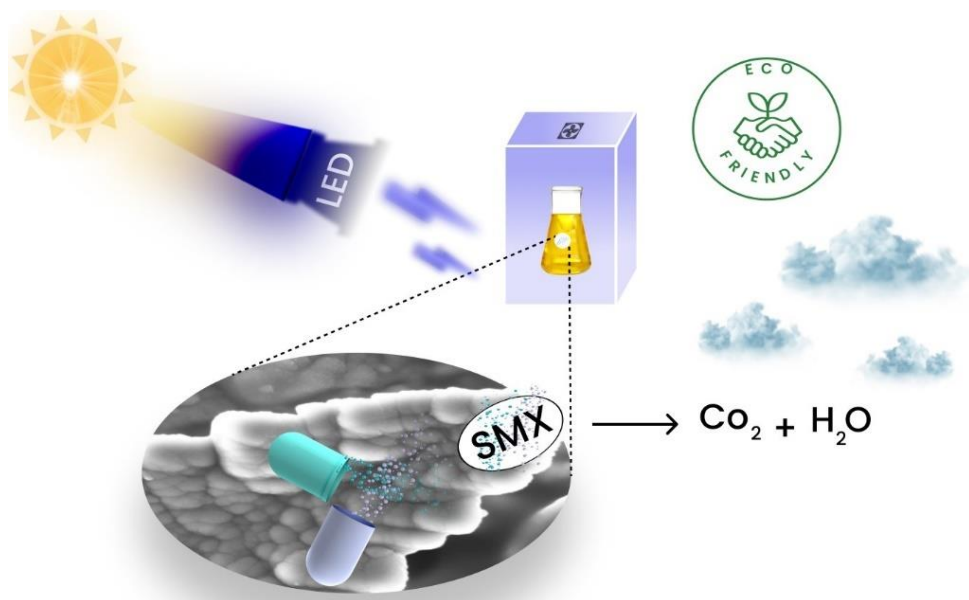
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**CHAPTER III: BiVO₄ BASED PHOTO-CATALYSTS
FOR THE DEGRADATION OF SMX FROM
WASTEWATER**



Graphical Abstract

3.1 ABSTRACT

BiVO₄ is an important n-type semiconductor used in photocatalysis due to its high capacity to absorb solar light in the 400-700 nm range, abundance, high chemical stability, non-toxicity, and low cost. However, research on physicochemical modifications to increase its catalytic activity via simple procedures is limited.

The main objective of this chapter was to evaluate the influence of different synthesis parameters, as calcination temperatures or silver doping, on the structural and physicochemical characteristic of the BiVO₄-based photocatalysts and their photocatalytic performance in degrading sulfamethoxazole in aqueous solution under blue-LED irradiation using a homemade slurry batch photoreactor. BiVO₄

photocatalysts were synthesized using the solvothermal method. Ag-BiVO₄ doped at the optimal calcination temperature (300 °C) showed the lowest recombination rate of photogenerated carriers and the highest photocatalytic efficiency under natural and neutral pH conditions. The LHHW theoretical model fitted very well to the experimental results.

3.2 EXPERIMENTAL

The solvothermal synthesis, calcination temperature, and characterization methodology of the BiVO₄-based photocatalysts, as well as photodegradation procedures of model molecule under blue-LED irradiation using a homemade slurry batch LED-reactor containing a dispersion of the photocatalyst, are presented in [Chapter II](#) of this thesis. The results are presented as follows:

3.3 RESULTS AND DISCUSSION

Figure 3.1 show powder samples after the synthesis protocol. The physical characteristics change when the powders are processed at different temperatures. Different yellow color intensities for fine powders with similar grain sizes are relatively easy to observe as the selected temperature (80, 300, 450, or 600 °C) increases during thermal treatment.

For all samples, the physicochemical properties of the particles induce significant changes in the color of the bulk powder. Physical changes can be observed, such as an opaquer color in samples treated at lower temperatures (80 and 300 °C). In contrast, those treated at higher temperatures exhibited a brighter appearance (450 and 600 °C).

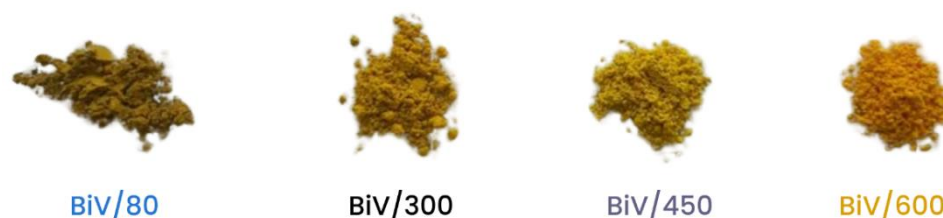


Figure 3.1. Photographs of undoped BiV/T (T = 80, 300, 450 and 600 °C) photocatalyst.

3.3.1 X-ray Diffraction (XRD)

Thermal treatments can significantly affect the crystalline structure of solids [1,2]. At low temperatures (below 500 °C), thermal expansion of crystals commonly occurs, altering their dimensions and leading to modifications in their physicochemical properties. At intermediate temperatures (between 500 °C and 1000 °C), both modifications in the physicochemical properties and partial recrystallization of the sample can occur [3].

For BiVO₄-based photocatalysts, the effect on the crystalline structure depends on the treatment temperature, heating time, and rate [4]. This solid can crystallize into three different structures: tetragonal zircon (*t-z*), monoclinic scheelite (*m-s*), and tetragonal scheelite (*t-s*). Several studies have shown that the monoclinic form is much more active in the visible spectrum region than the other crystalline forms, which is generally attributed to its small band-gap magnitude [5].

To initiate our studies and identify the photocatalyst with the best performance as a function of calcination temperature, the undoped samples were tested in the

photodegradation of SMX as a probe molecule. The relationship between photodegradation capacity and temperature indicates the temperature that maximizes photodegradation efficiency. As observed in **Figure 3.2**, The optimal temperature is 335 °C, achieving a significant photodegradation of approximately 50 %.

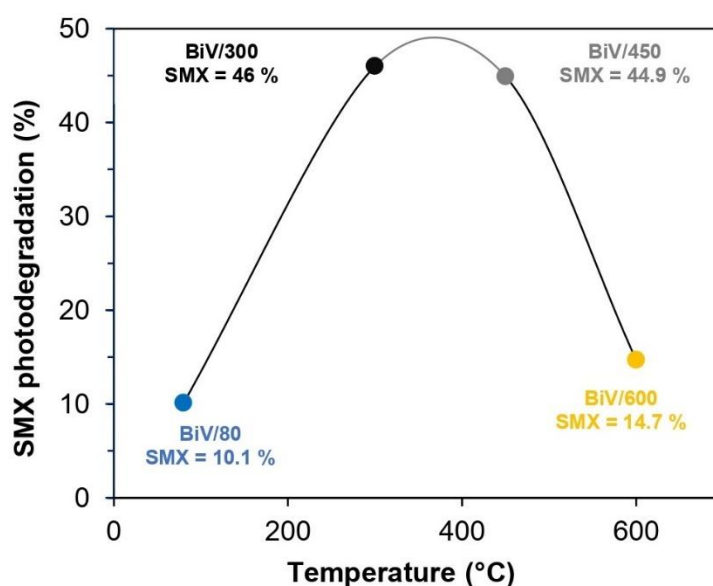


Figure 3.2. % of SMX photodegradation using undoped BiV/T (T = 80, 300, 450 and 600 °C) photocatalysts as a function of calcination temperature. The optimal temperature seems to be 335 °C.

Among the prepared photocatalysts, the sample treated at 300 °C, named BiV/300, was selected as the closest to the optimal temperature due to its proximity to the theoretical value of 335 °C, and for this reason the silver doped samples prepared were those named as Ag/BiV/80 and Ag/BiV/300 for the corresponding photo-degradation study.

Figure 3.3 shows the X-ray diffractogram of the BiV/T and Ag/BiV/T photocatalyst system (T = corresponds to the calcination temperature in °C) and the Miller indices attributed to the main peaks of the monoclinic scheelite phase (*m-s*) assigned to JCPDS No. 00-075-1866, detected in all photocatalysts [6].

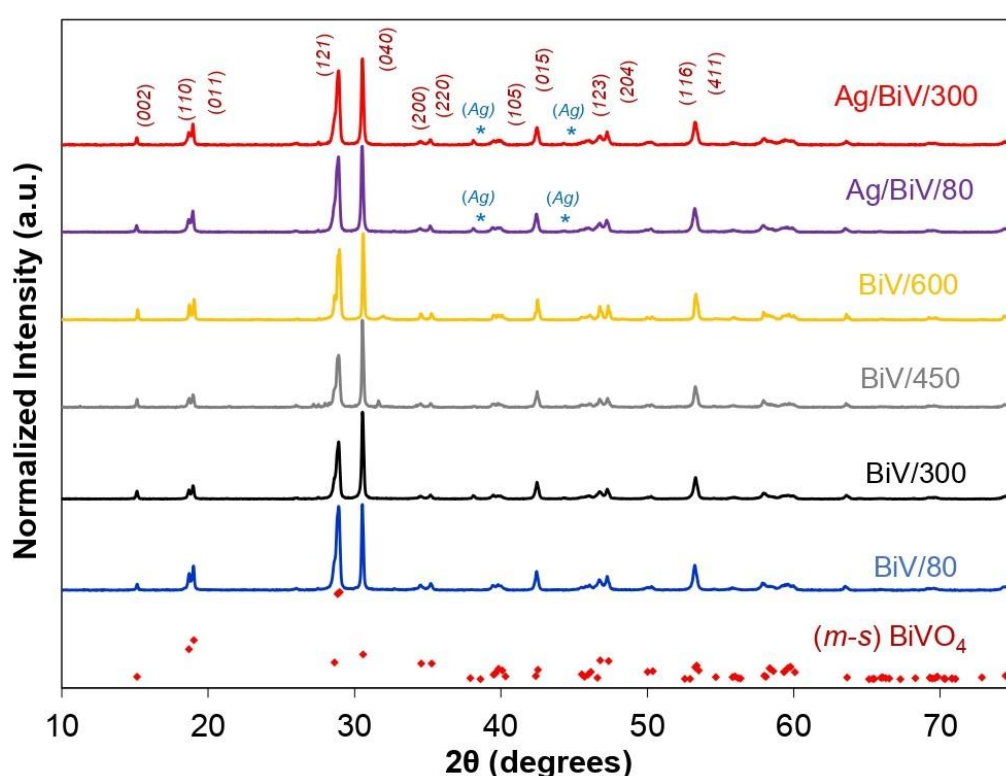


Figure 3.3. XRD pattern of undoped BiV/T (T = 80, 300, 450 and 600 °C) and doped Ag/BiV/T (T = 80 and 300 °C) photocatalysts.

Figure 3.4 presents an enlargement of the diffraction patterns in the 28-31.5 ° range. The intensities at 28.5 ° and 30.5 ° correspond to the crystalline planes (121) and (040), respectively.

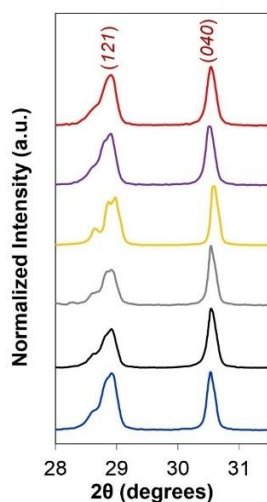


Figure 3.4 Enlargement of the 2θ degree area representing the (121) and (040) crystalline planes of (*m-s*) BiVO_4 .

In **Figure 3.4**, an increase in the intensity of the diffraction peak of the (040) crystalline plane concerning (121) was also observed as the temperature was increased from 80 to 300 °C, during the synthesis of the photocatalysts. The increase in the intensity of the (040) plane peak indicates higher crystallinity, which can significantly enhance the photocatalytic activity of the materials to degrade organic pollutants [7,8]. Regarding the photocatalysts containing Ag (Ag/BiV/80 and Ag/BiV/300), the main diffraction peaks attributed to metallic Ag ($2\theta = 38^\circ$ and 44°) (JCPDS No. 65-2871) were observed in both samples, but at low intensity, due to the low weight percentage of Ag added (3.5 wt.% Ag) [9].

Figure 3.5a and **b** show the correlations of the intensity ratio $I(121)/I(110)$ and $I(040)/I(110)$ concerning the synthesis temperature of the photocatalysts, for the BiV/T ($T = 80, 300, 450$, and 600 °C) and Ag/BiV/T ($T = 80$ and 300 °C) samples.

In **Figure 3.5a**, an increase of the intensity ratio $I(121)/I(110)$ was observed with increasing temperature from 80 to 300 °C. From 300 to 600 °C, the intensity ratio $I(121)/I(110)$ decreased slightly as the synthesis temperature increased. On the other hand, the increase in temperature during the synthesis of the photocatalysts showed a greater effect on the intensity ratio of $I(040)/I(110)$ for all the samples. For example, the intensity ratio $I(040)/I(110)$ increased from 4.6 to 8.5 (1.84 times) as the temperature increased from 80 to 300 °C. These results indicated that temperature can influence the orientation of the crystal growth during the synthesis of BiVO₄.

In **Figure 3.5b**, it can be seen that the intensity ratios $I(121)/I(110)$ and $I(040)/I(110)$ increased slightly as the synthesis temperature was raised from 80 to 300 °C. It can also be observed that the intensities $I(121)/I(110)$ are slightly higher, compared to the photocatalysts not containing Ag (See **Figure 3.5a**).

The average crystal size (dp) of the photocatalysts was determined using the Debye-Scherrer equation ([2.4.1 section](#)) [10] and the results are shown in **Table 3.1**. The dp varied from 16 to 20 nm as the temperature increased during the synthesis of the photocatalysts. These results can be attributed to the formation of crystal defects due to oxygen evolution and decomposition or destruction of the BiVO₄ crystal at high temperatures [11,12]. The photocatalysts containing Ag showed a larger dp size compared to those without Ag. The dp was 23 and 22 nm for Ag/BiV/80 and Ag/BiV/300, respectively.

Since the solvothermal synthesis temperature of all photocatalysts was 80 °C and the calcination temperature of 300 °C was the closest to optimal, the undoped materials treated at these temperatures were selected to be studied by nitrogen

adsorption-desorption at 77 K to analyze the textural changes between the freshly prepared precursor and the one that would subsequently be doped with silver

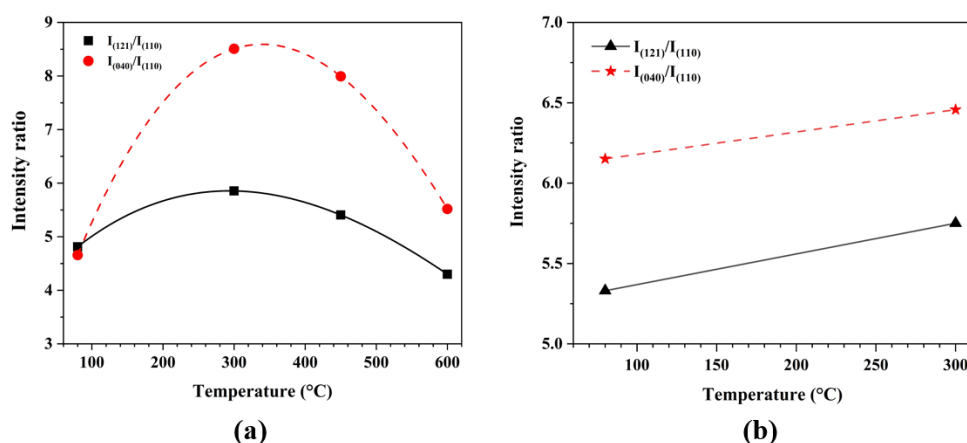


Figure 3.5. Correlation of the intensity ratio of $I(121)/I(010)$ and $I(040)/I(110)$ in the diffraction patterns of a) undoped BiV/T ($T = 80, 300, 450$ and 600 °C) and b) doped Ag/BiV/T ($T = 80$ and 300 °C) photocatalyst with synthesis temperature.

Table 3.1. Particle size (from XRD) and band-gap values of undoped BiV/T ($T = 80, 300, 450$, and 600 °C) and doped Ag/BiV/T ($T = 80$ and 300 °C) photocatalysts.

Photocatalyst	dp	Band Gap
	nm	eV
BiV/80	16	2.37
BiV/300	18	2.40
BiV/450	19	2.49
BiV/600	20	2.45
Ag/BiV/80	23	2.48
Ag/BiV/300	22	2.47

3.3.2 Nitrogen adsorption-desorption isotherms at 77 K

The textural properties of the samples BiVO₄ at lower temperatures (80 and 300 °C) are shown in **Figure 3.6** and **Table 3.2**. The **Figure 3.6** shows the nitrogen adsorption-desorption isotherms at 77 K for the photocatalysts. In both cases, the isotherms share similar characteristics and belong to type II according to the IUPAC classification, with an H3 hysteresis loop. This behavior commonly occurs when the adsorption curve differs from the desorption curve, which is a characteristic feature of non-porous samples [13,14].

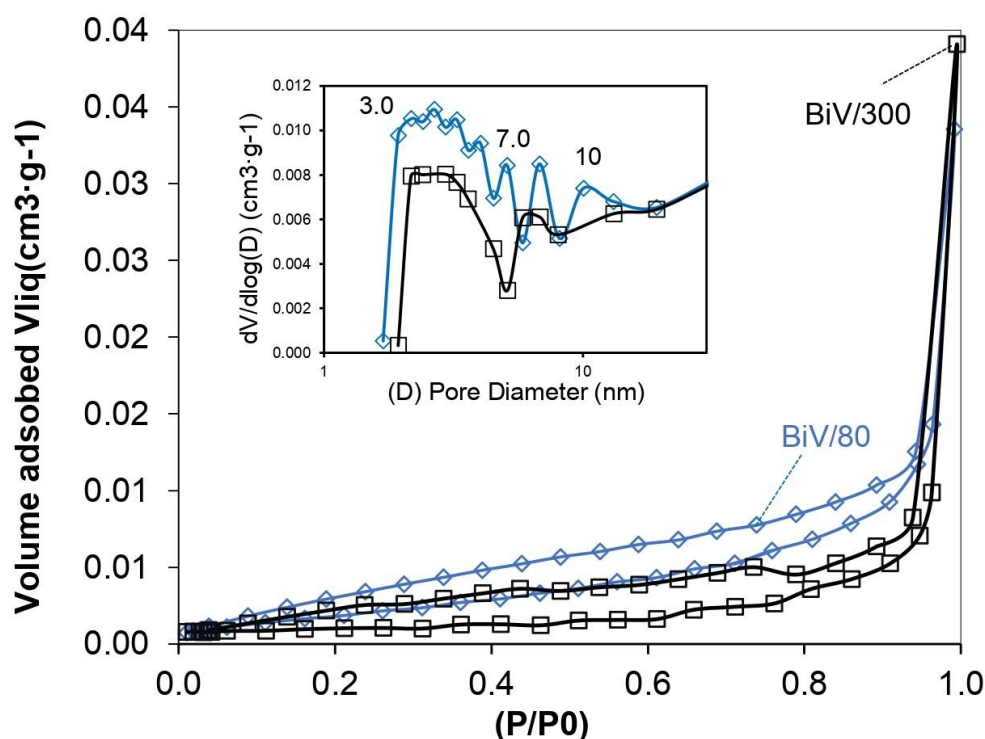


Figure 3.6. N₂ adsorption-desorption isotherms of undoped BiV/T (T = 80 and 300 °C) photocatalysts.

The inserted imagen in **Figure 3.6** shows the Barrett–Joyner–Halenda (BJH) pore size distributions. These results indicate that the pore diameters of the samples are primarily distributed in the range of 3-10 nm, a distribution similar to that presented by Shining [15].

However, the concentration of macropores is higher in the sample BiV/80 at lower temperatures, and their presence can be attributed to empty spaces between the grains of the sample.

Table 3.2 shows that the specific surface areas calculated from the S_{BET} equation were 5.1 and 2.2 $\text{m}^2 \text{g}^{-1}$ for BiV/80 and BiV/300, respectively. Based on the type and shape of the adsorption isotherm (see **Figure 3.6**), as well as the surface area BET calculation, it can be concluded that the samples are non-porous due to the negligible value of specific surface areas [13].

Table 3.2. The textural properties result of undoped BiV/T (T = 80 and 300 °C) photocatalysts.

	S_{BET}	S_{DR}	S_{mic}	$W_0 (\text{N}_2)$	$W_{0.95}$	V_{meso}	$L_0 (\text{N}_2)$
Photocatalyst	$\text{m}^2 \text{g}^{-1}$	$\text{m}^2 \text{g}^{-1}$	$\text{m}^2 \text{g}^{-1}$	$\text{cm}^3 \text{g}^{-1}$	$\text{cm}^3 \text{g}^{-1}$	$\text{cm}^3 \text{g}^{-1}$	nm
BiV/80	5.1	5.8	0.0	0.002	0.005	0.003	3.27
BiV/300	2.2	2.9	0.2	0.001	0.002	0.001	1.94

3.3.3 UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS)

Figure 3.7 shows the UV-Vis absorption spectra of the photocatalyst. Strong absorption in the UV-Vis region, confirming the optical response of these materials.

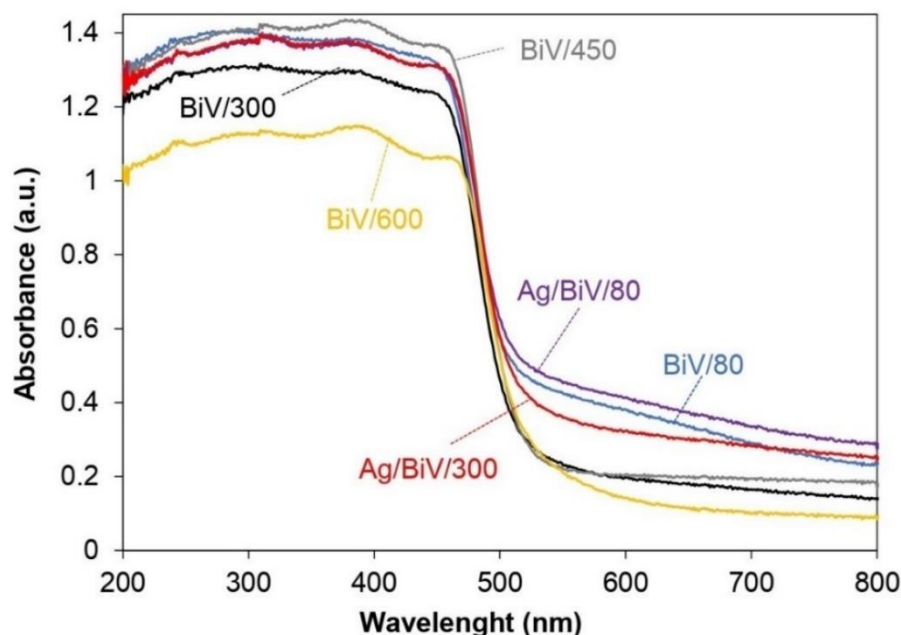


Figure 3.7. Diffuse Reflectance spectra of undoped BiV/T (T=80, 300, 450 and 600 °C) and doped Ag/BiV/T (T = 80 and 300 °C) photocatalysts.

A sample methodology for determining the E_g values of the photocatalyst system is shown in **Figure 3.8**. These values were obtained using the Kubelka-Munk method $[F(R)-E]^{1/2}$ [16]. The photocatalysts showed E_g values of 2.37 eV (BiV/80), 2.40 eV (BiV/300), 2.49 eV (BiV/450), 2.45 eV (BiV/600), 2.48 eV (Ag/BiV/80) and 2.47 eV (Ag/BiV/300) (see **Table 3.1**). These values slightly increase with the rise in synthesis temperature and correspond to the E_g values of the (*m-s*) BiVO₄ phase [7]. The E_g values for Ag/BiV/80 and Ag/BiV/300 were similar to those without Ag. This result might be due to the low weight percentage of Ag added. However, its presence, even in low weight percentages, can significantly enhance the photocatalytic activity [17].

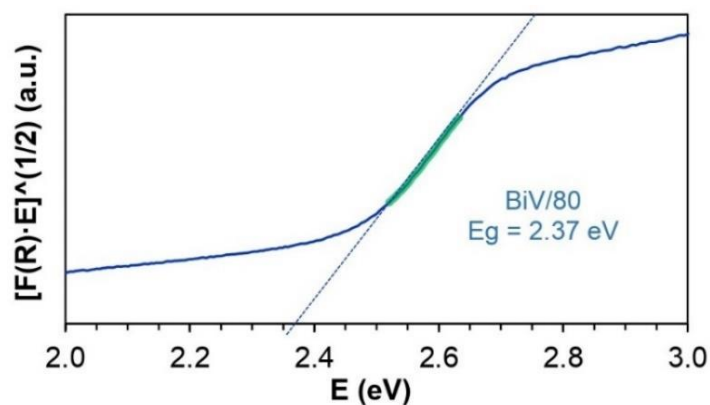


Figure 3.8. Sample methodology for determining the band-gap (E_g) in undoped photocatalyst at synthesis temperature (BiV/80).

3.3.4 Scanning Electron Microscopy (SEM)

To investigate the morphological changes due to the effect of calcination temperature, the SEM images [18] of all undoped photocatalysts are presented in **Figure 3.9**. The morphology of the samples is closely linked to the thermal treatment temperature. **Figure 3.9a-b** for the sample at 80 °C (BiV/80) shows agglomerated shapes with dimensions between 1 and 3 μm , while individual particles, nearly spherical in shape, have sizes around 150 nm.

At calcination temperature of 300 °C (BiV/300), **Figure 3.9c-d** show few differences compared with the precursor; agglomerated shapes remain due to the union of individual particles. An important morphological feature corresponds to its pine-like architecture, as observed by Le-Duy [19]. However, this sample exhibits the smallest sizes among all the samples; some individual particles have reduced their size to values below 100 nm.

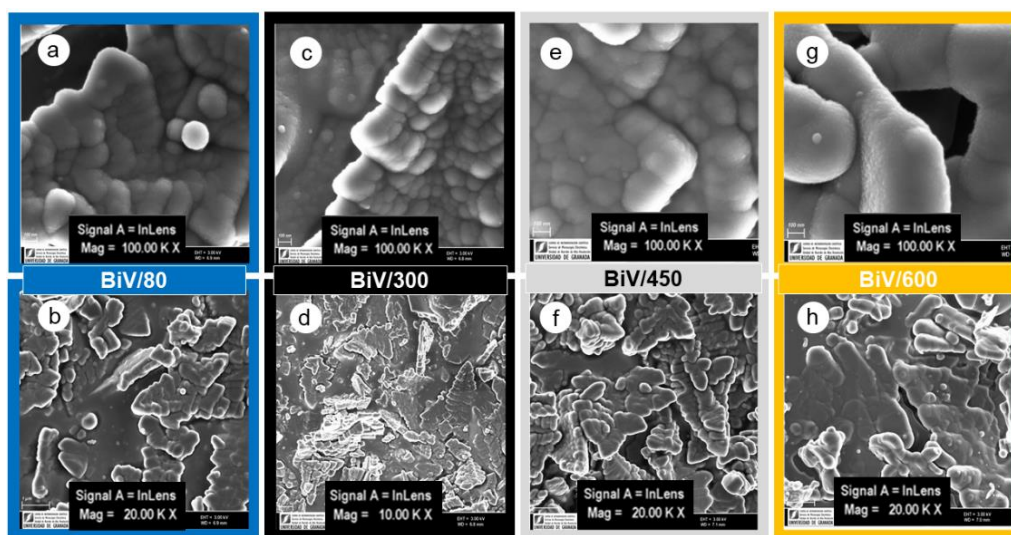


Figure 3.9. SEM images of undoped BiV/T (T = 80, 300, 450 and 600 °C).

For the sample treated at 450 °C (BiV/450), the images in **Figure 3.9e-f** show a significant change in the aggregate size. Contrary to the phenomenon observed in BiV/80 and BiV/300, the aggregates are now much larger, with sizes above 150 nm. At 600 °C, the effect of temperature is noticeable when observing the images in **Figure 3.9g-h** for the BiV/600 sample. There is a significant loss of porosity; now the aggregates are much larger and less porous, with sizes reaching several microns. For example, **Figure 3.9g** shows that at this temperature, the aggregates scarcely exhibit shapes below 100 nm and are much larger. This difference in sizes can be explained by the crystallization processes to which the samples were subjected.

3.3.5 High Resolution Transmission Electron Microscopy (HRTEM)

Due to its superior performance in the photodegradation of the probe molecule, the sample containing Ag calcined at 300 °C (Ag/BiV/300) was analyzed by HRTEM.

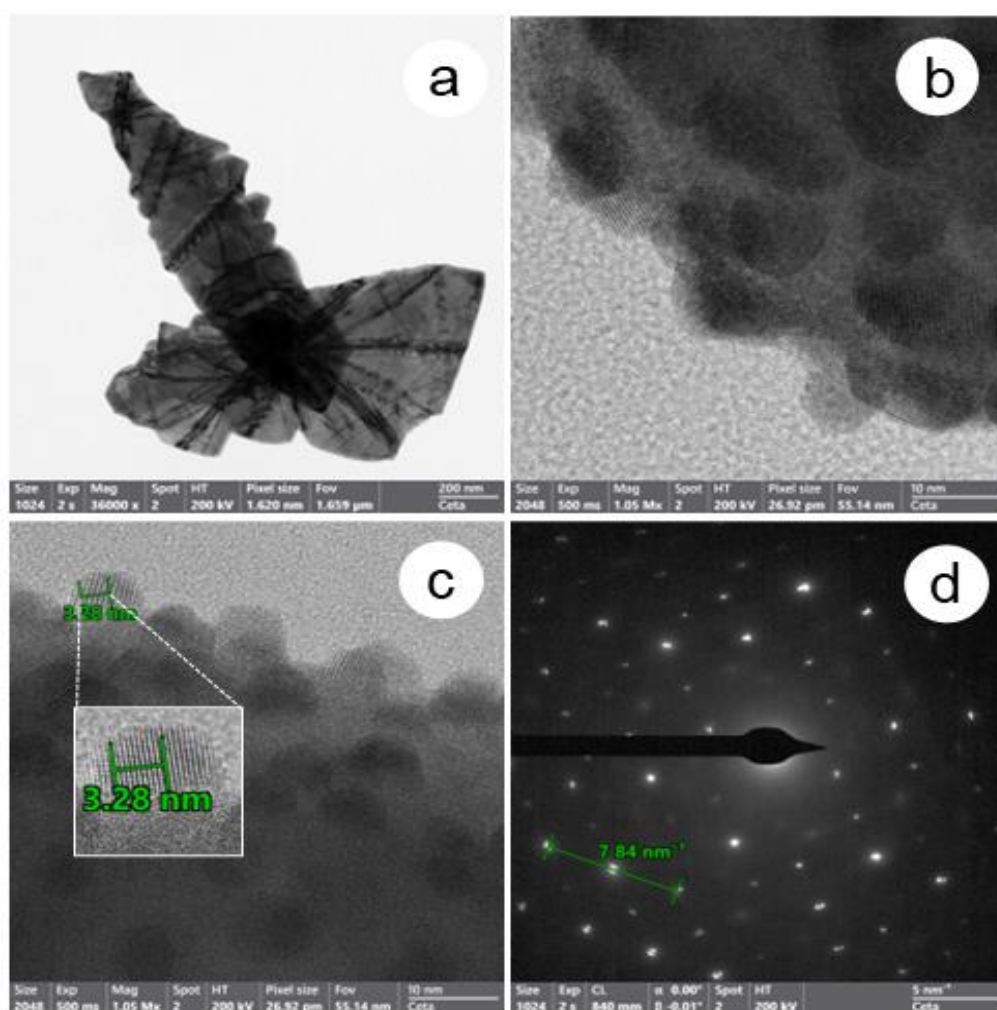


Figure 3.10. HRTEM image of doped Ag/BiV/T (T = 300 °C).

Figure 3.10a shows a single particle of the sample, highlighting its irregular characteristics, formed by the aggregation of smaller plate-like particles with heterogeneous shapes. The micrographs in **Figure 3.10b-c** show the lattice fringes of BiVO₄ with an approximate dimension of 0.36 nm, corresponding to the crystallographic planes (101) [20]. **Figure 3.10d**, shows the symmetrical arrangement of the white diffraction points, confirming the polycrystalline nature of BiVO₄.

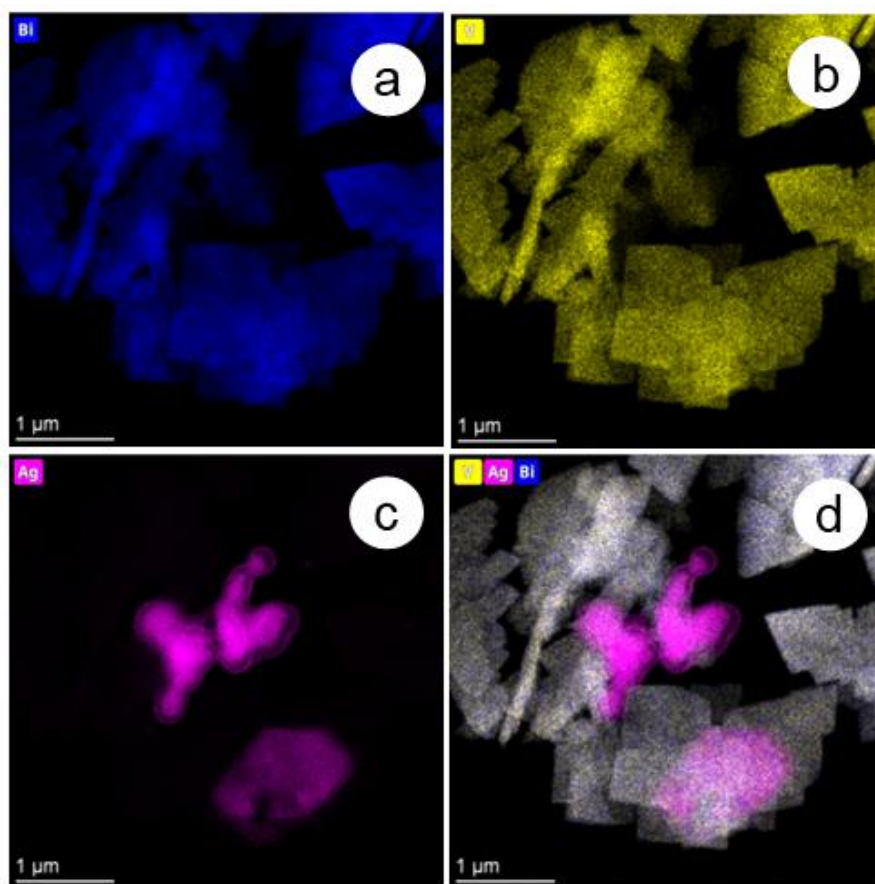


Figure 3.11. EDS-HRTEM image of doped Ag/BiV/T (T = 300 °C).

To identify the elemental composition of the sample, elemental mapping was performed using EDS technique. The images corresponding to the presence of bismuth (blue color), vanadium (yellow color), and silver (pink color) are presented in **Figure 3.11**. This morphology confirms that, after calcination, the crystallinity of the silver-doped sample was preserved. This is evidenced by the formation of silver metallic nanoparticles, as confirmed by X-ray diffraction, where the characteristic crystallographic plane (111) of Ag^0 was observed (see **Figure 3.3**). These characteristics suggest that Ag^{+1} cations has been reduced to Ag^0 during the thermal treatment process and that silver nanoparticles were possibly coated on the BiVO_4 surface, as shown in **Figure 3.11c-d**.

3.3.6 X-ray Photoelectron Spectroscopy (XPS)

In order to study the chemical nature for all samples, the surface chemistry properties were analysed by XPS. High-resolution spectra were obtained for the BiVO_4 photocatalyst treated at various temperatures and those doped with silver, initially focusing on the four elements: C, Bi, V, and O.

These elements were represented by the C_{1s} , Bi_{4f} , V_{2p} , and O_{1s} spectrums, respectively, as shown in **Figure 3.12** and **Figure 3.13**. Additionally, **Figure 3.13e** illustrates the $\text{Ag}_{3d5/2}$ band, which was used to determine the silver content in the doped samples. **Table 3.3** displays the surface element content, binding energy, and percentage of the components used to fit the C_{1s} , Bi_{4f} , V_{2p} , O_{1s} , and $\text{Ag}_{3d5/2}$ spectral regions of the BiVO_4 samples.

Three peaks were necessary to accurately model the C_{1s} spectral region at 284.6, 285.8, and 288.1 eV, identified as C-C, C-O, and COO^- , respectively (see

Figure 3.12a and **Figure 3.13a** and **Table 3.3**). Among them, the peak at 284.6 eV was used to calibrate the surface charge, which is characteristic of adventitious carbon and was used for internal calibration for all binding energies corresponding to sp^3 hybridization [21]. The adsorption of CO_2 molecules increases, leading to the formation of carbon intermediates due to the presence of oxygen vacancies, which can significantly impact the interaction between the surface and CO_2 [22,23]. It is important to note that the carbon content appears to depend on the surface area of the samples. Subsequently, the deconvolution of the $Bi4f$ spectra for both silver undoped and doped samples (**Figure 3.12b** and **Figure 3.13b**) reveals two main peaks at the binding energy values of 158.7 and 159.4 eV, with an orbital splitting of 0.7 eV. These peaks are attributed to the $Bi4f_{7/2}$ and $Bi4f_{5/2}$ lines of Bi^{+3} [6,24].

Figure 3.12c and **Figure 3.13c** displays the deconvolution of the high-resolution XPS spectrum of V_{2p} , revealing well-defined binding energy peaks located at 516.1 eV and 523.8 eV for both silver undoped and doped $BiVO_4$. These peaks are attributed to V^{5+} indicating the presence in $BiVO_4$ [24].

Figure 3.12 and **Figure 3.13d** depict the high-resolution O_{1s} binding energy peak, with the main peaks located at 529.3 and 530.6 eV, respectively, show in **Table 3.3**. These peaks correspond to the bond between Bi and O in the crystal lattice and surface of $BiVO_4$. The peak at 529.3 eV could be assigned to the total oxygen atoms in the stoichiometric form, while the peak at 530.6 eV corresponds to superficial oxygen, forming functional groups, mainly hydroxyl (OH^-) groups whereas the peak at 532.5eV could be assigned C-O bonds of the oxygenated surface groups of the carbon phase [25].

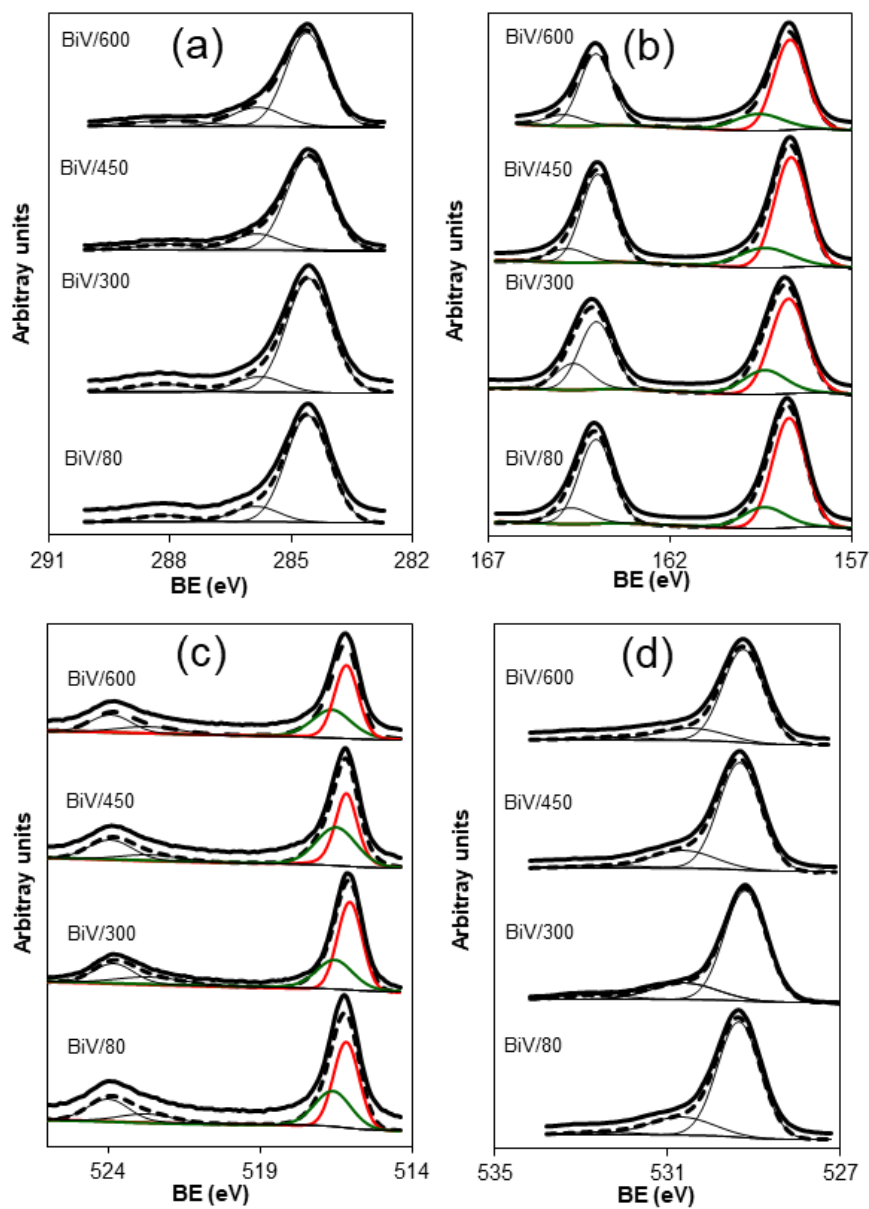


Figure 3.12. XPS spectra of undoped BiV/T (T=80, 300, 450 and 600 °C) photocatalysts a) C_{1s}, b) Bi_{4f}, c) V_{2p} and, d) O_{1s}.

Figure 3.13e comparatively shows the spectra for samples treated at 80 and 300 °C, both undoped and silver-doped, confirming the presence of silver.

The high-resolution spectrum of Ag exhibits the characteristic 3d doublet structure with a binding energy of 367.8 eV and a doublet splitting of 5.8 eV (to 373.6 eV). The major peak at 367.8 eV indicates the presence of pure metallic silver in the Ag⁰ state and corresponds to the Ag_{3d5/2} spectrum. The minor peak at 368.1 eV could be attributed to the presence of silver (II) oxide [26,27].

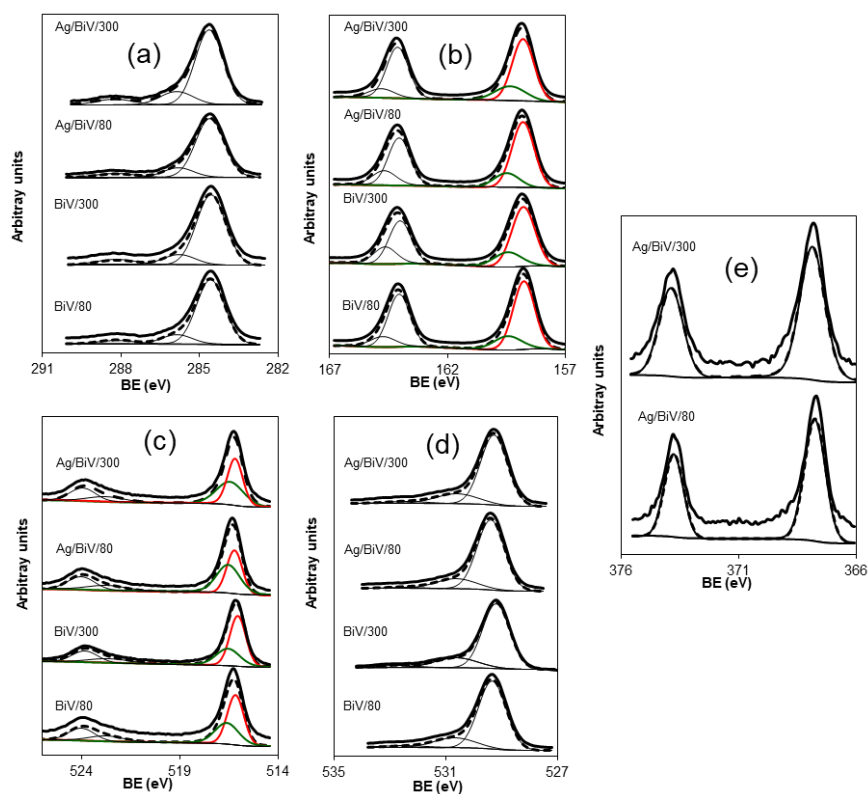


Figure 3.13. XPS spectra of doped with silver Ag/BiV/T (T = 80 and 300 °C) photocatalyst a) C_{1s}, b) Bi_{4f}, c) V_{2p} and, d) O_{1s} and, e) Ag_{3d5/2}.

The atomic percentage found for all elements in all samples was adjusted to match the theoretical percentage expected according to the values are shown in **Table 3.3**.

Overall, the presence of silver in the samples, ranging between 1.3 and 1.8 wt.%, for Ag/BiV/80 and Ag/BiV/300, respectively, enhances the photocatalytic activity of BiVO₄ samples, which can be advantageous for improving its photocatalytic behavior due to the formation of Ag⁰ nanoparticles.

Table 3.3. XPS results of undoped BiV/T (T = 80, 300, 450 and 600 °C) and doped Ag/BiV/T (T = 80 and 300 °C) photocatalyst: the surface element content, binding energy and percentage of the components used to fit the C1s, Bi4f, V2p, O1s and, Ag3d5/2 spectral regions of BiVO₄ samples.

Sample	C _{1s}	peak	C	C	O _{1s}	peak	O	O
	eV	%	wt.%	at.%	eV	%	wt.%	at.%
BiV/80	284.6	81	12.5	44.0	529.3	80	13.4	35.2
	285.9	13			530.7	18		
	288.2	6			532.5	2		
BiV/300	284.6	80	14.4	48.0	529.2	78	13.2	32.9
	285.8	12			530.6	18		
	288.2	7			532.7	4		
BiV/450	284.6	79	12.1	43.4	529.3	77	13.2	35.4
	285.8	15			530.7	20		
	288.0	7			532.6	3		
BiV/600	284.6	74	14.8	48.7	529.3	80	12.9	31.9
	285.8	18			530.5	17		
	288.1	7			532.3	4		

Table 3.3 (continued)

Sample	V _{2p3/2} eV	peak %	V wt. %	V at. %	Bi _{4f7/2} eV	peak %	Bi wt. %	Bi at. %
BiV/80	516.2	44	9.3	7.7	158.7	45	64.8	13.1
	516.6	29			159.4	12		
BiV/300	516.1	47	8.8	6.9	158.8	43	63.5	12.1
	516.6	25			159.4	14		
BiV/450	516.2	40	9.1	7.7	158.7	45	65.6	13.5
	516.5	34			159.4	13		
BiV/600	516.2	44	9.6	7.5	158.7	46	62.7	11.9
	516.7	30			159.6	12		

Table 3.3 (continued)

Sample	C _{1s} eV	O _{1s} eV	peak %	O wt. %	O at. %	V _{2p3/2} eV	peak %	V wt. %	V at. %
Ag/BiV/80	284.6	529.4	80	13.6	36.2	516.2	35	9.9	8.3
	285.8	530.6	18			516.5	37		
	288.2	532.5	2						
Ag/BiV/300	284.6	529.3	79	13.2	32.1	516.2	38	9.7	7.4
	285.9	530.6	18			516.5	35		
	288.2	532.4	3						

Table 3.3 (continued)

Sample	Bi _{4f7/2} eV	peak %	Bi wt. %	Bi at. %	Ag _{3d5/2} eV	Ag wt. %	Ag at. %
Ag/BiV/80	158.8	46	63.4	12.9	367.8	1.3	0.5
	159.5	11					
Ag/BiV/300	158.8	43	60.4	11.3	367.9	1.8	0.6
	159.3	14					

3.3.7 Photodegradation Results

Figure 3.14 displays all the photodegradation experimental points and a graphical representation of the selected best-fit LHHW model. Before initiating the photodegradation reaction, adsorption experiments were conducted in the dark for 12 h to assess the potential SMX adsorption on the surface of BiVO_4 samples.

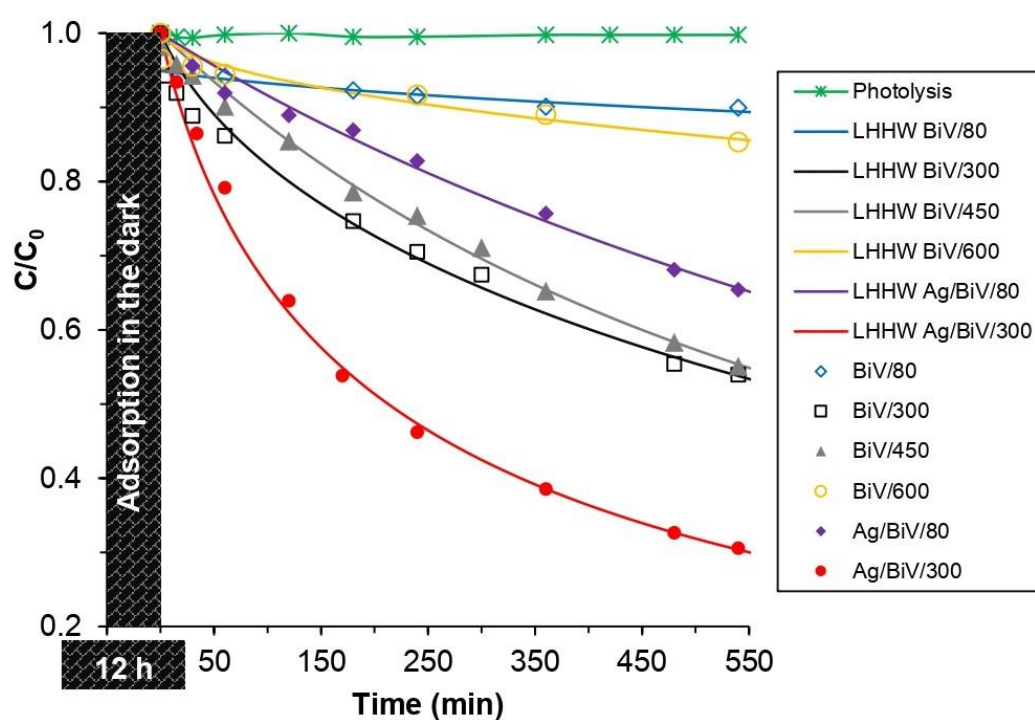


Figure 3.14. Photodegradation results for SMX degradation using undoped BiV/T ($T = 80, 300, 450$, and $600\text{ }^{\circ}\text{C}$) and doped Ag/BiV/T ($T = 80$ and $300\text{ }^{\circ}\text{C}$) photocatalysts (dots) under blue-LED irradiation. The best-fit LHHW mathematical models (continuous color lines) are shown to compare the theoretical and experimental trends.

In all cases, there was no noticeable change in the concentration of SMX, indicating the non-porosity of the samples. In addition, this figure illustrates that in the absence of the photocatalyst (photolysis, represented by the green line), the SMX concentration remained unchanged after 540 min of irradiation.

Table 3.4 presents the photodegradation results after 540 min. BiV/80 induced only 10.1 % photodegradation, which is consistent with the trend reported by Le-Duy et al. [19]. Conversely, the undoped sample BiV/300, treated at 300 °C, demonstrated the most efficient calcination temperature, leading to 46 % photodegradation. BiV/450, treated at 450 °C, resulted in 44.9 % photodegradation of SMX. However, only 14.7 % photodegradation of SMX was achieved using the BiV/600 sample. Ag/BiV/80 ranked as the fourth best sample, as the addition of Ag as a dopant agent increased the photodegradation to 34.6 %.

The Ag/BiV/300 photocatalyst emerged as the top performer for degrading the SMX antibiotic, reaching 69.7 % in 540 min. This sample achieved the same photodegradation percentage as the sample without Ag nanoparticles (BiV/300) but in only 171 min. This significant reduction in degradation time highlights the enhanced efficiency conferred by the presence of Ag nanoparticles.

Among the undoped photocatalysts treated at the lowest and highest temperatures, BiV/80 and BiV/600, respectively, exhibited slightly similar photodegradation efficiency percentages of 10.1 % and 14.7 %. However, these magnitudes differed significantly when compared with samples treated at intermediate temperatures (300 and 450 °C), achieving efficiencies of 46 % and 44.9 %, respectively.

Table 3.4. % of SMX photodegradation using undoped and doped BiVO₄ calcinated photocatalyst, pseudo-reaction order (n), kinetic constants A and B of the best-fit LHHW models and correlation factor (R^2). The initial aqueous concentration of SMX was 5 mg L⁻¹.

Photocatalyst	% SMX degradation	reaction order n	A (10 ⁻³)	B (10 ⁻³)	R^2
BiV/80	10.1	2	56.6186	0.0029	0.9643
BiV/300	46.0	1	198.6829	0.3980	0.9969
BiV/450	44.9	1	164.4503	0.6171	0.9986
BiV/600	14.7	1	193.5677	0.0234	0.9849
Ag/BiV/80	34.6	1	94.8051	0.4769	0.9959
Ag/BiV/300	69.7	2	20.3644	0.8087	0.9992

Regarding the doped samples, silver nanoparticles significantly enhanced the photodegradation of SMX due to the synergistic effect between the optimal calcination temperature and the dopant. Consequently, the capacity for SMX degradation for the precursor treated at 80 °C increased threefold to 34.6 % with the silver-doped sample at the same temperature. Similarly, BiVO₄ treated at 300 °C improved by 1.5 times, increasing from 46 % to 69.7 %.

3.3.8 Mathematical model of photodegradation results

The methodology for validating the best-fit mathematical model for the photodegradation experiments involves two distinct sets: The first set corresponds to the classical Power-Law model, which is described by **Equation 3-1**, where r_A , K_{app} , and C_A represent the reaction velocity, apparent rate constant, and residual concentration (mg L⁻¹) of chemical species A (In our study A is SMX) at any time

of irradiation (t), respectively. The values for the parameter n which denotes the pseudo-Nth order of reaction, were selected to be 0, 1, or 2.

$$-r_A = \frac{dC_A}{dt} = k_{app} C_A^n$$

Equation 3-1. Reaction rate law for the Power-Law model for the nth pseudo-reaction order (n).

Second set corresponds to the Langmuir-Hinshelwood-Hougen-Watson (LHHW) heterogeneous catalytic model, which is a more realistic model that considers both mass transfer and surface chemical reactions on solid photocatalysts. In summary, the following steps can be identified during the solid-liquid reaction: 1) diffusion of pollutant molecules from the liquid solution to the external surface of the photocatalyst, 2) diffusion or penetration of the pollutant into the pores of the solid photocatalyst to the reaction sites, 3) adsorption of the pollutant onto the photocatalyst surface, 4) surface chemical reaction, 5) desorption of the degraded products from the photocatalyst surface to the liquid phase, 6) diffusion or outlet of degraded products from the pores of the solid photocatalyst to the exterior, and 7) diffusion of degraded products into the liquid solution. In many chemical reactions, only the early steps are slower than the others, making them the determining step for the total reaction rate.

Therefore, due to their heterogeneous nature, our catalysts must provide a surface for the surface chemical reaction to occur at some point in the reaction mechanism, which occurs after the SMX pollutant is adsorbed onto the photocatalyst surface and subsequently desorbed into degraded products. The

surface phenomena corresponding to steps 3, 4, and 5 of the reaction mechanism are as follows: 1) adsorption of SMX onto the modified-BiVO₄ photocatalyst, 2) surface chemical reaction for the degradation of SMX, and 3) desorption of the degraded species.

LHHW model, which is described by **Equation 3-2**, where A and B are two different kinetic rate constants derived from the assumption that the desorption process is negligible compared with the adsorption and reaction steps. Specifically, $A = K_A/K_{sr}$ and $B = K_A C_t$, where K_A and K_{sr} are the adsorption and reaction constants, respectively, and C_t is the concentration of active sites on the catalyst surface [28].

$$-r_A = \frac{dC_A}{dt} = \frac{BC_A^n}{(1 + AC_A^n)}$$

Equation 3-2. Reaction rate law for the LHHW heterogeneous catalytic model for the n th pseudo-reaction order (n).

Upon solving differential **Equation 3-1** Equation 3-2 for the three reaction orders ($n = 0, 1$, and 2) six mathematical expressions for modeling SMX photodegradation were obtained, as shown in **Table 3.5**.

The experimental results using undoped BiV/T ($T = 80, 300, 450$ and 600 °C) and doped Ag/BiV/T ($T = 80$ and 300 °C) photocatalyst were graphically compared with each mathematical model. All Power-Law-based models showed a similar trend, with correlation factors below 75 %. Alternative methods suggested $n = 2.2$ as the best pseudo-reaction order in several cases, but much greater than 2.2 for the

precursor sample, which has no physical significance. In addition, this general model does not consider the steps involved in the kinetics of heterogeneous reactions, indicating that it inadequately describes the photodegradation process.

Table 3.5. Mathematical expressions for modeling photodegradation under Power-Law and LHHW models at n pseudo-reaction orders ($n = 0, 1$, and 2).

n	Power-Law	LHHW
0	$t = -\frac{C_{A0}}{k} (X - 1)$	$t = \frac{AC_{A0}}{B} (1 - X) - \frac{C_{A0}}{B} (X - 1)$
1	$t = \frac{1}{k} \ln \left(\frac{1}{X} \right)$	$t = \frac{AC_{A0}}{B} (1 - X) + \frac{1}{B} \ln \left(\frac{1}{X} \right)$
2	$t = -\frac{1}{kC_{A0}} \left(1 - \frac{1}{X} \right)$	$t = \frac{AC_{A0}}{B} (1 - X) - \frac{1}{BC_{A0}} \left(1 - \frac{1}{X} \right)$

In contrast, the realistic LHHW model, which considers the surface chemical reaction, offered the best correlation factor in all cases (see **Table 3.4**). The kinetic constants were obtained by establishing an objective function (**Equation 3-3**) to minimize the sum of the quadratic differences between the calculated values and the experimental measurements.

$$F_{objective} = \sum (t_{calculated} - t_{measured})^2$$

Equation 3-3. Objective function to minimize the difference between the calculated value of t by the LHHW model and that found experimentally.

Kinetic constants A and B were calculated from the equations in **Table 3.5** using the conjugate gradient method and Excel [28,29]. A summary of the results, including the kinetic constants, is presented in **Table 3.4**. For the best-performing photocatalyst, the kinetic constants A and B were $20.3644 \cdot 10^{-3}$ and $0.8087 \cdot 10^{-3}$, respectively, with an R^2 of 0.9992.

LHHW catalytic models showed superior adjust with the experiments, with R^2 correlations exceeding 96 % between theoretical predictions and experimental values. The best-fit models were for orders $n = 1$ and $n = 2$, corresponding to **Equation 3-4a-b**.

$$t = \frac{AC_{A0}}{B}(1-X) + \frac{1}{B} \ln\left(\frac{1}{X}\right)$$

(a)

$$t = \frac{AC_{A0}}{B}(1-X) - \frac{1}{BC_{A0}} \left(1 - \frac{1}{X}\right)$$

(b)

Equation 3-4. Mathematical expressions for LHHW heterogeneous catalytic model: (a) $n = 1$ (b) $n = 2$.

The non-zero kinetic rate constant A for all samples (see **Table 3.4**) indicates a significant relationship between the reaction velocity and the SMX concentration. This suggests that the mass transfer process from the aqueous solution to the catalyst surface significantly influences the overall photodegradation, highlighting the importance of SMX adsorption onto the photocatalytic surface.

This behavior, previously discussed by Scotti et al. [30], indicates a preference for the first-order mechanism in the LHHW model to describe the photochemical reaction on a heterogeneous surface is the determining step, and that the reaction velocity is directly proportional to the SMX concentration.

3.4 CONCLUSIONS

Bismuth vanadate photocatalysts were synthesized using the hydrothermal method with modifications at different calcination temperatures and dopant introduction. Within the used experimental conditions these photocatalysts achieved 46 % efficiency in the photodegradation of sulfamethoxazole solution under blue-LED without dopant at the optimal calcination temperature (300°C). After doping with Ag the efficiency increased to 69.7 % enhancing the degradation capacity by an additional 23.7 %.

X-ray diffraction confirmed that with the hydrothermal synthesis method the monoclinic phase (*m-s*) was successfully crystallized keeping stable even after the thermal treatments at 300, 450, and 600 °C; monoclinic phase was obtained also with silver doped samples. The band-gap (*E_g*) values obtained using the Kubelka-Munk method ranged from 2.37 to 2.49 eV, with the best-performing sample showing a band-gap of 2.47 eV.

The small *E_g* of 2.40 eV and the average particle size of 18 nm of the catalyst treated at 300 °C could justify its most efficient photocatalytic behavior among the undoped samples. HRTEM confirms DRX results as well as the presence of silver into the doped samples.

The very low Ag superficial contents (determined by XPS) enhance a lot the photocatalytic performance of the BiVO₄ based catalysts.

Before blue-LED irradiation on the SMX solution, physical adsorption on the photocatalysts was negligible. Thus, the observed SMX photodegradation was

attributed to the presence of the photocatalyst, as confirmed by direct photolysis tests without the catalyst. The high photoactivity of the samples is likely due to the stabilization of the monoclinic phase during thermal treatment and the reduction of e^-/h^+ recombination by stabilizing the active sites.

Two sets of mathematical models were applied to the SMX degradation results. The Power-Law model, with the lowest correlation factors, showed that this model inadequately describes the photodegradation process. In contrast, the best model for all tests was the Langmuir-Hinshelwood-Hougen-Watson model despite the low apparent surface areas of these materials. In all tests, the non-zero kinetic rate constant $A = K_A/K_{sr}$ indicates that the mass transfer process from the aqueous solution to the catalyst surface directly influences the overall photodegradation of sulfamethoxazole.

Due to their simple preparation and right stabilization of the monoclinic active phase controlling both, temperature and dopant addition, these BiVO_4 based photocatalysts are an economical and potentially accessible option for the photodegradation of emerging contaminants in water using solar light under ambient conditions, and with low toxicity as secondary effects in comparison with other water treatment technologies.

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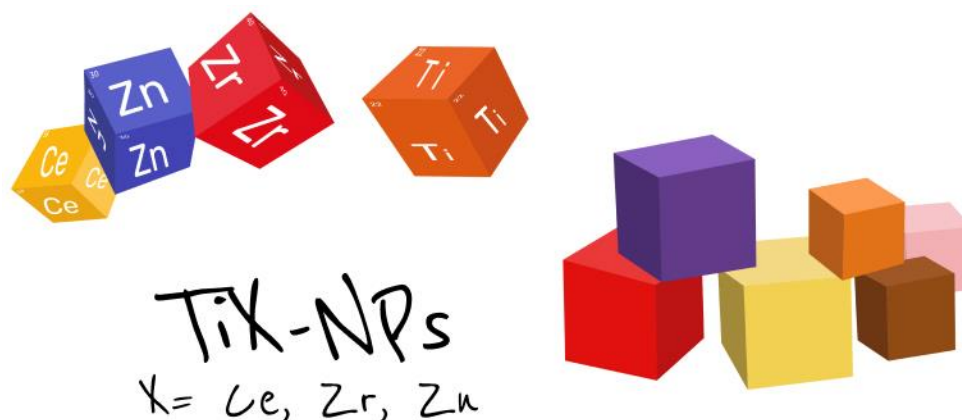
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**CHAPTER IV: TiX (X = Ce, Zr, Zn) BIMETALLIC
NANOPARTICLES WITH SYNERGISTIC
PHOTOCATALYTIC ACTIVITY IN THE
DEGRADATION OF SULFAMETHOXAZOLE
UNDER BLUE-LED IRRADIATION**



Graphical Abstract

4.1 ABSTRACT

Water contamination due to the presence of various emerging contaminants is a serious environmental problem today. These contaminants have been detected in groundwater, surface water, wastewater effluents, and drinking water, and their presence can have adverse effects on the health of humans and aquatic organisms. Heterogeneous photocatalysis is a widely used method for the decontamination and removal of toxic organic compounds from wastewater. Semiconductor metal nanoparticles, either as dopants or in composite mixed systems, are considered potential photocatalysts due to their individual or combined physicochemical properties.

In this work, the synergistic effect on the photocatalytic activity of mixed metal NPs based on TiZr, TiZn, and TiCe in the photodegradation of sulfamethoxazole using visible light, simulated by blue-LED light irradiation, was evaluated.

4.2 EXPERIMENTAL

The inverse microemulsion synthesis, calcination temperature, and characterization methodology of the monometallic and bimetallic nanoparticles photocatalysts, as well as photodegradation procedures of model molecule under blue-LED irradiation using a homemade slurry batch LED-reactor containing a dispersion of the photocatalyst, are presented in [Chapter II](#) of this thesis. The oxides corresponding to the four semiconductor materials of titanium, zirconium, cerium, and zinc studied were commercially acquired to be compared during both physicochemical characterization and kinetic studies when evaluating the performance of the nanoparticles prepared. The results are presented as follows:

4.3 RESULTS AND DISCUSSION

Figure 4.1 shows that all nanoparticles exhibit different colors, even when compared with the corresponding commercial oxides (M-com, M = Ti, Ce, Zr, and Zn).

This indicates that the visible light absorption capability varies for each material, and the coloration of the materials in the mixed phase does not match what would be expected by simple intuition, assuming that the final color is the result of a physical mixture of the corresponding monometallic metal nanoparticles. For example, on the left side of **Figure 4.1**, monometallic titanium and zirconium nanoparticles have slightly different light colors from each other, whereas the mixed phase between them has a dark color, which is far from what would be intuitively expected. However, this characteristic is not shown by the other mixed

oxides, suggesting that other factors determine the final coloration of the nanoparticles.

This could be a consequence of particle size, the interaction between different chemical species presents in the mixed NPs, or the presence of crystalline or non-crystalline structures. In any case, these results indicate that the final coloration cannot be easily predicted, and a more detailed analysis of the structures and physicochemical properties is necessary.



Figure 4.1. Photographs of semiconductor nanoparticles synthesized in monometallic and mixed phases. The corresponding commercial oxides are shown in the corner for comparison.

4.3.1 X-ray Diffraction (XRD)

Figure 4.2 depicts the diffraction patterns of monometallic and mixed cerium and zirconium nanoparticles, with the diffraction patterns of commercial oxides provided for comparison.

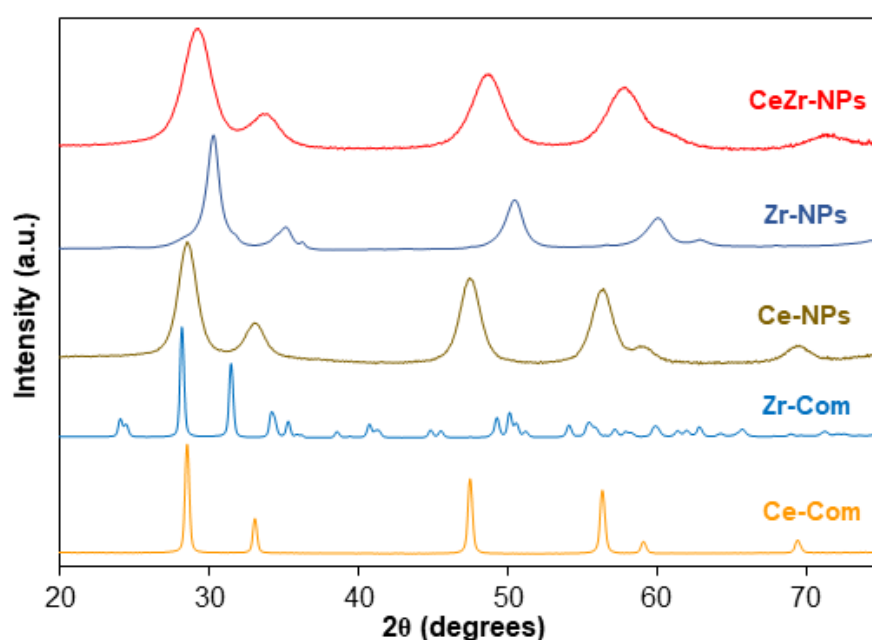


Figure 4.2. XRD patterns of mixed cerium and zirconium nanoparticles

The fluorite structure is common in inorganic compounds containing metals with an IV oxidation state, characterized by metallic ions arranged in a cubic lattice and surrounded by eight oxygen anions. Compounds such as cerium dioxide (CeO_2) [1], UO_2 (uranium dioxide), and ThO_2 (thorium dioxide) commonly exhibit this structure. In our study of commercial cerium oxide (Ce-com) [6], we determined that the main diffraction peaks correspond to the fluorite phase, with a strong peak

at 28.7 degrees in 2θ . However, the diffraction pattern of a commercial zirconium oxide (Zr-com) presented in the same figure, reveals that it belongs to the orthorhombic system. This system is described as a crystal lattice composed of compact hexagonal layers of Zr and O atoms, with each layer consisting of three sublayers of O atoms surrounded by Zr atoms, arranged one above the other and held together by valence bonds between Zr and O atoms [2,3].

For monometallic cerium oxide nanoparticles (Ce-NPs), distinct peaks appear along the 2θ axis at positions 28.5°, 33.0°, 47.4°, 56.24°, 58.98°, and 69.28°. These peaks correspond to the lattice parameters of a cubic crystalline system and are attributed. In the case of monometallic zirconium oxide nanoparticles (Zr-NPs), a series of intense peaks located along the 2θ axis at positions 30.28°, 35.1°, 50.48°, and 60° are assigned to the tetragonal structure of zirconium oxide (t-ZrO₂), in agreement with JCPDS diffraction file No. 88-1007 [4]. Notably, the characteristic peaks of the monoclinic phase are absent, indicating a high-purity material with lattice parameters of $a=0.511$ nm, $b=0.511$ nm, $c=0.511$ nm; $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=90^\circ$ [4].

Analysis of the mixed cerium and zirconium oxides (CeZr-NPs) revealed the emergence of a new crystallographic phase, evident from the shifts in peaks along the 2θ axis compared with the diffraction patterns of the monometallic phases obtained using the same methodology.

Figure 4.3 shows the X-ray diffraction patterns of the zirconium and zinc oxides mixed nanoparticles (ZrZn-NPs) are depicted. Zinc oxide (ZnO) can exhibit various crystalline structures, including zinc blende, hexagonal wurtzite, and monoclinic wolframite [5], with wurtzite being the most common [6,7].

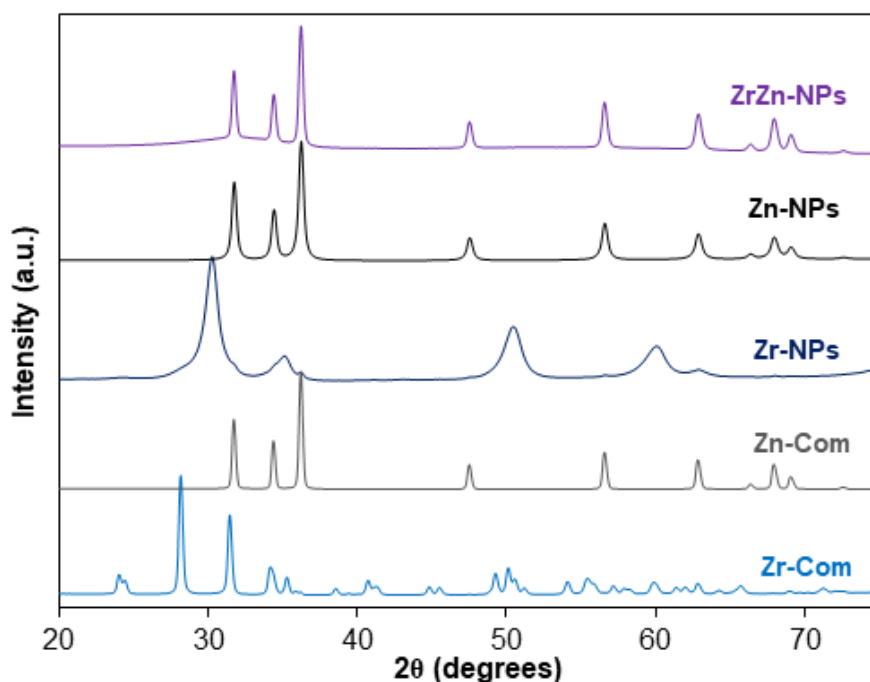


Figure 4.3. XRD patterns of mixed zirconium and zinc nanoparticles

To compare the physicochemical properties of the prepared nanoparticles, a commercial sample of ZnO (Zn-com) was utilized, demonstrating a monoclinic hexagonal structure as identified through the JCPDS No. 36-1451 diffraction file [8,9]. Analysis of the diffraction pattern of the ZrZn-NPs mixed phase confirmed that the peak positions on the 2θ axis precisely match those of zinc nanoparticles in monometallic phase (Zn-NPs). This suggests that the synthesis method employed did not yield a mixed phase, but potentially resulted in either the monometallic semiconductor phase or a phase doped with zirconium atoms.

Figure 4.4 illustrates the X-ray diffraction patterns corresponding to the mixed phase of cerium and zinc nanoparticles (CeZn-NPs).

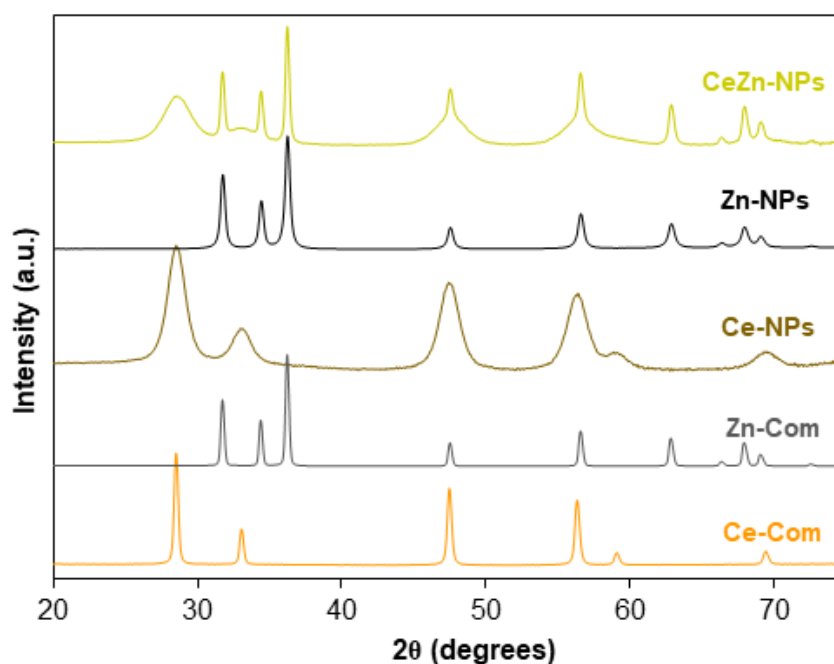


Figure 4.4. XRD patterns of mixed cerium and zinc nanoparticles

For this material, characteristic peaks corresponding to zinc oxide and cerium oxide appear in the pattern of the mixed phase. This suggests that the synthesized material may correspond to a physical mixture of cerium and zinc nanoparticles and that the attainment of a mixed phase, as initially proposed, may not have been achieved.

Figure 4.5 depicts the diffraction patterns of the mixed nanoparticles of titanium and zinc (TiZn-NPs). It is known that titanium dioxide (TiO_2) is an inorganic solid that occurs in three different crystallographic phases: anatase, rutile, and brookite. Both anatase and rutile have a tetragonal structure, whereas brookite is orthorhombic [3,10].

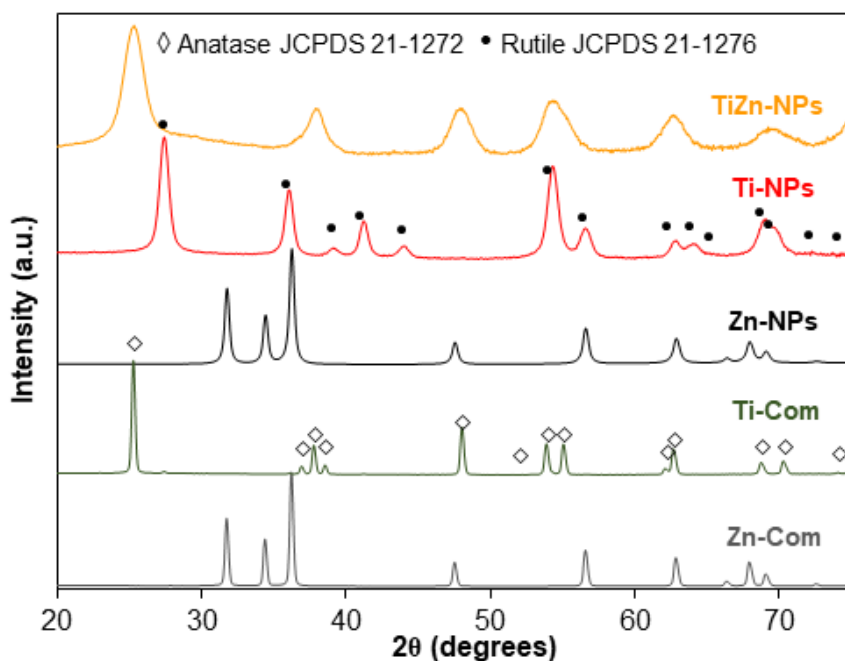


Figure 4.5. XRD patterns of mixed titanium and zinc nanoparticles

In the X-ray diffraction study, it was identified that commercial titanium oxide (Ti-com) crystallized in the anatase phase, identified with the JCPDS No. 21-1272 diffraction file [1]. On the other hand, for titanium oxide nanoparticles (Ti-NPs), the diffraction pattern show all the characteristic peaks of the rutile phase (JCPDS No. 21-1276) [11], with lattice parameters $a=0.46118$ nm, $b=0.46118$ nm, $c=0.29817$ nm; $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=90^\circ$. with lattice parameters $a=0.46118$ nm, $b=0.46118$ nm, $c=0.29817$ nm; $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=90^\circ$.

These nanoparticles are likely to be of high purity because no other diffraction peaks were observed [12], as confirmed by Zubieta and colleagues using the same synthesis method [13].

The X-ray diffraction pattern of the TiZn-NPs mixed phase shows a set of diffraction peaks different from those exhibited by TiO₂ and ZnO nanoparticle. This confirms the attainment of a mixed crystalline phase combining the two semiconductor metals. Although no peaks different from the anatase phase are observed, a shift in the peak positions along the 2θ axis is noticeable. Therefore, this material may correspond to zinc titanate, a binary compound characterized by the presence of TiO₂-ZnO, which typically exhibits four crystalline phases depending on the synthesis process [8,14]. The first is a spinel-type structure corresponding to zinc protitanate [14], while two cubic and hexagonal phases correspond to zinc metatitanate. The last phase, Zn₂Ti₃O₈, has a spinel structure with defects [15].

It is important to highlight that TiO₂ exhibits different crystalline phases, such as rutile, anatase [16], brookite [17], and hollandite [18], with rutile being more stable than anatase at room temperature [18]. However, the rutile phase can transform into the anatase phase in the presence of stimuli such as heat treatment, acids, or leaching with alkaline solutions.

Figure 4.6 shows the XRD patterns corresponding to the mixed phase of titanium and cerium nanoparticles (TiCe-NPs). In the next figure, when observing the X-ray diffraction pattern of the TiCe-NPs mixed phase, it is possible to identify the characteristic peaks of the three crystalline phases. The first is attributed to the presence of cerium oxide, which can be confirmed by comparing its diffraction pattern with that of both commercial cerium oxide (Ce-com) and cerium nanoparticles (Ce-NPs). The other two crystalline phases are attributed to the rutile and anatase phases of titanium dioxide, which can be confirmed by comparison

with the diffraction patterns of commercial titanium oxide (Ti-com) and nanoparticles (Ti-NPs).

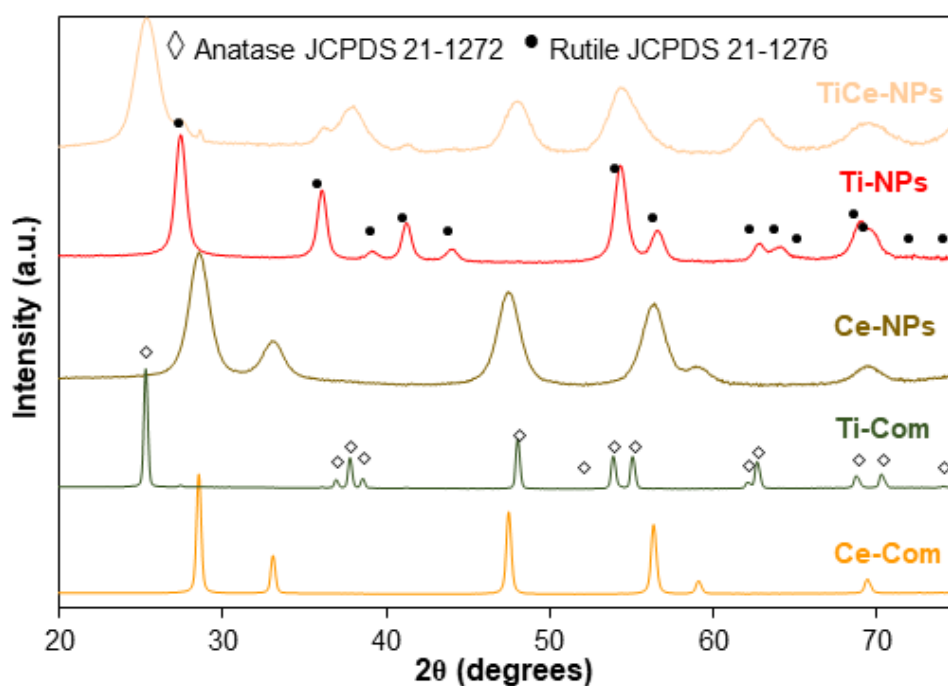


Figure 4.6. XRD patterns of mixed titanium and cerium nanoparticles

Figure 4.7 shows the X-ray diffraction patterns corresponding to the mixed phase of titanium and zirconium nanoparticles (TiZr-NPs). In the next figure, the characteristic peaks of the anatase phase are evident in commercial titania (TiO_2), whereas the rutile phase is detected in monometallic titanium nanoparticles [19]. In the TiZr-NPs XRD pattern, an additional broad peak around 28° in 2θ is observed, suggesting the possible presence of low-crystallinity zirconium oxide nanoparticles [20].

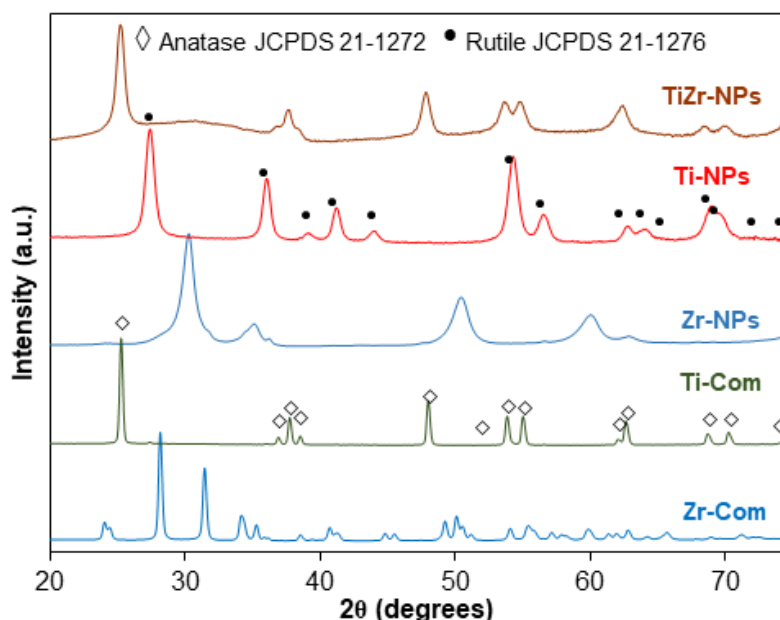


Figure 4.7. XRD patterns of mixed titanium and zirconium nanoparticles

This observation raises the possibility of obtaining a mixed phase of zirconium titanate. However, since initially only the peaks specific to the anatase phase are observed, it is conceivable that zirconium may act as a dopant.

To determine the crystal size (dp), the peaks of maximum intensity in the X-ray diffraction patterns were used, following the technique described in the experimental Section and applying the Scherrer equation (see **Equation 2-1**). The results are presented in **Table 4.1**.

Table 4.1 show that, regarding commercial oxides, the obtained crystal sizes of 21.4, 26.2, 28.8, and 28.8 nm for cerium, zirconium, zinc, and titanium oxides, respectively, indicate variations in their particle sizes. A smaller crystal size

typically suggests a higher specific surface area and chemical reactivity, whereas a larger crystal size may indicate the opposite [21].

Table 4.1. Crystal properties of materials.

Photocatalyst	New phase formation	Crystallographic Phase	dp nm
Ce-Com	-	fluorite	24.1
Zr-Com	-	orthorhombic	26.2
Zn-Com	-	monoclinic hexagonal	28.8
Ti-Com	-	anatase	28.8
Ce-NPs	-	cubic	6.0
Zr-NPs	-	tetragonal	8.5
Zn-NPs	-	monoclinic hexagonal	19.3
Ti-NPs	-	rutile	10.8
CeZr-NPs	yes	anatase	3.8
ZrZn-NPs	not	---	25.6
CeZn-NPs	not	---	28.0
TiZn-NPs	yes	anatase	8.0
TiCe-NPs	yes	anatase/rutile/CeO ₂	4.9
TiZr-NPs	yes	anatase/ZrO ₂	10.6

For monometallic semiconductor nanoparticle, their sizes range from 6 to 19.3 nm, indicating that smaller particle sizes have been achieved compared with commercial oxides. The table also demonstrates that the six mixed phase materials exhibit diverse sizes, ranging from 3.8 nm for CeZr-NPs to 28 nm for CeZn-NPs. CeZn-NPs and ZrZn-NPs, being the largest NPs, did not form mixed phases. However, CeZr-NPs, TiCe-NPs, TiZn-NPs, and TiZr-NPs, with sizes of 3.8, 4.9, 8, and 10.6 nm, respectively, are considered to be more effective in photocatalysis due to their larger available surface area. Finally, **Table 4.1** also shows that the

formation of a new phase was confirmed in four of the six mixed NPs, namely CeZr-NPs, TiZn-NPs, TiZr-NPs, and TiCe-NPs.

4.3.2 Nitrogen adsorption-desorption isotherms at 77 K

In the next figures we will see that these types of materials show quasi type II isotherms with a micropore contribution in most of the bimetallic oxides based samples.

Table 4.2. Textural properties of photocatalyst.

Photocatalyst	S _{BET}	S _{DR}	S _{mic}	W _o (N ₂)	V _{0.95}	V _{MESO}	L _o (N ₂)
	m ² g ⁻¹	m ² g ⁻¹	m ² g ⁻¹	cm ³ g ⁻¹	cm ³ g ⁻¹	cm ³ g ⁻¹	nm
Ce-Com	0	0	0	0.000	0.012	0.000	0.000
Zr-Com	0	0	0	0.000	0.011	0.000	0.000
Zn-Com	9	13	0	0.005	0.019	0.014	3.718
Ti-Com	17	13	0	0.005	0.019	0.015	2.720
Ce-NPs	126	131	3	0.046	0.178	0.131	2.047
Zr-NPs	101	124	0	0.044	0.124	0.080	2.103
Zn-NPs	84	47	0	0.017	0.112	0.095	3.601
Ti-NPs	78	95	0	0.034	0.216	0.082	3.193
CeZr-NPs	146	166	12	0.059	0.175	0.116	1.923
ZrZn-NPs	97	106	0	0.038	0.152	0.114	2.233
CeZn-NPs	71	80	2	0.029	0.083	0.054	2.033
TiZn-NPs	220	252	13	0.090	0.199	0.110	1.968
TiZr-NPs	182	224	0	0.080	0.180	0.103	2.270
TiCe-NPs	101	109	78	0.039	0.140	0.101	1.080

These findings align with previous literature, which suggests that metal oxides typically have moderate specific surface areas and a small pore size distribution, indicating nitrogen adsorption at specific sites on the material surface. **Table 4.2**

collects the textural characterization data. In general, commercial monometallic oxide samples have virtually no apparent surface areas, but the synthesised monometallic nanoparticles increase all textural parameters with respect to their counterparts: Ce-NPs and Zr-NPs have the highest textural values while Zn-NPs and Ti-NPs the lowest ones.

Moreover, when the nanoparticles based samples are formed micro- and/or mesopores are developed in all cases. On the other hand, bimetallic oxide based samples show some micropores and mesoporosity. Sample CeZn-NPs clearly developed poor textural characteristics than its separated based components. It should be remarked the special high development of textural characteristics in the case of bimetallic oxides containing titanium even with Zn as partner. In fact, TiZn-NPs and TiZr-NPs have the highest values of apparent surface areas because they developed the largest micropore volumes.

Figure 4.8-Figure 4.13 depict the adsorption and desorption isotherms of both monometallic and the corresponding bimetallic samples, along with the pore size distribution images obtained using the BJH method. The comparison of the isotherms among the bimetallic and monometallic phases, especially the variations in the hysteresis loops suggests potential differences in their structural characteristics. It should be noted that pore size distributions have been calculated as $dV/d\log(D)$; therefore, logarithmic units may distort the quantitative analysis of the curves. In this way, mean pore diameters of non-containing Ti bimetallic samples are higher than the other bimetallic ones, following the order: CeZn(18nm) > ZrZn (6 nm) > CeZr (4.5nm), while the Ti-containing bimetallic samples have same values of 3.5 nm.

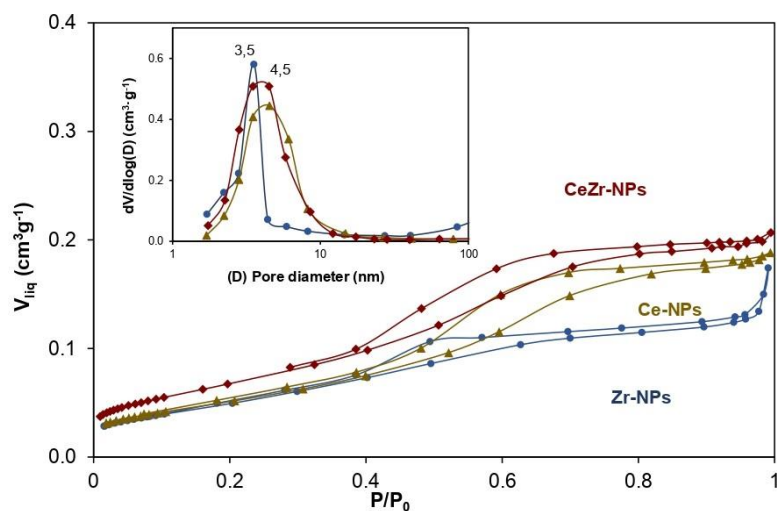


Figure 4.8. N_2 adsorption-desorption isotherms and pore size distribution of CeZr-NPs and their corresponding monometallic samples.

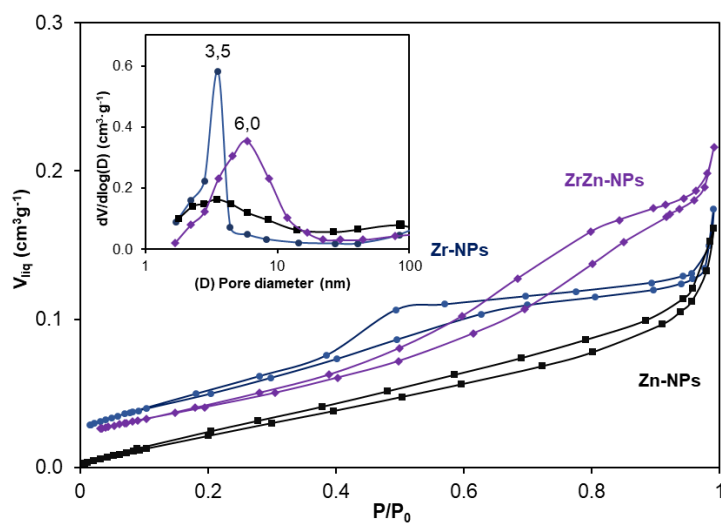


Figure 4.9. N_2 adsorption-desorption isotherms and pore size distribution of ZrZn-NPs and their corresponding monometallic samples.

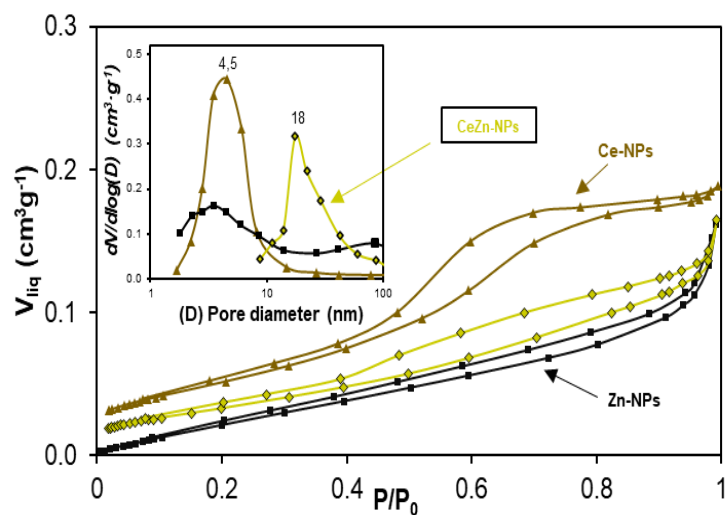


Figure 4.10. N_2 adsorption-desorption isotherms and pore size distribution of CeZn-NPs and their corresponding monometallic samples.

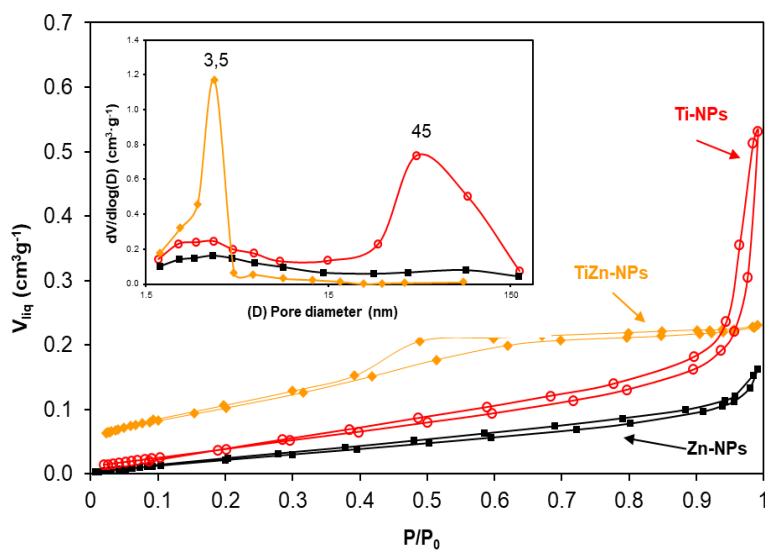


Figure 4.11. N_2 adsorption-desorption isotherms and pore size distribution of TiZn-NPs and their corresponding monometallic samples

All isotherms correspond to type II [22], indicating the presence of micropores and mesopores. However, the mixed phase exhibits the highest concentration of micropores, with pore sizes centered around 3.5 nm. In addition, in the case of Ti-NPs, mesopores centered around 45 nm are evident.

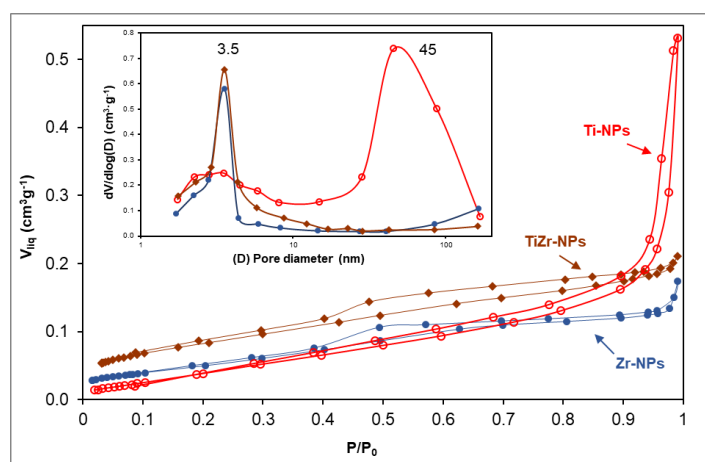


Figure 4.12. N₂ adsorption-desorption isotherms and pore size distribution of TiZr-NPs and their corresponding monometallic samples

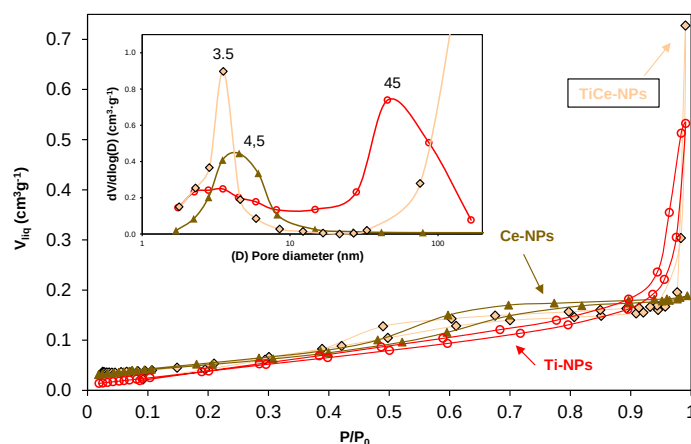


Figure 4.13. N₂ adsorption-desorption isotherms and pore size distribution of titanium and cerium samples

Table 4.2 presents notable differences in the BET surface area values. For instance, zinc nanoparticles have a surface area of $84 \text{ m}^2 \text{ g}^{-1}$, significantly lower than that of the mixed phase TiZn-NPs, which has a surface area of $220 \text{ m}^2 \text{ g}^{-1}$, representing a 162 % increase in the BET area.

The mixed titanium and zirconium nanoparticle (TiZr-NPs) system, shown in **Figure 4.12**, it can be observed that its surface area corresponds to $182 \text{ m}^2 \text{ g}^{-1}$ (see **Table 4.2**).

4.3.3 UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS)

Figure 4.14 depicts the UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS) spectra of commercial oxides of cerium, zirconium, zinc, and titanium.

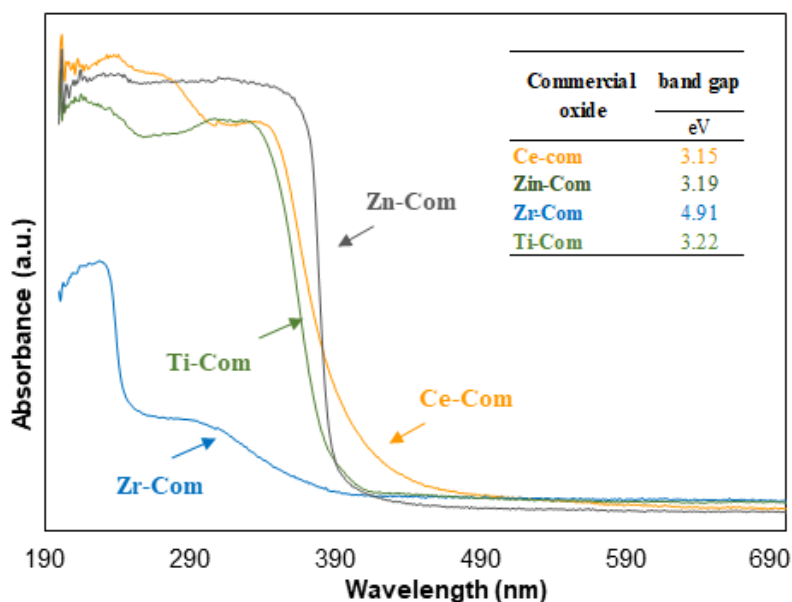


Figure 4.14. Diffuse reflectance spectra of commercial oxides

In the previous figure, all the materials demonstrated a unique absorption band according to their crystalline structures and optical properties. The inset table displays the E_g values for each oxide [23]

Figure 4.15 illustrates the UV-Vis DRS spectra for all monometallic nanoparticles. **Table 4.3** depicts the E_g values. Consequently, nanoparticles such as Ti-NPs and Ce-NPs, which have low E_g values, could be readily activated by light, exhibiting higher photocatalytic activity.

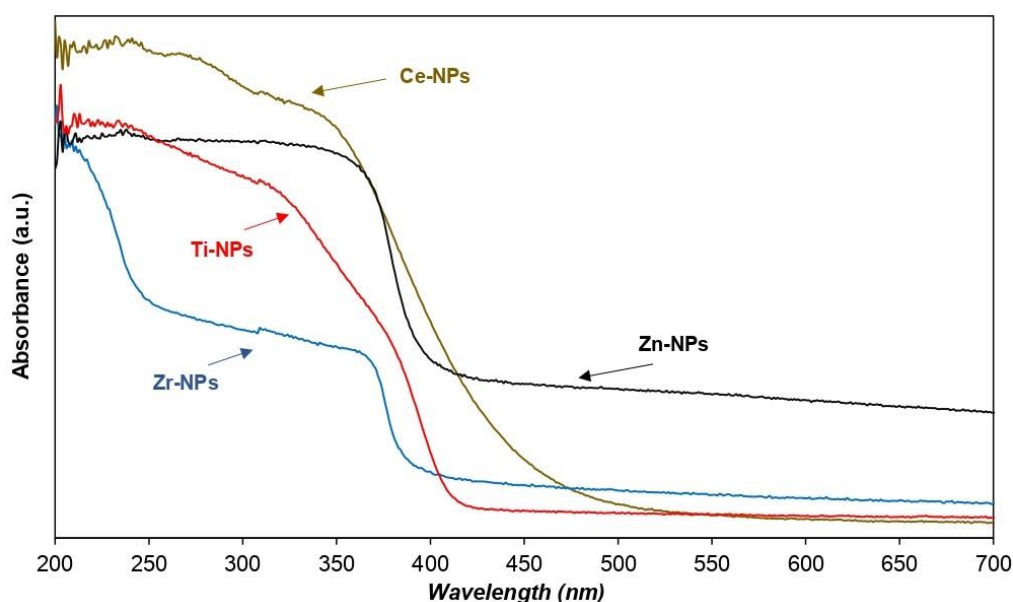
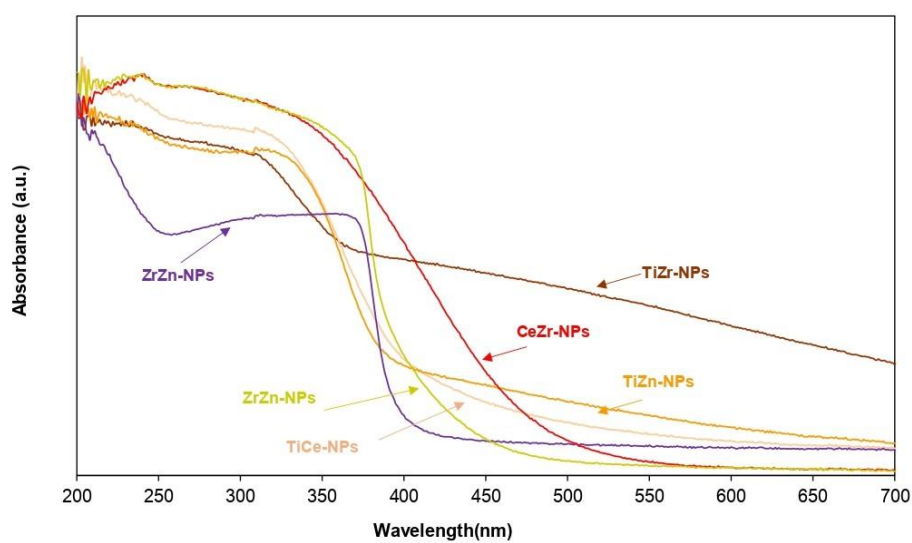


Figure 4.15. Diffuse reflectance spectra of monometallic nanoparticles

Ce-NPs and Ti-NPs have the same E_g magnitude of 2.88 eV, indicating that both require a similar amount of energy to excite their electrons. Meanwhile, the zinc and zirconium based nanoparticles have E_g values of 3.01 and 3.15 eV, respectively, suggesting that they need similar energy to be activated.

Table 4.3. Band Gap values of photocatalysts.

Photocatalyst	Band Gap
	eV
TiZn-NPs	3.11
TiZr-NPs	2.73
Ti-NPs	2.88
TiCe-NPs	3.01
ZrZn-NPs	3.11
Zr-NPs	3.15
Zn-NPs	3.01
CeZn-NPs	3.04
CeZr-NPs	2.60
Ce-NPs	2.88

**Figure 4.16.** Diffuse reflectance spectra of mixed nanoparticles

According to **Table 4.3** and **Figure 4.16**, cerium and zirconium nanoparticles (CeZr-NPs) demonstrate a smaller E_g , with a value of 2.60 eV. This suggests that

this mixed system is particularly suitable for photocatalytic applications. However, it is essential to consider that this conclusion may be influenced by other factors, such as the stability and catalytic efficiency of the nanoparticle. Consequently, as shown in the photodegradation study, other systems, such as the mixed titanium and zirconium oxide (TiZr-NPs), exhibit promising performance in photocatalysis.

4.3.4 Transmission Electron Microscopy (TEM)

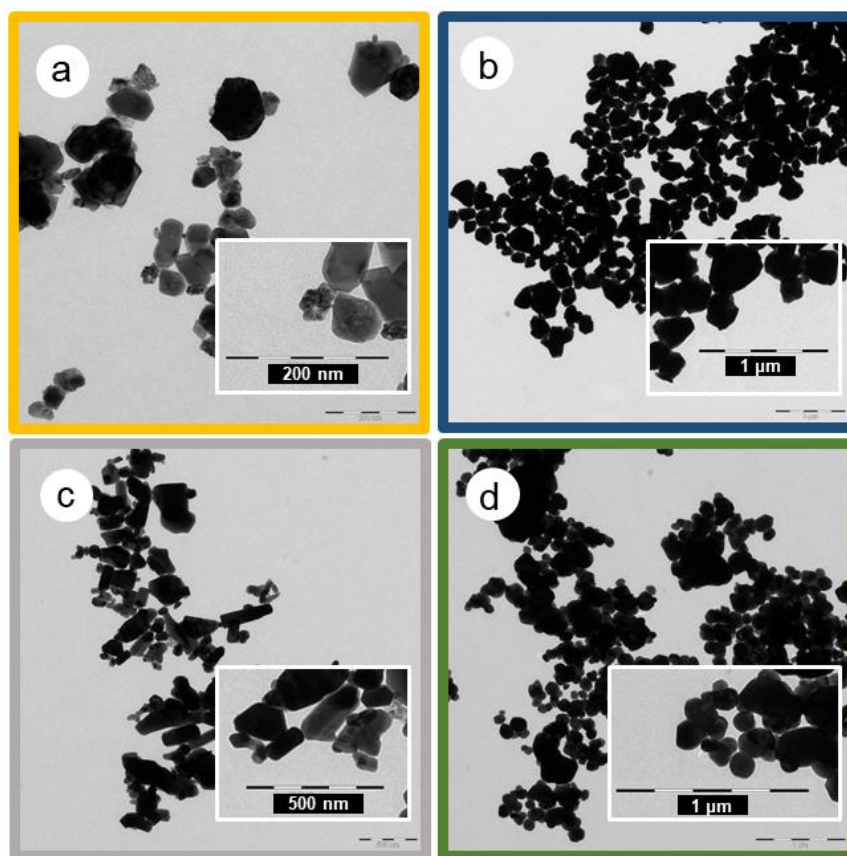


Figure 4.17. TEM images of commercial oxides (a) cerium, (b) zirconium, (c) zinc and (d) titanium.

In **Figure 4.17a**, the microphotograph of commercial cerium oxide reveals heterogeneous aggregates ranging from 50 to 100 nm in size.

Although irregular shapes with an average size of 16 nm, their morphology appears polygonal and rough. In **Figure 4.17b**, commercial titanium oxide displays overlapping shapes with regular and ordered geometries, albeit obscured by aggregates, indicating sizes of approximately 100 nm.

Figure 4.17c presents commercially sourced zirconium oxide, characterized by more homogeneous shapes and a dark hue attributed to its atomic number. Its transparency correlates with thickness, and its size is approximately 150 nm. Finally, **Figure 4.17d** depicts zinc oxide, with sizes around 40 nm, alongside aggregations of various geometries and shapes.

The size of these aggregates could significantly influence the practical application of these commercial materials as photocatalysts. Although the presence of heterogeneous aggregates and irregular shapes might impact their effectiveness in photocatalysis, greater homogeneity suggests superior performance in this regard.

In **Figure 4.18a**, the microphotographs of cerium oxide nanoparticles (Ce-NPs) reveal an average size of 10 nm with a spherical shape, albeit somewhat asymmetrical, as noted previously [12]. Ce-NPs and Zr-NPs seem to be formed as individual aggregates (**Figure 4.18a-b**), reaching sizes in the micrometer range. The individual nanoparticles vary in size between 4 and 6 nm and exhibit both spherical and non-spherical shapes. **Figure 4.18c** displays Zn-NPs forming aggregates with diverse geometries, including plate-like and spherical shapes, with

sizes extending to the micrometer scale. These particles measure between 7 and 15 nm, characterized by a rough texture and minimal symmetry.

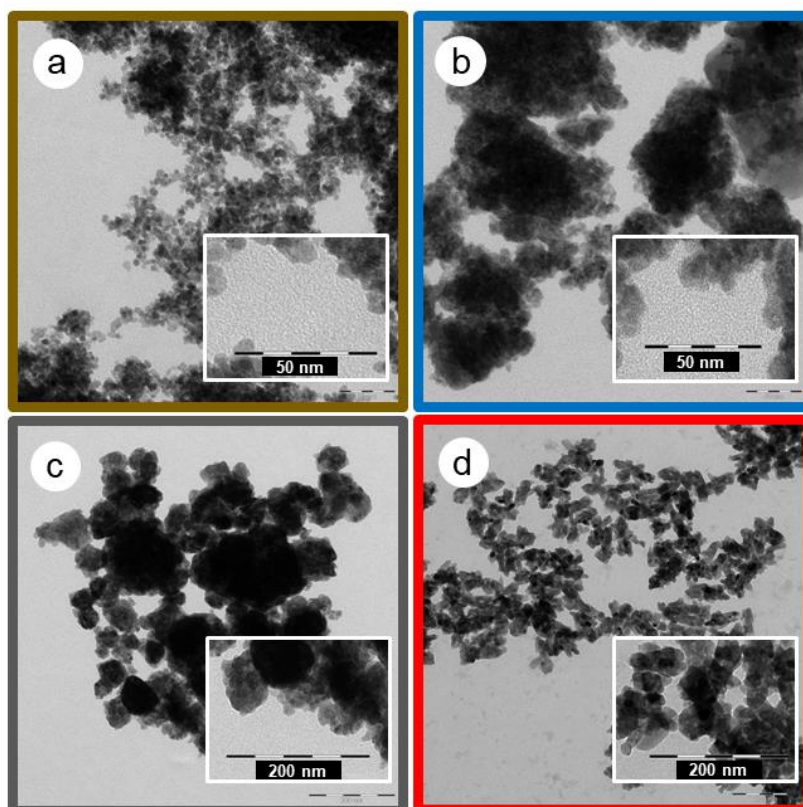


Figure 4.18. TEM images of monometallic nanoparticles (a) Ce-NPs, (b) Zr-NPs, (c) Zn-NPs and (d) Ti-NPs.

Finally, in **Figure 4.18d**, Ti-NPs exhibits varied geometries, forming flat plates and rods, as noted in prior literature [12]. The individual rods measure approximately 38 nm in length and 17 nm in width, although particle aggregations lead to nonuniform dimensions.

In **Figure 4.19a**, microphotographs of CeZr-NPs reveals individual particles with an average diameter of 5 nm and spherical geometry alongside particle clusters. In **Figure 4.19b**, ZrZn-NPs appears with rod-shaped geometries, reaching lengths of up to 1 μm , alongside smaller particles averaging 4 nm in diameter.

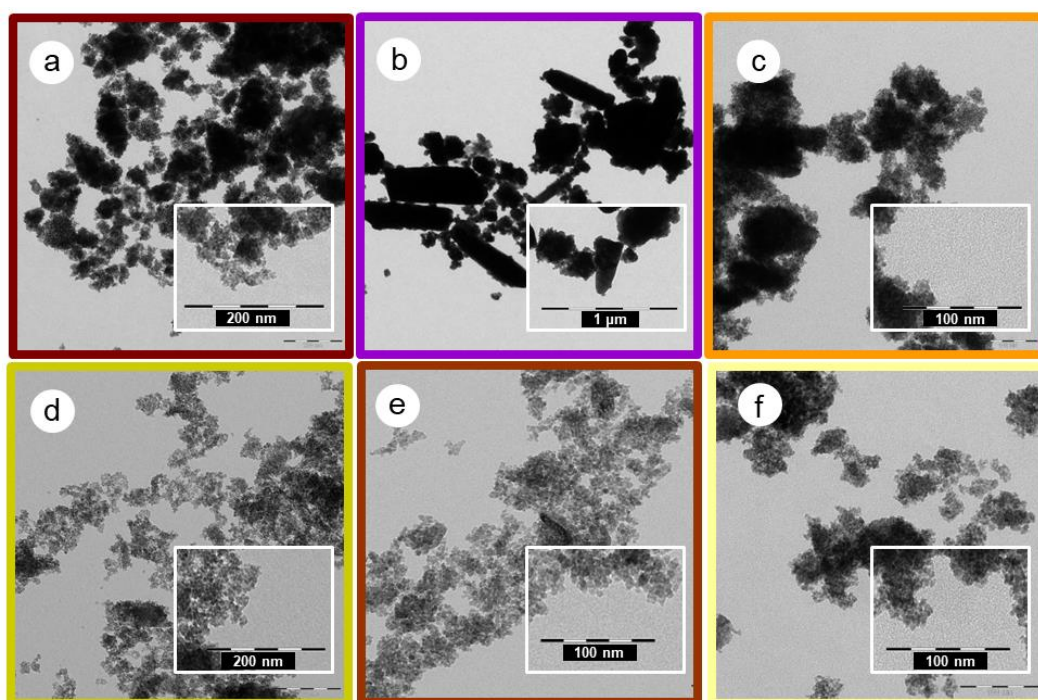


Figure 4.19. TEM images of bimetallic nanoparticles (a) CeZr-NPs, (b) ZrZn-NPs, (c) CeZn-NPs, (d) TiZn-NPs, (e) TiZr-NPs and (f) TiCe-NPs

In **Figure 4.19c**, CeZn-NPs is depicted as spherical aggregates with an average diameter of 35 nm, alongside smaller aggregates averaging 4 nm. The material demonstrates homogeneity across nearly 90 % of its surface. **Figure 4.19d** displays sample TiZn-NPs with sizes hovering around 4 nm. Notably, aggregates and

individual particles are evenly distributed throughout the sample, distinguishable with defined geometries.

A comparative analysis of the sizes of the nanoparticles composed by bimetallic phases and the corresponding monometallic ones reveals significant differences. Bimetallic NPs produced smaller particles with well-defined geometries, suggesting that the presence of both metals (titanium and zinc) during synthesis plays a fundamental role in shaping the final material.

These characteristics indicate that the smaller nanoparticles possess a larger specific surface area, as shown in **Table 4.2**, indicating a potential enhancement in the photocatalytic performance. Thus, TiZn-NPs are presumed to exhibit higher photocatalytic activity owing to their smaller size compared to nanoparticles in the monometallic phase.

In **Figure 4.19e**, mixed titanium and zirconium nanoparticles (TiZr-NPs) exhibit a more dispersed distribution compared to other mixed oxides, featuring average sizes of 5 nm and spherical geometries. Conversely, the last image in **Figure 4.19**, depicting titanium and cerium nanoparticles (TiCe-NPs), reveals cluster formations and irregular sizes.

4.3.5 X-ray Photoelectron Spectroscopy (XPS)

The surface chemistry composition was analysed by XPS. High resolution spectra were obtained for nanoparticles that were calibrated with the adventitious carbon, C_{1s}, at a displacement of 284.6 eV. The spectra of the most representative elements are shown below.

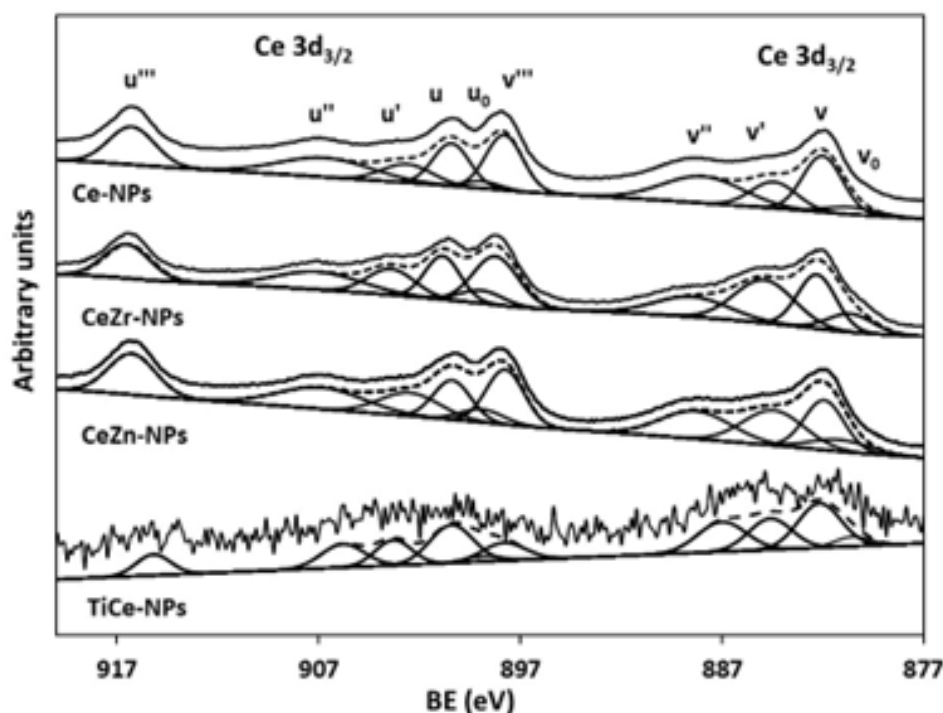


Figure 4.20. XPS spectra for Ce3d core level regions

The XPS spectra of cerium (**Figure 4.20**) we can see that the main oxidation state is Ce^{4+} , although a small amount of Ce^{3+} appears. The position of the peaks can be seen in the Tables 4.5 and 4.6. According to the studies of Burroughs *et al.* [24], the peaks V, V'', V''', U, U'' and U''' are referred to Ce^{4+} $3d_{3/2}$ and $3d_{5/2}$; respectively, and the peaks U_0 , U' , V_0 and V'' are assigned to Ce^{3+} as labelled in the **Figure 4.20**.

The ratio of Ce^{3+} to Ce^{3+} and Ce^{4+} cations can be estimated as the ratio of the area under the Ce^{3+} peaks to the total area under the spectrum and is given in **Table**

4.4. The amount of Ce^{3+} in the samples is approximately 30 wt.% in all of them, with no large variations from one sample to another.

The amount of Ce^{3+} in the samples is approximately 30 wt.% in all samples, with no great variation from one sample to another. This indicates that the preparation of the composites has not affected the Ce^{3+} and Ce^{4+} ratio of the Ce-NPs compared to the mixed metal nanoparticles.

Table 4.4. Ratio $\text{Ce}^{3+}/\text{Ce}^{4+}$ for the nanoparticles.

Photocatalyst	wt.% Ce^{4+}	wt.% Ce^{3+}
Ce-NPs	70	30
CeZr-NPs	67	33
CeZn-NPs	70	30
TiCe-NPs	73	27

Three peaks have been found in the O_{1s} spectra (Tables 4.5 and 4.6). The first one peak located around at a binding energy of 529 eV is assigned to the lattice oxygen in Ce^{4+} [25]. The second peak (~ 530 eV) is related to the Ce^{3+} oxide on the surface, and the third one that appear around 532 eV, has arisen to oxygen chemisorbed on the surface in forms as CO or CO_2 .

In the CeZn-NPs sample also must include the component $\text{Zn}^{2+}\text{-O}$, of the ZnO oxide, in the peak about 529 eV. The same way, the oxygen components of TiZn-NPs, the components $\text{Ti}^{4+}\text{-O}$ and Ti-O-Ti are included in the peak at 529 eV and 530 eV, respectively.

In the **Figure 4.21** we can see the Zn (A) and Ti (B) deconvoluted spectra of the 2p region, and the **Table 4.7** and **Table 4.8** show of the peaks positions in eV.

The two strong peaks at around 1021.5 eV and 1045.5 eV appeared in Zn_{2p} , which are consistent with the binding energies of $\text{Zn}_{2p_{3/2}}$ and $\text{Zn}_{2p_{1/2}}$ of Zn^{2+} [26]. It is worth noting the low surface concentration of Zn in the TiZn-NPs sample, which may be due to the Zn^{2+} being incorporated into the TiO_2 structure.

Table 4.5. Assigned peaks of deconvoluted Ce_{3d} , O_{1s} and M (Zr_{3d}) XPS regions.

Sample	O_{1s}	Assig.	% peak	Ce_{3d}	Assig.	% peak	M	Assig.	% peak
Ce-NPs	528.8	$\text{Ce}^{4+}-\text{O}$	59	880.6	$\text{Ce}^{3+}_{5/2}$	3			
	530.6	$\text{Ce}^{3+}-\text{O}$	36	882.0	$\text{Ce}^{4+}_{5/2}$	16			
	532.2	O-C	5	884.4	$\text{Ce}^{3+}_{5/2}$	8			
				888.0	$\text{Ce}^{4+}_{5/2}$	15			
				897.8	$\text{Ce}^{4+}_{5/2}$	14			
				898.9	$\text{Ce}^{3+}_{3/2}$	2			
				900.4	$\text{Ce}^{4+}_{5/2}$	11			
				902.6	$\text{Ce}^{3+}_{3/2}$	6			
				906.7	$\text{Ce}^{4+}_{5/2}$	13			
				916.3	$\text{Ce}^{4+}_{5/2}$	12			
CeZr-NPs	529.1	$\text{Ce}^{4+}-\text{O}$	48	880.5	$\text{Ce}^{3+}_{5/2}$	5	181.6	$\text{Zr}_{3d_{5/2}}$	56
	530.4	$\text{Ce}^{3+}-\text{O}$	44	882.2	$\text{Ce}^{4+}_{5/2}$	13	184.0	$\text{Zr}_{3d_{3/2}}$	44
	531.8	O-C	7	884.8	$\text{Ce}^{3+}_{5/2}$	16			
				888.5	$\text{Ce}^{4+}_{5/2}$	10			
				898.1	$\text{Ce}^{4+}_{5/2}$	14			
				898.8	$\text{Ce}^{3+}_{3/2}$	4			
				900.9	$\text{Ce}^{4+}_{5/2}$	10			
				903.3	$\text{Ce}^{3+}_{3/2}$	8			
				907.0	$\text{Ce}^{4+}_{5/2}$	10			
				916.4	$\text{Ce}^{4+}_{5/2}$	10			

The O_{1s} peaks can be deconvoluted into three peaks. The binding energies at about 529.3 eV, 530.7 eV and 532.1 eV can be assigned to the surface lattice oxygen, adsorbed oxygen on the vacancies and hydroxyl peaks respectively [27].

Table 4.6. Assigned peaks of deconvoluted Ce_{3d}, O_{1s} and M (Zn, Zr)_{2p}, XPS regions.

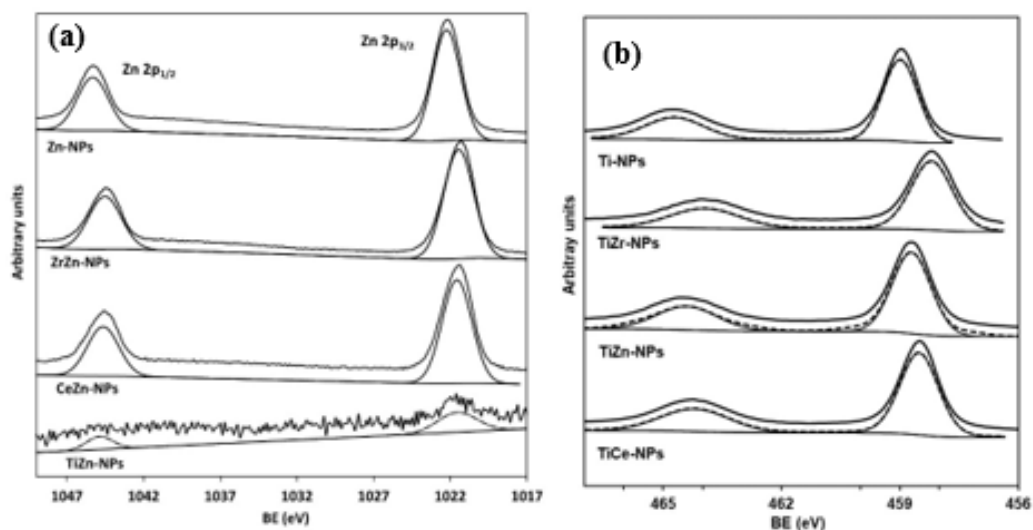
Sample	O _{1s}	Assig.	% peak	Ce _{3d}	Assig.	% peak	M	Assig.	% peak
CeZn-NPs	528.8	Ce ⁴⁺ -O/ Zn ²⁺ -O	30	881.2	Ce ³⁺ _{5/2}	4	1021.6	Zn _{2p3/2}	66
	530.0	Ce ³⁺ -O	44	881.9	Ce ⁴⁺ _{5/2}	12	1044.6	Zn _{2p1/2}	34
	531.7	O-C	25	884.4	Ce ³⁺ _{5/2}	13			
				888.3	Ce ⁴⁺ _{5/2}	12			
				897.8	Ce ⁴⁺ _{5/2}	13			
				898.9	Ce ³⁺ _{3/2}	3			
				900.4	Ce ⁴⁺ _{3/2}	9			
				902.5	Ce ³⁺ _{3/2}	9			
				906.9	Ce ⁴⁺ _{3/2}	11			
				916.3	Ce ⁴⁺ _{3/2}	12			
TiCe-NPs	529.7	Ce ⁴⁺ -O/ Ti ⁴⁺ -O	59	880.5	Ce ³⁺ _{5/2}	3	458.5	Ti ³⁺ _{2p3/2}	68
	530.1	Ce ³⁺ -O/ Ti-O-Ti	27	882.2	Ce ⁴⁺ _{5/2}	19	464.2	Ti ³⁺ _{2p1/2}	32
	531.3	O-C	14	884.6	Ce ³⁺ _{5/2}	13			
				887.0	Ce ⁴⁺ _{5/2}	14			
				897.8	Ce ⁴⁺ _{5/2}	8			
				898.8	Ce ³⁺ _{3/2}	2			
				900.4	Ce ⁴⁺ _{3/2}	16			
				903.3	Ce ³⁺ _{3/2}	9			
				905.8	Ce ⁴⁺ _{3/2}	10			
				915.2	Ce ⁴⁺ _{3/2}	7			

Table 4.7. Assigned peaks of deconvoluted Zn_{2p}, O_{1s} and M (Zr_{3d}, Ti_{2p}, Ce_{3d}) XPS regions.

Sample	O _{1s}	Assig.	% peak	Zn _{2p}	Assig.	% peak	M	Assig.	% peak
Zn-NPs	530.1	Zn ²⁺ -O	33	1021.8	Zn _{2p3/2}	64.8			
	531.4	C-O/-OH	58	1044.9	Zn _{2p1/2}	35.2			
	532.4	O-C/C-COO ⁻	9						
ZrZn-NPs	530.2	Zn ²⁺ -O	64	1021.5	Zn _{2p3/2}	65.5	181.7	Zr _{3d5/2}	52.2
	531.7	C-O/-OH	30	1044.5	Zn _{2p1/2}	34.5	184.0	Zr _{3d3/2}	47.8
	533.0	O-C/C-COO ⁻	6				181.6	Zr ³⁺ _{3d5/2}	46
							183.93	Zr ³⁺ _{3d3/2}	38

Table 4.7 (continued)

TiZn-NPs	529.9	Ti ⁴⁺ -O/Zn ²⁺ -O	55.2	1021.5	Zn2p _{3/2}	69.8	457.3	Ti ³⁺ _{2p3/2}	62.3
	530.9	-OH/Ti-O-Ti	38.2	1044.9	Zn2p _{1/2}	30.2	458.7	Ti ³⁺ _{2p3/2}	28.1
	532.5	O-C/C-COO ⁻	6.6				460.1	Ti ⁴⁺ _{2p3/2}	2.7
							462.8	Ti ³⁺ _{2p1/2}	2.2
							464.4	Ti ³⁺ _{2p1/2}	2.8
							465.9	Ti ⁴⁺ _{2p1/2}	1.8
CeZn-NPs	528.8	Ce ⁴⁺ -O/Zn-O	30	1021.6	Zn2p _{3/2}	66	881.2	Ce ³⁺ _{3d5/2}	4.3
	530.0	Ce ³⁺ -O	44	1044.6	Zn2p _{1/2}	34	881.9	Ce ⁴⁺ _{3d5/2}	12.3
	531.7	O-C/C-COO ⁻	25				884.4	Ce ³⁺ _{3d5/2}	13
							888.3	Ce ⁴⁺ _{3d5/2}	12
							897.8	Ce ⁴⁺ _{3d5/2}	13
							898.9	Ce ³⁺ _{3d3/2}	3
							900.4	Ce ⁴⁺ _{3d3/2}	9
							902.5	Ce ³⁺ _{3d3/2}	9
							906.9	Ce ⁴⁺ _{3d3/2}	11
							916.3	Ce ⁴⁺ _{3d3/2}	12

**Figure 4.21.** XPS spectra for (a) Zn_{2p} and (b) Ti_{2p} core level regions

In the same way that in the other TiCe-NPs (Table 4.6), the components $\text{Ti}^{4+}\text{--O}$ and Ti--O--Ti are included in the peak at 520 eV and 531 eV, respectively, to the TiZn-NPs (Table 4.7).

Table 4.8. Assigned peaks of deconvoluted Ti_{2p} , O_{1s} and M (Zn_{2p} , Zr_{3d} and Ce_{3d}) XPS regions.

Sample	O_{1s}	Assig.	% Peak	Ti_{2p}	Assig.	% Peak	M	Assig.	% Peak
Ti-NPs	530.0	$\text{Ti}^{4+}\text{--O}$	85	459.0	$\text{Ti}^{4+}_{2p3/2}$	67.32	—		
	531.3	--OH/Ti--O--Ti	13	464.7	$\text{Ti}^{4+}_{2p1/2}$	32.68			
	532.3	O--C	2						
TiZn-NPs	529.9	$\text{Ti}^{4+}\text{--O}$	55	457.3	$\text{Ti}^{3+}_{2p3/2}$	62.3	1021.5	$\text{Zn}_{2p3/2}$	69.8
	530.9	--OH/Ti--O--Ti	38	458.7	$\text{Ti}^{3+}_{2p3/2}$	28.1	1044.9	$\text{Zn}_{2p1/2}$	30.2
	532.5	O--C	7	460.1	$\text{Ti}^{4+}_{2p3/2}$	2.7			
				462.8	$\text{Ti}^{3+}_{2p1/2}$	2.2			
				464.4	$\text{Ti}^{3+}_{2p1/2}$	2.8			
				465.9	$\text{Ti}^{4+}_{2p1/2}$	1.8			
TiZr-NPs	529.8	$\text{Ti}^{4+}\text{--O}$	61	458.4	$\text{Ti}^{3+}_{2p3/2}$	68.2	182.1	$\text{Zr}_{3d5/2}$	51.1
	531.2	--OH/Ti--O--Ti	35	464.1	$\text{Ti}^{3+}_{2p1/2}$	31.8	182.8	$\text{Zr}_{3d5/2}$	9.4
	532.5	O--C	4				184.5	$\text{Zr}_{3d3/2}$	33.2
							185.0	$\text{Zr}_{3d3/2}$	6.3
TiCe-NPs	529.7	$\text{Ti}^{4+}\text{--O/Ce}^{4+}\text{--O}$	59	458.5	$\text{Ti}^{3+}_{2p3/2}$	68	880.5	$\text{Ce}^{3+}_{3d5/2}$	3
	530.1	$\text{--OH/Ti--O--Ti/Ce}^{3+}\text{--O}$	27	464.2	$\text{Ti}^{3+}_{2p1/2}$	32	882.2	$\text{Ce}^{4+}_{3d5/2}$	19
	531.3	O--C	14				884.6	$\text{Ce}^{3+}_{3d5/2}$	13
							887.0	$\text{Ce}^{4+}_{3d5/2}$	14
							897.8	$\text{Ce}^{4+}_{3d5/2}$	8
							898.8	$\text{Ce}^{3+}_{3d3/2}$	2
							900.4	$\text{Ce}^{4+}_{3d3/2}$	16
							903.3	$\text{Ce}^{3+}_{3d3/2}$	9
							905.8	$\text{Ce}^{4+}_{3d3/2}$	10
							915.2	$\text{Ce}^{4+}_{3d3/2}$	7

The **Table 4.8** shows the assigned peaks of deconvoluted Ti_{2p} , O_{1s} and M (Zn_{2p} , Zr_{3d} and Ce_{3d}) XPS regions. The $Ti_{2p_{3/2}}$ region (Figure 4.21 B) was deconvoluted in one peak centered at around 430.0 eV assigned to Ti^{4+} .

The O_{1s} spectra show the components $Ti^{4+}-O$, $Ti-O-Ti$ for the peaks at 530 and 531 eV, in all the TiX-NPs samples.

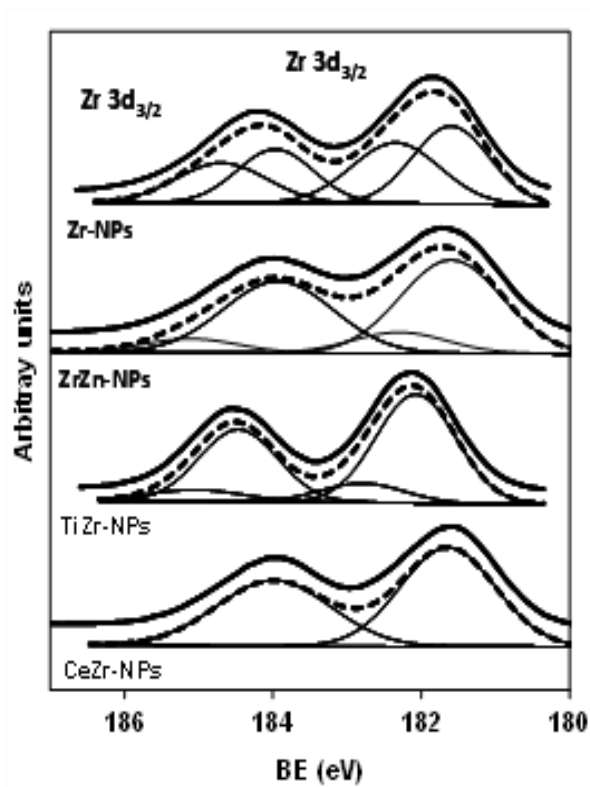


Figure 4.22. XPS spectra for Zr_{3d} core level regions

The deconvoluted Zr_{3d} spectra of the Zr-NPs and the ZrM-NPs samples (M: Zn, Ce and Ti) are shown in **Figure 4.22**. **Table 4.10** show the peak positions in

eV. In both Zn-NPs and ZrM-NPs there are two peaks at 181.6 eV and 182.6 eV, which are attributed to Zr^{+4} in stoichiometric ZrO_2 and non-stoichiometric oxides (ZrO_y : $0 < y < 2$). Nonstoichiometric zirconium oxides can show peaks at higher binding energies than monometallic ZrO_2 phases which happen in all Zr containing bimetallic samples except for CeZr-NPs.

Table 4.9. Mass ratio of metals and oxygen in nanoparticles (wt.%). Atomic percentages in brackets (at.%). For the calculation of these percentages carbon contents has not been considered.

Sample (M_1M_2 -NPs)	M_1	M_2	O
TiZn-NPs	64 (38)	0.3 (0.1)	36 (62)
TiZr-NPs	27 (20)	46 (18)	28 (62)
Ti-NPs	64 (38)	-	36 (62)
TiCe-NPs	55 (30)	1.3 (0.2)	44 (70)
ZrZn-NPs	58 (26)	18 (11)	24 (63)
Zr-NPs	80 (41)	-	20 (59)
Zn-NPs	75 (26)	-	25 (74)
CeZn-NPs	52 (15)	18 (11)	30 (74)
CeZr-NPs	33 (10)	43 (23)	24 (66)
Ce-NPs	73 (24)	-	27 (76)

Figure 4.10 provides the ratio of metals to oxygen that compose the nanoparticles. M_1 and M_2 are the metals in the nanoparticles samples in the order they are listed in the catalyst name, e.g. for TiZn-NPs M_1 =Ti and M_2 =Zn. Free of Zn samples with atomic content of oxygen (O_{at}) close to 66 % would indicate stoichiometric metal/oxygen composition, and the majority of these range relatively close to this value. Samples TiZn-NPs, TiZr-NPs and Ti-NPs has values lower O_{at} than 66 % indicating the possibility of presence of oxygen vacancies into the external structure. Moreover, sample TiZn-NPs has not practically Zn atoms on the

external structure while in the case of TiZr-NPs the proportion of both metals is very similar. On the other hand, due to the ZnO stoichiometric, in samples containing Zn the O_{at} of the stoichiometric bimetallic samples should be around 58 %; this means that in the rest of the Zn containing samples the amount of O_{at} is higher than the expected ones and so probably a lot of oxygen has been chemisorbed on the external surface of these nanoparticles.

Table 4.10. Assigned peaks of deconvoluted O_{1s} , Zr_{3d} and M (Ti_{2p} and Ce_{3d}), XPS regions.

Sample	O_{1s}	Assig.	% Peak	Zr_{3d}	Assig.	% Peak	M	Assig.	% Peak
Zr-NPs	529.7	$Zr^{4+}-O$	61	181.6	ZrO_2	52.7			
	531.1	$-OH/Zr-O-Zr$	35	182.3	ZrO_x	47.3			
	532.5	$O-C$	4						
ZrZn-NPs	530.2	$Zn^{2+}-O$	64	181.6	$Zr_{3d\ 5/2}$	46	1021.5	$Zn_{2p3/2}$	65
	531.7	$C-O/-OH$	30	183.9	$Zr_{3d\ 3/2}$	38	1044.5	$Zn_{2p1/2}$	35
	533.0	$O-C/C-COO^-$	6	182.3	$Zr_{3d\ 5/2}$	10			
				185.1	$Zr_{3d\ 3/2}$	6			
TiZr-NPs	529.8	$Ti^{4+}-O$	61	182.1	$Zr_{3d5/2}$	51.1	458.4	$Ti_{2p3/2}$	68.2
	531.2	$-OH/Ti-O-Ti$	35	182.8	$Zr_{3d5/2}$	9.4	464.1	$Ti_{2p1/2}$	31.8
	532.5	$O-C$	4	184.5	$Zr_{3d3/2}$	33.2			
				185.0	$Zr_{3d3/2}$	6.3			
CeZr-NPs	529.1	$Ce^{4+}-O$	48	181.6	$Zr^{4+}_{5/2}$	55.6	880.5	$Ce^{3+}_{3d5/2}$	5.3
	530.4	$Ce^{3+}-O$	44	184	$Zr^{4+}_{3/2}$	44.4	882.2	$Ce^{4+}_{3d5/2}$	13.4
	531.8	$O-C$	7				884.8	$Ce^{3+}_{3d5/2}$	16.5
							888.5	$Ce^{4+}_{3d5/2}$	9.6
							898.1	$Ce^{4+}_{3d5/2}$	14.1
							898.8	$Ce^{3+}_{3d3/2}$	3.6
							900.9	$Ce^{4+}_{3d3/2}$	9.8
							903.3	$Ce^{3+}_{3d3/2}$	7.9
							907.0	$Ce^{4+}_{3d3/2}$	9.8
							916.4	$Ce^{4+}_{3d3/2}$	10.0

Zr-NPs seem to be quite oxygen deficient just the opposite of Ce-NPs, while CeZr-NPs shows a stoichiometric balance of oxygen with more Zr than Ce on the external surface. Similar than TiZn-NPs, in TiCe-NPs the external structure is clearly dominated for Ti atoms on the lattice positions. This is also observed with less extension in sample ZrZn-NPs. Therefore, Zn atoms tend to be situated mainly in the core structure of these types of bimetallic nanoparticles.

4.3.6 Photodegradation Results

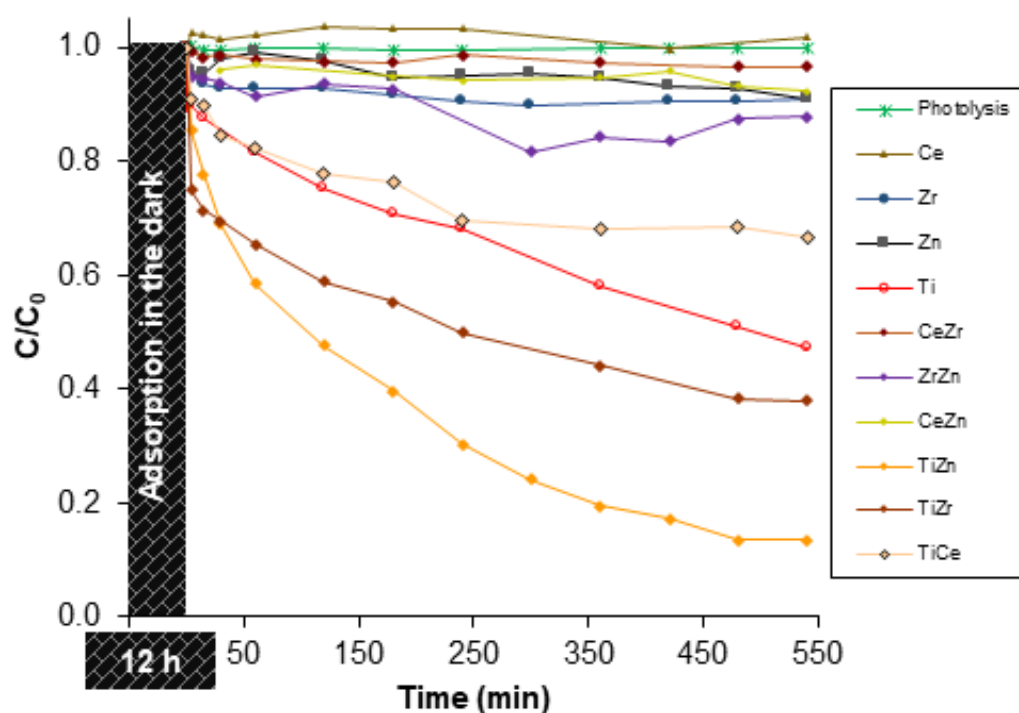


Figure 4.23. Photodegradation results for SMX degradation using NPs and blue-LED irradiation for 540 minutes.

The synthesized catalysts were tested for degradation of SMX using blue-LED irradiation (465 nm). For this, the nanoparticles were previously saturated in dark with a solution of the proper concentration to achieve a final concentration of 5 mg L⁻¹. The SMX photodegradation tendency of all photocatalysts are plotted in **Figure 4.23** and SMX degradation percent are shown in **Table 4.3**.

Table 4.11. % of SMX photodegradation.

Photocatalyst	% SMX degradation
TiZn-NPs	86.6
TiZr-NPs	66.0
Ti-NPs	53.0
TiCe-NPs	33.6
ZrZn-NPs	12.2
Zr-NPs	9.2
Zn-NPs	9.0
CeZn-NPs	7.6
CeZr-NPs	3.5
Ce-NPs	0.0

The information provided in **Figure 4.13** highlights the varying effectiveness of different nanoparticles in the photodegradation of contaminants. Specifically, TiZn-NPs demonstrated the highest percentage of contaminant photodegradation at 86.6 %. TiZr-NPs and monometallic-phase titanium nanoparticles (Ti-NPs) also exhibited significant removal rates, of 66 % and 53 %, respectively. Conversely, titanium and cerium nanoparticles (TiCe-NPs) exhibit a slightly lower removal rate of 33.6 %.

In contrast, mixed nanoparticles of cerium and zirconium (CeZr-NPs), monometallic zirconium (Zr-NPs), and monometallic zinc (Zn-NPs) demonstrated the lowest removal values, with 3.5 %, 9.2 %, and 9 %, respectively. Additionally, the monometallic cerium phase (Ce-NPs) did not exhibit activity in degrading the contaminant. Some mixed nanoparticles show relatively similar removal rates, such as those corresponding to cerium and zinc (CeZn-NPs) with 7.6 %, and zirconium and zinc (ZrZn-NPs) with 12.2 %. The results of photodegradation using commercial semiconductor oxides did not show significant activities; therefore, they have not been included in the previous figure.

The obtained XMS degradation results don't follow apparently any full trend in line with the textural characteristics even with the band-gap values. In fact, TiZn-NPs shows one of the highest band-gap values among the samples, although it has one of the highest values of surface area. Nevertheless, it should be noted that the most active samples TiZn-NPs, TiZr-NPs and Ti-NPs are the ones that clearly contain oxygen vacancies as the XPS indicated by both, binding energies of the different deconvoluted peaks and atomic content of oxygen and metals. Moreover, the samples with poor photodegradation capacity were those with O_{at} higher than 66 %, and as general trend above this value, the higher the O_{at} the lower the photoactivity. This means that the type of structure of these nanoparticles combined with the possibility of vacancies generation seem to be a clue for designing high performance photocatalysts based on bimetallic oxides.

4.4 CONCLUSIONS

We evaluated the synergistic effect on the photodegradation capacity of novel coupled semiconductors using SMX as the probe molecule under blue irradiation.

The synthesis of mixed nanoparticles using the reversed two-emulsion technique demonstrated varying degrees of success in achieving mixed phases. CeZr-NPs displayed a shift in peaks on the 2θ axis, indicating successful synthesis. Similarly, TiZn-NPs exhibited a typical X-ray diffraction pattern of the anatase phase, suggesting zinc doping in TiO_2 crystalline structure. TiZr-NPs also showed promise, with zirconium likely acting as a dopant in anatase.

However, the TiCe-NPs show evidence of both mixed and monometallic phases of titanium dioxide and cerium oxide. In contrast, ZrZn and CeZn NPs failed to produce mixed oxides, displaying only the characteristic peaks of individual components. These findings underscore the complexity of synthesizing mixed-phase nanoparticles and highlight the importance of precise control over the synthesis parameters for the desired material properties.

Investigation of the textural properties of the synthesized materials revealed that the mixed nanoparticles studied, TiZn-NPs and TiZr-NPs, have the highest surface areas, measuring 220 and 182 $\text{m}^2 \text{g}^{-1}$, respectively. In addition, the crystal sizes were 8 and 11.9 nm, respectively. These findings could suggest that the photocatalytic efficacy of these materials may be enhanced by their smaller particle sizes, however the main reason for why the most photo-active samples are TiZn-NPs and TiZr-NPs would be related with the oxygen vacancies generation capacity.

We demonstrated that intentionally combining coupled semiconductors in a single crystalline structure enables us to leverage the advantages of both and enhance the efficiency of photocatalysis always that the generation of oxygen vacancies can occur and keeping low their oxygen chemisorption capacity. As general composition distribution tendencies found within this type of bimetallic

oxides we can conclude that Ti atoms tend to be well present on the shell part of the nanoparticles while Zn use to be forming part mainly of the core.

Finally, TiZr-NPs were selected for further study in [Chapter V](#), with the objective of optimizing both size miniaturization and TiO₂-ZrO₂ content. Meanwhile, TiZn-NPs are investigated in [Chapter VI](#) as coated materials in a recirculation 3D-printed LED-reactor.

4.5 BIBLIOGRAPHY

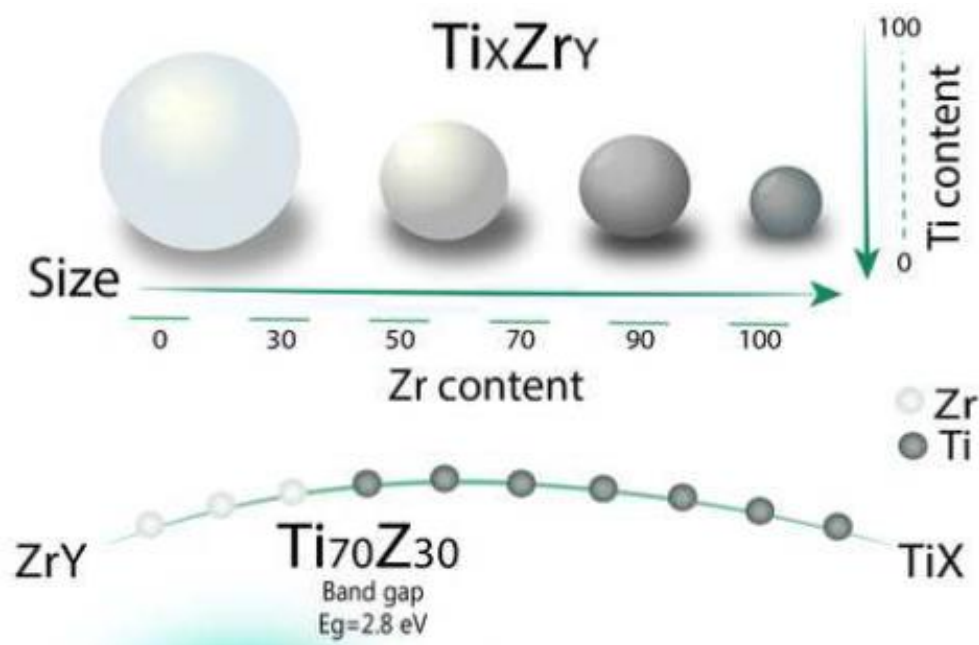
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**CHAPTER V: SIZE-MINIATURIZATION OF TiO₂-
ZrO₂ COUPLED SEMICONDUCTORS TO
DEVELOP HIGHLY EFFICIENT VISIBLE-
DRIVEN PHOTOCATALYSTS FOR THE
DEGRADATION OF DRUGS IN WASTEWATE**



Graphical Abstract

5.1 ABSTRACT

Solar photocatalysis has emerged as a cost-effective and efficient approach to address water remediation challenges. Nonetheless, there is a pressing requirement to innovate and design novel photocatalysts capable of utilizing solar or visible light. In this study, morphology control and surface sensitization techniques were integrated to engineer titania-based photocatalysts that operate efficiently under blue-LED light. This is accomplished through the synthesis of $\text{Ti}_a\text{Zr}_b\text{O}_c$ materials (Ti_xZr_y) with finely tuned nano-scale dimensions, employing meticulous control through the inverse two-emulsion technique. This innovative approach has yielded remarkable performance in the removal of pharmaceutical contaminants. Zr contents highly affect the size and, thus, the active surface of the photocatalysts.

XRD results indicate that a low Zr content zirconium titanates are formed whereas at high Zr contents zirconia cubic phase is the main crystalline structure detected. The heterojunction created between the zirconium titanate and the titania anatase phases can be responsible of the band gap reduction observed ($E_g = 2.8$ eV). A SMX degradation percent as high as 80.1 % with a decrease of the treated water toxicity was obtained for Ti70Zr30 under blue-LEDs irradiation which is explained based on the formation of zirconium titanates observed by XRD and XPS and the high active surface area.

5.2 EXPERIMENTAL

The inverse microemulsion synthesis, and characterization methodology of the coupled nanoparticles photocatalysts, as well as photodegradation procedures of model molecule under blue-LED irradiation using a homemade slurry batch LED-reactor containing a dispersion of the photocatalyst, are presented in [Chapter II](#) [1,2] of this thesis. In this chapter the samples were labeled with the notation Ti_xZr_y , where X and Y represent the weight percentages of TiO_2 and ZrO_2 in the sample, respectively. For instance, Ti10Zr90 signifies that the nanoparticles contain 10 wt. % of TiO_2 and 90 % of ZrO_2 . Here, toxicity assessments were conducted using the LUMISTox 300 coupled with a LUMISTherm incubator. The results are presented as follows:

5.3 RESULTS AND DISCUSSION

5.3.1 High Resolution Transmission Electron Microscopy (HRTEM)

The morphology and particle size of the coupled semiconductors were analyzed by TEM (**Figure 5.1**). Rod-like nanoparticles of an average length of 26

nm were observed for monometallic TiO_2 nanoparticles, Ti100 (**Figure 5.1a**). Spherical-shaped and smaller nanoparticles appear by adding Zr in the nanoparticle formulation.

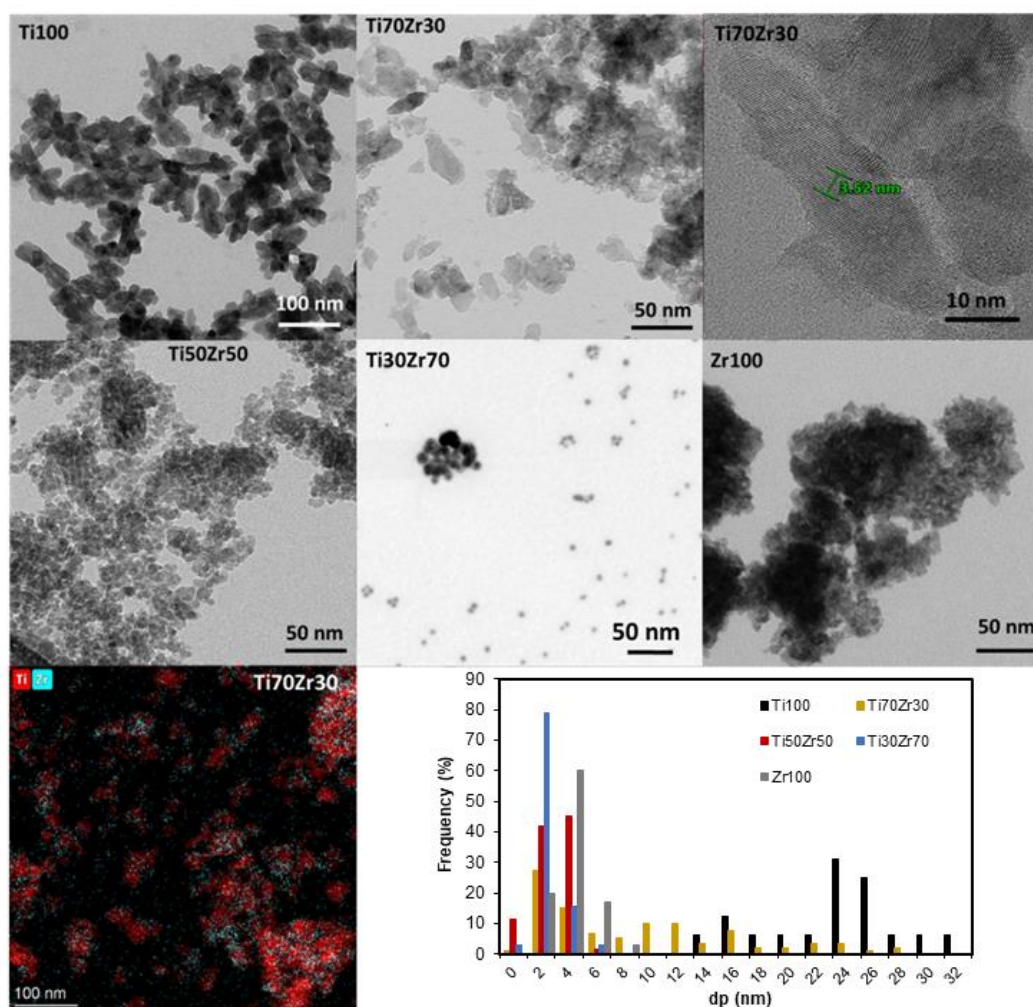


Figure 5.1. (a-f) TEM images, (g) TEM mapping and (h) particle size distributions of monometallic (Ti100 and Zr100) and mixed (Ti_xZr_y) oxides nanoparticles.

A mixture of rod-like and spherical-shaped nanoparticles is obtained for Ti₇₀Zr₃₀ photocatalyst (**Figure 5.1b**) whereas just spherical-shaped nanoparticles are observed at Zr contents higher than 30 % (**Figure 5.1d-f**). The higher the Zr content the lower the particle size and narrower pore size distributions are obtained (**Figure 5.1h**). The average particle size (**Table 5.1**) decreases from 26 nm for Ti₁₀₀ to 3.4 for Ti₃₀Zr₇₀, and then increases to 4.9 nm for monometallic Zr₁₀₀. TEM mapping was performed on the Ti₇₀Zr₃₀ photocatalyst in order to analyze the Ti and Zr distribution on the nanoparticle surface (**Figure 5.1g**). As it was expected, Ti is the major component of the particles and Zr is homogeneously distributed along the nanoparticles surface.

5.3.2 X-ray diffraction (XRD)

The crystallinity of nanoparticles was analyzed by XRD. **Figure 5.2** displays the diffractograms, while **Table 5.1** presents the particle size and d-spacing values obtained by applying the Scherrer equation and the Bragg law, respectively, to the most intense diffraction peak. Note that the crystallite size obtained by XRD is higher than the particle size obtained by TEM (**Table 5.1**) at low Ti contents, because these photocatalysts are formed mainly by particles of size lower than 5 nm and analyzing crystalline domain sizes below 5 nm using XRD, is challenging due to both broad peaks and low signal-to-noise ratios. In this sense, only the biggest particles are detected by XRD. At high Ti contents, TEM and XRD particle sizes are similar, since size distributions are centered at higher sizes. It is important to highlight that no diffraction peaks are obtained for Ti₃₀Zr₅₀ photocatalyst, since particles with sizes lower than 4 nm are obtained, as it was observed from TEM images (**Figure 5.1h**).

On the other hand, the anatase phase is detected in commercial titania, whereas the rutile phase is stabilized in Ti100 nanoparticles. Moreover, peaks become wider in the Ti100 photocatalyst regarding Ti-com, denoting a smaller particle size (10.8 nm vs 28.8 nm, **Table 5.1**). The d-spacing was 0.3252 nm for Ti100 and 0.3523 nm for Ti-com which aligns well with the (110) and (101) crystallographic planes of rutile and anatase TiO_2 , respectively [3].

TiO_2 physicochemical properties are deeply affected by the crystal structure. Rutile TiO_2 exhibits a narrower bandgap, greater dielectric constant, and higher refractive index compared to anatase TiO_2 , all of which are favorable attributes for various photonic applications.

The rutile phase can be obtained from methods that favor the direct precipitation of TiO_2 from a liquid phase, such as hydrothermal methods. Aside from this method, rutile is just obtained through anatase phase thermal transition [4,5]. However the transformation from anatase to rutile phase typically requires elevated temperatures, often ranging from 600 to 800 °C [6,7].

The average crystal size seems to be a crucial factor, affecting the anatase to rutile transformation [5,8–10]. Anatase exhibits the highest thermodynamic stability at sizes smaller than 11 nm, while brookite prevails for crystal sizes ranging from 11 to 35 nm. Rutile, on the other hand, is most stable when crystal sizes exceed 35 nm [8,11]. Thus, anatase can be synthesized at ultrafine sizes [11]. However, nanosized TiO_2 could transform to rutile by heating, and this transition temperature is affected by the initial particle size. Li *et al.* [9] observed that the lowest transition starting temperature and thermal stability was obtained with 12 nm anatase, compared with 17 and 23 nm photocatalysts.

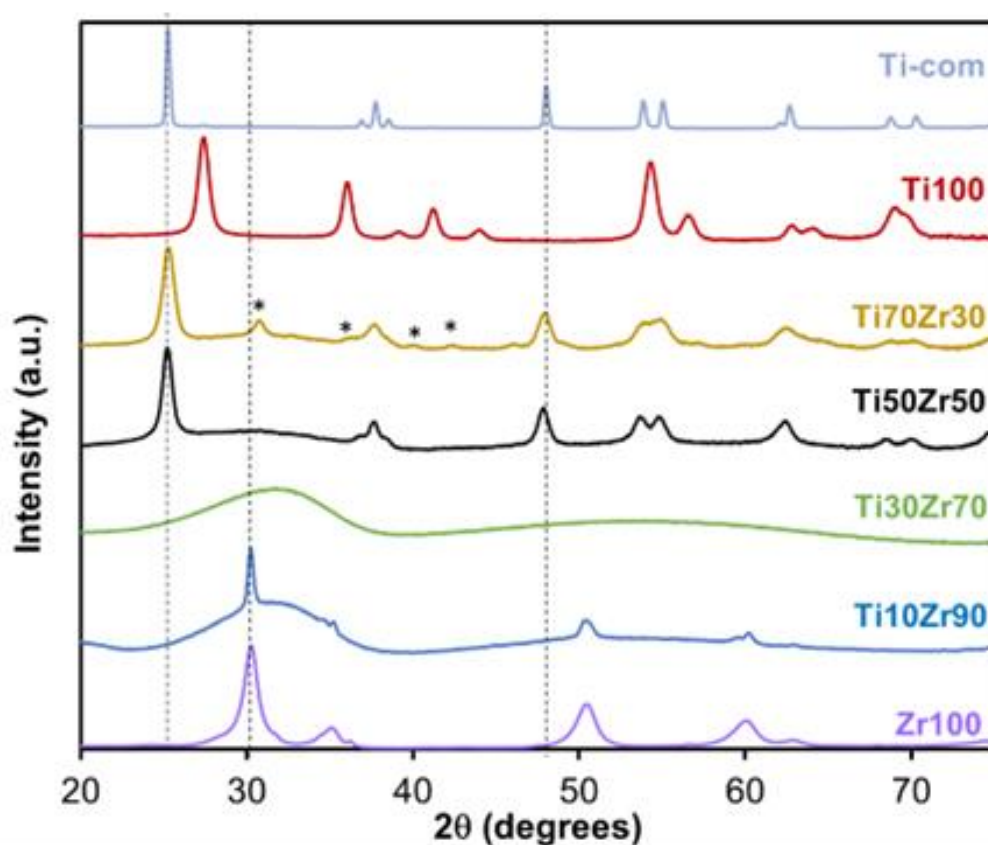


Figure 5.2. XRD patterns of Ti_xZr_y nanoparticles.

Here, TiO_2 nanoparticles of an average crystallite size of 10.8 nm were obtained in Ti100 after a calcination at 400 °C. A priori, at this crystal size, anatase phase could be expected rather than a rutile one. Moreover, the calcination temperature is low enough to produce an anatase to rutile transformation. However, the ultrafine TiO_2 particles obtained by the two-emulsion method, could decrease the transformation temperature since size affects the number of particle-particle contacts within a given volume, favoring the phase transition and consequently the stabilization of small rutile nanoparticles.

The incorporation of Zr to the titania formulation, changes the diffraction pattern in comparison with Ti100. Ti70Zr30 shows a diffraction pattern similar to anatase TiO_2 but new peaks emerge at 30.8° , 35.9° , 40.9° and 42.1° which could be identified as zirconium titanates, $\text{Ti}_{0.33}\text{Zr}_{0.67}\text{O}_2$ (JCPDS 46-1265) [12,13] and ZrTiO_4 (34-0415) [14]. These peaks almost disappear by increasing the Zr content. For high Zr contents ($>50\%$), the zirconia cubic phase (JCPDS 49-1642) is the main crystalline structure detected. In these cases, the monoclinic zirconia phase could be expected, since the stable phase is at temperatures below 1200°C , whereas tetragonal and cubic phases are stable at temperatures above 1200°C and 2400°C , respectively [15]. However, the zirconia phase stabilization is also size-dependent. Consequently, the cubic phase can be stabilized at a crystallite size lower than 11 nm [16]. A crystallite size of 8.5 nm was obtained for Zr100 which could explain the stabilization of the cubic phase. The d-spacing corroborates that the anatase phase predominates for photocatalysts with high Ti content ($\geq 50\%$) whereas the zirconia cubic phase with a d-spacing of 0.295 nm is predominant at higher content of Zr ($> 50\%$) [17].

5.3.3 Nitrogen Adsorption-Desorption Isotherms at 77 K

The porous structure of the photocatalysts was examined through N_2 adsorption-desorption analysis and results are collected in **Figure 5.3** and **Table 5.1**.

Type II isotherm is obtained for Ti100 typical of microporous materials whereas hybrid type I-IV isotherms were observed for the Ti_xZr_y photocatalysts, exhibiting a distinct hysteresis loop that indicates the presence of mesopores. The N_2 adsorption at low pressures is likely related to adsorption on the external surface

of the nanoparticles, while the presence of mesopores can be attributed to interparticle voids.

Table 5.1. Results from the characterization of the catalysts through N₂ adsorption and XRD.

Photocatalyst	N ₂ -isotherm			XRD		TEM
	S _{BET} m ² g ⁻¹	V _{0.95} cm ³ g ⁻¹	V _{MESO}	dp nm	d-spacing nm	dp nm
Zr100	101	0.124	0.082	8.5	0.2949	4.9
Ti10Zr90	171	0.134	0.080	n.a.	0.2951	-
Ti30Zr70	190	0.101	0.043	n.a.	n.a.	3.4
Ti50Zr50	182	0.180	0.103	10.6	0.3531	3.8
Ti70Zr30	165	0.248	0.194	10.1	0.3517	11.2
Ti100	78	0.216	0.082	10.8	0.3252	26.0
Ti-com	17	0.019	0.015	28.8	0.3523	-

S_{BET}: BET surface area, *dp* (XRD): crystallite size determined by Scherrer equations.

Note that the surface area (S_{BET}) is directly related to the nanoparticle size. The lower the *dp* (TEM) the higher the S_{BET}, that is, nanoparticles expose more external surface-per-volume. The N₂-adsorption at higher relative pressures and the hysteresis loop also depend on the Zr content and, consequently, the particle size. Interparticle voids left by the big particles (26 nm) of Ti100, should be in the range of wide mesopores or macropores which explains the fast N₂-uptake at P/P₀ close to 1.

As it was observed by TEM, the addition of Zr decreases the particle size below 11 nm, and consequently, narrower interparticle voids are left, increasing the N₂-adsorption at moderate relative pressures proper of mesoporous materials.

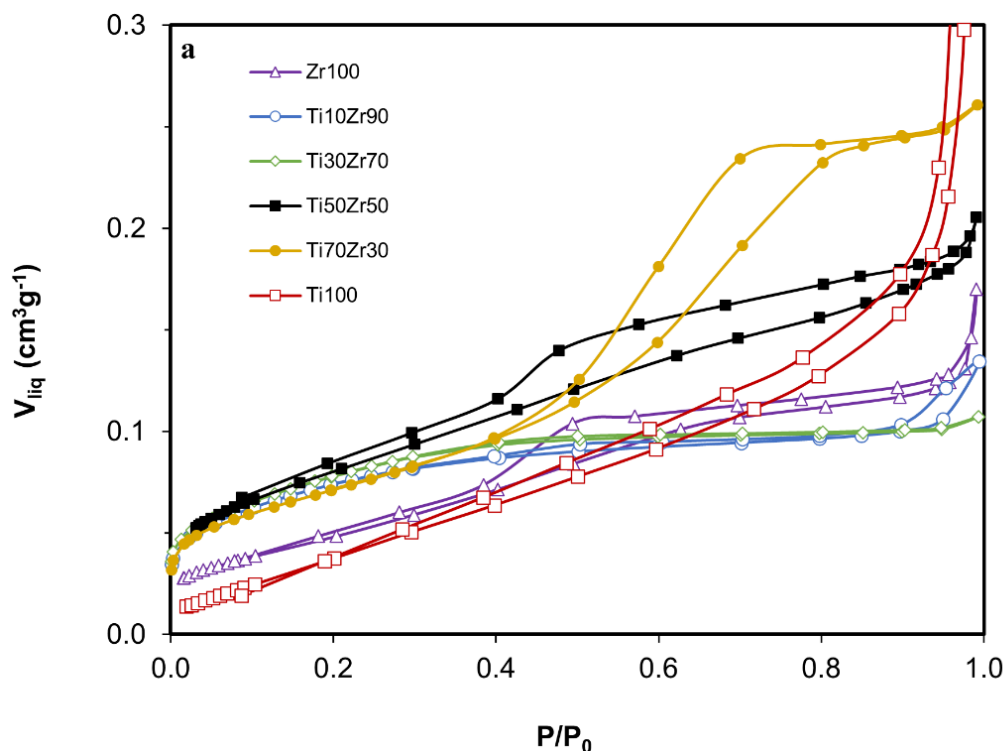


Figure 5.3. N_2 adsorption-desorption isotherms of Ti_xZr_y photocatalysts.

This N_2 -adsorption at moderate relative pressures and the hysteresis loop, decreases by increasing the Zr content due to the particle size decrease up to almost disappearing at high Zr contents ($\text{Ti}_{30}\text{Zr}_{70}$, $\text{Ti}_{10}\text{Zr}_{90}$, and even Zr_{100}), denoting that the interparticle voids left by these small particles ($< 4 \text{ nm}$) are in the micropores range.

5.3.4 Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS)

The band gap (E_g) of the prepared photocatalysts was studied by diffuse reflectance spectroscopy. The band gap of photocatalysts can be evaluated using the Kubelka–Munk function, $F(R)$. The E_g value could be obtained by plotting

$(F(R)E)^n$ as a function of E ($h\nu$). A value of $n = 1/2$ was considered for permitted direct transitions. The Kubelka Munk plot of photocatalysts is presented in **Figure 5.4** and the obtained E_g is collected in **Table 5.2**.

Table 5.2. Band Gap.

Photocatalyst	Band Gap
	eV
Zr100	4.55
Ti10Zr90	3.42
Ti30Zr70	3.32
Ti50Zr50	2.82
Ti70Zr30	2.90
Ti100	2.98

The E_g value obtained for Ti-commercial was 3.22 eV which closely aligns with the reported value for the titania anatase phase (3.20 eV) [18,19]. The E_g decreases to 2.98 eV for Ti100 nanoparticles which can be attributed to the stabilization of the rutile phase showing a reported band gap of 3.0 eV [19]. For monometallic ZrO_2 photocatalysts (**Figure 5.4b**), the band gap decreases from 5.0 eV to 4.5 eV for monoclinic Zr-com and cubic Zr100. The TiO_2/ZrO_2 heterojunction decreases the band gap of photocatalysts.

The higher the content of Ti, the lower the band gap of the Ti_xZr_y photocatalysts, achieving the optimal value with a content of Ti of 50-70 %. This red shift of the optical absorption edge of the material, could be explained by the Ti doping of bulk ZrO_2 . Gallino *et al.* [20] demonstrated that the introduction of Ti into bulk ZrO_2 , results in the creation of an unoccupied Ti_{3d} band, positioned approximately 0.5 eV below the bottom of the conduction band which induces a decrease of the band gap.

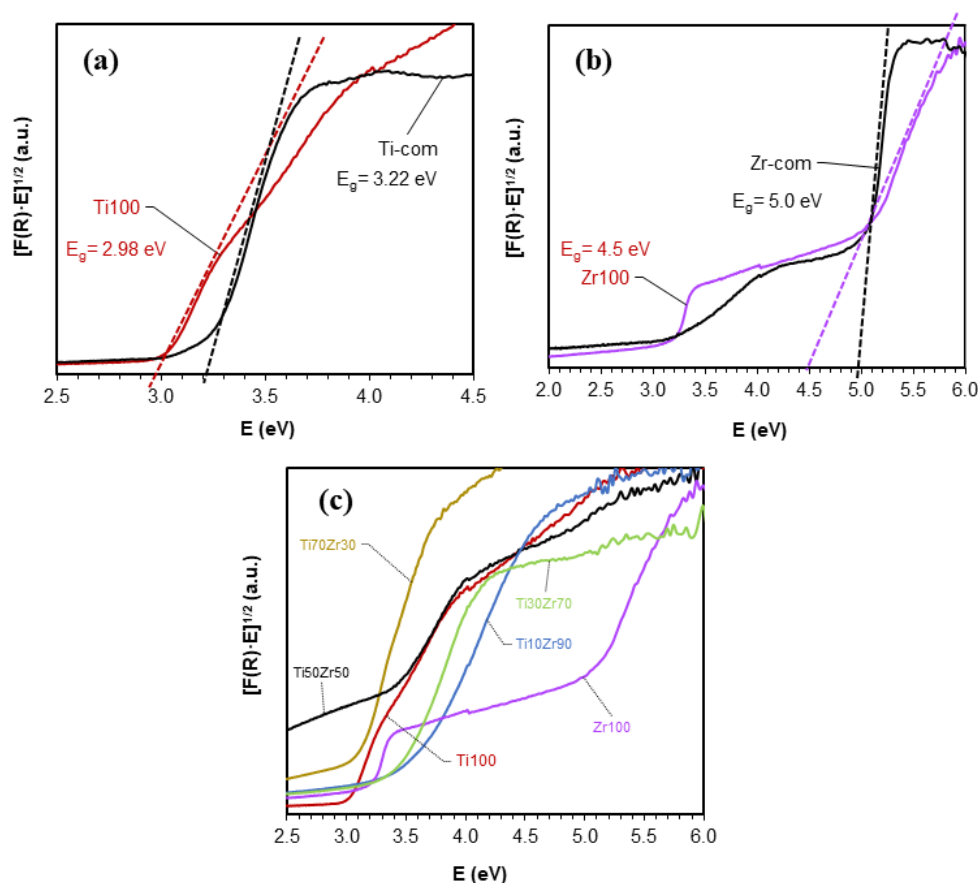


Figure 5.4. Diffuse reflectance spectra of (a) monometallic TiO_2 photocatalysts, (b) monometallic ZrO_2 photocatalysts and (c) Ti_xZr_y nanoparticles.

Consequently, the inclusion of ZrO_2 into TiO_2 results in intermediate band gap values between the parent oxides (TiO_2 and ZrO_2). However, it's worth noting that an unconventional decrease in band gap values was observed when Zr was incorporated into TiO_2 (Ti50Zr50 and Ti70Zr30) photocatalysts due to the formation of zirconium titanate phases (see XRD plot).

The creation of a heterojunction between the zirconium titanate phases and the titania anatase phase, can be attributed to the reduction in band gap values [21,22].

5.3.5 X-ray Photoelectron Spectroscopy (XPS)

The surface chemistry of the photocatalysts was analyzed by XPS. C_{1s} , O_{1s} , Ti_{2p} , and Zr_{3d} spectral regions are depicted in **Figure 5.5** and data obtained from their deconvolutions are collected in **Table 5.3**.

Adventitious carbon was used as a reference for the calibration of the binding energies. There is evidence suggesting that CO or CO_2 species may be involved in the gradual accumulation of carbon on pristine oxide surfaces [23]. Oxygen vacancies can significantly impact the interaction between the surface and CO_2 , thereby increasing the adsorption of CO_2 molecules and leading to the formation of carbon intermediates [24–28].

Oxygen vacancies formed on the surface of titania are directly involved in the activation of CO_2 , resulting in the formation of carbonate species. Thus, the amount of carbon fixed could be related to the exposed surface of the material and its surface chemistry.

Three peaks were necessary to accurately model the C_{1s} spectral region at 284.6, 285.8, and 288.5 eV identified as C-C, C-O, and COO^- . The carbon content (C_{1s} , **Table 5.3**) seems to depend on the surface area of the materials. The lower the particle size, the more exposed the defect-rich surface, and the higher the adventitious carbon fixed.

Note also that carbonate species are present in nanoparticles where they are not detected in Ti-com, probably indicating a more oxygen vacancies concentration on the nanoparticles surface. The amount of carbonate (COO^-) increases in the mixed oxides, is probably due to the heterojunction of Ti-Zr which creates a more oxygen-deficient structure. The presence of these oxygen vacancies can be also observed by analyzing the O_{1s} region (**Figure 5.5b**).

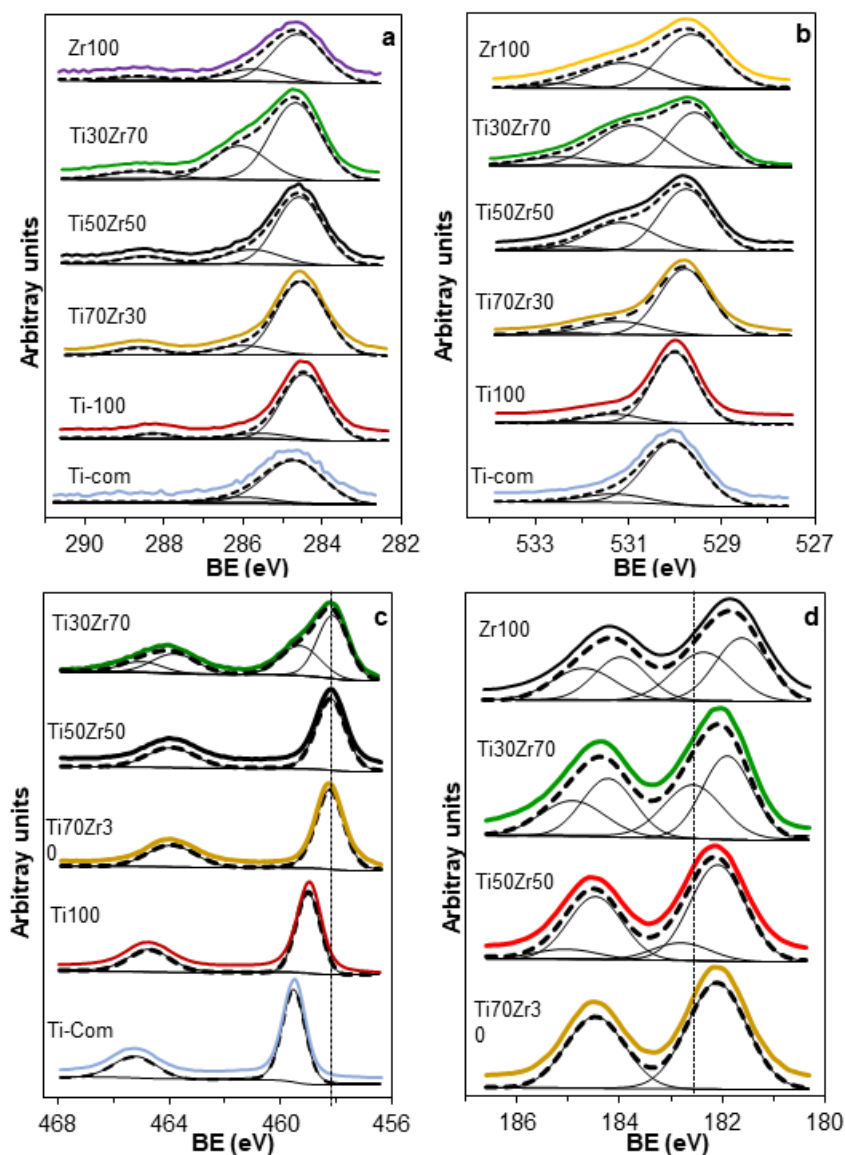


Figure 5.5. XPS spectra. (a) C_{1s}, (b) O_{1s}, (c) Ti_{2p} and (d) Zr_{3d}

Three peaks are also observed in the O_{1s} region at 529.8, 531.1, and 532.5 eV assigned to lattice oxygen (O_L), adsorbed oxygen on the vacancies (O_{ads}), and C-O species, respectively [29,30].

The O_{ads} component of Ti_xZr_y photocatalysts is much higher than that of the monometallic Ti photocatalysts, denoting a more oxygen-vacancies-rich surface as was pointed out from the C_{1s} region.

Table 5.3. XPS results of Ti_xZr_y photocatalysts: surface content, binding energy and percentage of the components used to fit the C_{1s} , O_{1s} , Ti_{2p} and Zr_{3d} spectral regions of Ti_xZr_y .

Sample	C_{1s}	Assig.	FWHM (eV)	% Peak	% C	O_{1s}	Assig.	% Peak	% O
Ti-com	284.7	C-C	1.74	88	6.0	530.1	$Ti^{4+}-O$	87	30.7
	286.0	C-O		12		531.3	$-OH/Ti-O-Ti$	13	
Ti100	284.7	C-C	1.31	86	7.5	530.0	$Ti^{4+}-O$	85	31.2
	285.8	C-O		9		531.3	$-OH/Ti-O-Ti$	13	
	288.5	COO^-		5		532.3	O-C	2	
Ti70Zr30	284.5	C-C	1.45	79	8.8	529.8	$Ti^{4+}-O$	75.7	28.6
	286.0	C-O		12		531.2	$-OH/Ti-O-Ti$	20.9	
	288.6	COO^-		9		532.4	O-C	3.3	
Ti50Zr50	284.6	C-C	1.39	74	9.8	529.8	$Ti^{4+}-O$	61	24.3
	285.8	C-O		18		531.2	$-OH/Ti-O-Ti$	35	
	288.5	COO^-		8		532.5	O-C	4	
Ti30Zr70	284.7	C-C	1.46	62	11.9	529.6	$Ti^{4+}-O$	44	23.3
	286.1	C-O		29		530.9	$Ti^{3+}-O$	46	
	288.6	COO^-		9		532.5	O-C	9	
Zr100	284.6	C-C	1.54	73	4.9	529.7	$Zr^{4+}-O$	61	19.5
	285.8	C-O		19		531.1	$-OH/Zr-O-Zr$	35	
	288.7	COO^-		8		532.5	O-C	4	

Table 5.3 (Continued)

Sample	Ti _{2p}	Assig.	% Peak	% Ti	Zr _{3d}	Assig.	% Peak	% Zr
Ti-com	460	Ti ⁴⁺ _{3/2}	100	63	—			
	465	Ti ⁴⁺ _{1/2}						
Ti100	459	Ti ⁴⁺ _{3/2}	100	61	—			
	465	Ti ⁴⁺ _{1/2}						
Ti70Zr30	458.4	Ti ³⁺ _{3/2}	100.0	41.0	182.1	Zr-O-Ti	100.0	21.6
	464.1	Ti ³⁺ _{1/2}			184.5			
Ti50Zr50	458	Ti ³⁺ _{3/2}	100	32	182	Zr-O-Ti	84	36
	464	Ti ³⁺ _{1/2}			183	ZrO ₂	16	
					184			
					185			
Ti30Zr70	458	Ti ³⁺ _{3/2}	62	19	182	Zr-O-Ti	50	46
	459	Ti ⁴⁺ _{3/2}	38		182	ZrO ₂	50	
	464	Ti ³⁺ _{1/2}			184			
	465	Ti ⁴⁺ _{1/2}			185			
Zr100	—				182	ZrO ₂	53	76
					182	ZrO _x	47	

For monometallic TiO₂ photocatalysts (Ti100 and Ti-com), the Ti_{2p3/2} region (**Figure 5.5c**) was deconvolved in one peak, centered at around 430.0 eV attributed to Ti⁴⁺. A new peak appears at 458.2 eV for Ti_xZr_y photocatalysts which can be ascribed to Ti³⁺/zirconium titanates species [31,32]. The same conclusions can be obtained by analyzing the Zr_{3d5/2} region (**Figure 5.5d**). For monometallic ZrO₂ (Zr100), two peaks appear at 181.6 eV and 182.6 eV which are ascribed to Zr⁴⁺ in stoichiometric ZrO₂ and non-stoichiometric oxides (ZrO_y: 0<y<2), respectively

[32]. Two peaks, which are shifted 0.8 eV to higher B.E, were also required to deconvolve the $Zr_{3d5/2}$ region for Ti_xZr_y photocatalysts, but the relative intensity of both peaks is different, depending on the Ti content. The peak at 181.7 eV can be attributed to the $Zr_{3d3/2}$ in hybridized ZrO_2-TiO_2 nanostructure, whereas the peak at 182.6 eV can be attributed to $Zr_{3d3/2}$ in free ZrO_2 . It is important to highlight that the contribution of this hybridized ZrO_2-TiO_2 peak was 100, 84.4 and 49.9 % for $Ti_{70}Zr_{30}$ (stoichiometric hybridized ZrO_2-TiO_2), $Ti_{50}Zr_{50}$ and $Ti_{30}Zr_{70}$, respectively which is in good agreement with the main contribution of the 458.2 eV $Ti_{2p3/2}$ signal in $Ti_{70}Zr_{30}$ and $Ti_{50}Zr_{50}$ photocatalysts ascribed to Ti^{3+} /zirconium titanates species. Thus, the hybridized ZrO_2-TiO_2 nanostructure seems to increase with the Ti content in accordance with the XRD results to be maximum for the $Ti_{70}Zr_{30}$ (stoichiometric zirconium titanate).

5.3.6 Photodegradation Results

The synthesized catalysts were tested in the degradation of SMX using blue-LED irradiation (465 nm). For that, the nanoparticles were previously saturated in the dark with a solution of the proper concentration to achieve a final concentration of 5 mg L⁻¹. The SMX photodegradation tendency of all photocatalysts are plotted in **Figure 5.6**.

From **Figure 5.6** it can be observed that Ti-com is not photoactive because the energy of the blue-LED is not enough to promote an electron from the valence band to the conduction band, which is caused by the wide band gap. However, the miniaturization of titania size in Ti_{100} increases the photoactivity to 49.3 %, despite the less photoactive crystal phase (rutile) being obtained. Conversely, the Zr_{100} photocatalyst is poorly active due to the high band gap of the photocatalyst.

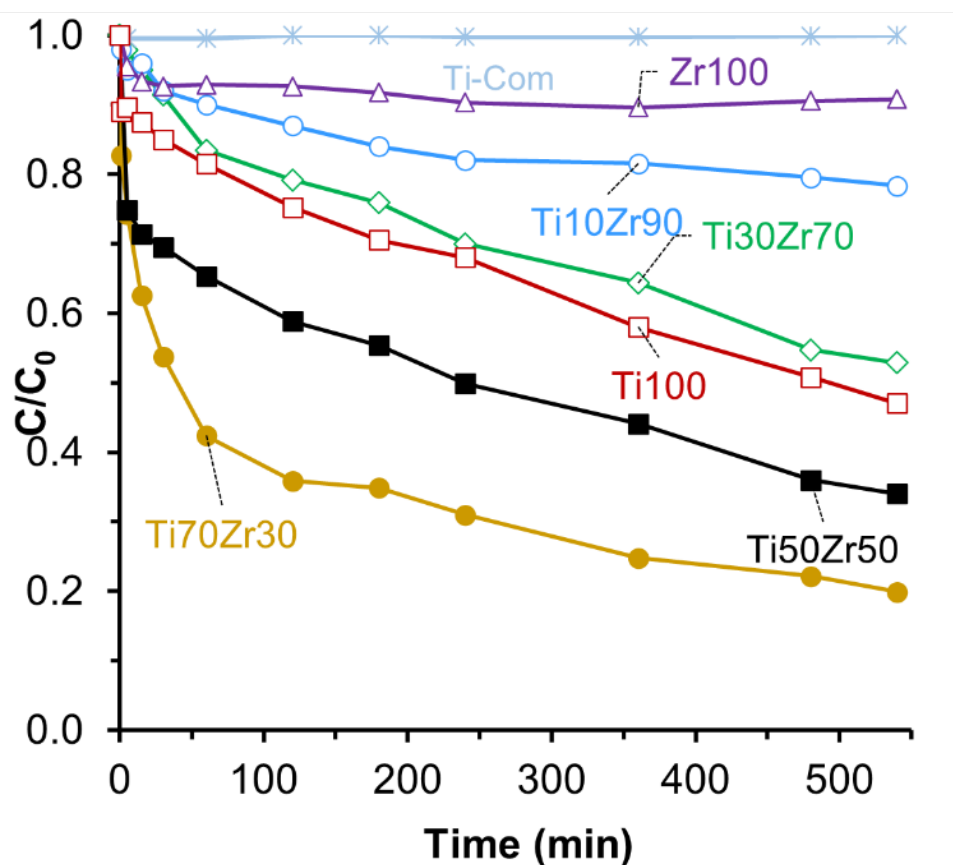


Figure 5.6. Photodegradation results for SMX degradation using Ti_xZr_y photocatalysts under blue-LED irradiation.

The activity increases by adding Ti to the photocatalyst which could be explained based on the decrease of the band gap and the decrease of the particle size. The decrease of the particle size enhances the photocatalytic performance due to i) the increase of the photo-catalytically active surface area for the degradation of SMX and ii) the minimization of the distance that photogenerated electrons and holes need to cross to reach the surface where the reaction occurs, and consequently, the minimization of the electron-hole recombination probability.

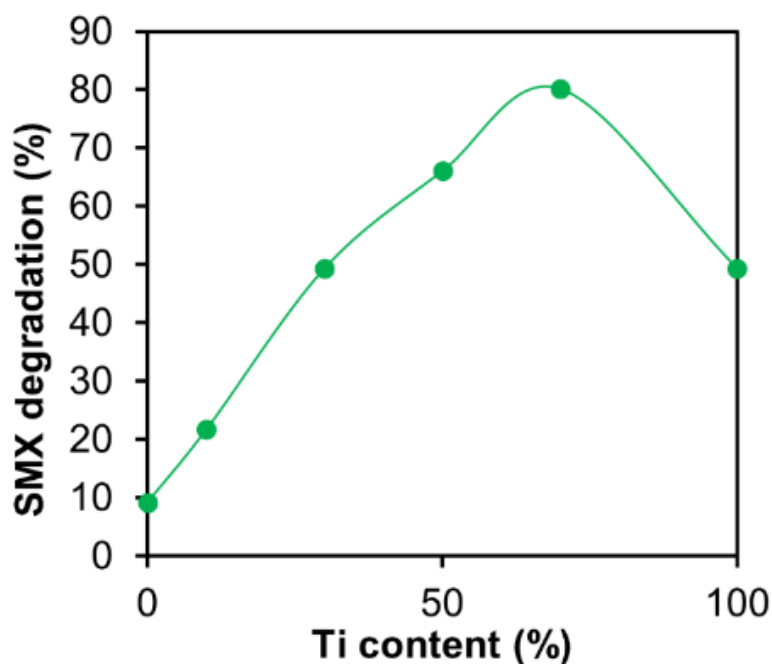


Figure 5.7. % of SMX photodegradation achieved at 540 min as a function of the Ti content in the Ti_xZr_y photocatalysts.

Note that by only adding 30 % of Ti to the Zr nanoparticle composition the degradation activity achieved (49.3 %) is similar to the obtained for Ti100 (53 %). However, a synergistic effect is obtained for nanoparticles with a 50 % and 70 % of Ti. If segregated phases were obtained, a dilution effect would be expected by increasing the Ti content, and an average activity between the obtained for Ti-100 and Zr-100 would be obtained for the Ti50Zr50 photocatalyst. However, the activity highly increases from 53 % (Ti100) to 66 % for Ti50Zr50 which could be explained based on, as commented, the active surface area increasing along with the reduction in the band gap. However, a SMX degradation percent as high as 80.1 % was obtained for Ti70Zr30 under blue-LED irradiation, although the surface area

has decreased, and the band gap has increased in this photocatalyst, compared to the Ti50Zr50 one.

This activity enhancement is explained, based on the formation of zirconium titanates observed by XRD and XPS. The heterojunction comprising $\text{ZrTiO}_4/\text{ZrTi}_2\text{O}_6/\text{TiO}_2$ extends the lifespan of photogenerated charge carriers, thereby enhancing photoactivity [31,32]. Briefly, the optimal SMX degradation (**Figure 5.7**) in photocatalyst Ti70Zr30 is achieved due to an optimal combination of surface area, band gap, and formation of hybridized zirconium titanates nanostructured.

SMX exhibits a UV-visible absorption spectrum characterized by a solitary peak, which reaches its maximum absorption at 258 nm. This distinctive peak can be attributed to a $\pi-\pi^*$ transition, most likely associated with the aniline group. UV-visible absorption spectroscopy was employed to assess the extent of transformation induced in SMX. **Figure 5.8a** illustrates a notable reduction in the distinctive absorption peak of SMX for the Ti70Zr30 photocatalyst over varying irradiation periods ranging from 0 to 540 min.

This decline ultimately means the complete disappearance of the SMX absorption band. It's worth mentioning that a rise in absorbance within the wavelength range of 300-450 nm in the spectrum, indicates the generation of byproducts [33,34]. The emergence of a new absorption band at 250 nm can be also ascribed to the degradation of SMX leading to the formation of byproducts. This occurrence suggests that the phenyl and pyrimidine bands have not entirely disappeared, as some remnants of their structure persist in the degradation byproducts, notably the C-N and C=N bonds [35]. Analyzing **Figure 5.8a-b**, the

appearance of a new band at 250 nm is not observed and only a slight increase of absorption in the 300-400 range is observed for Ti70Zr30 low irradiation times (< 60 min) which then decreases at longer irradiation times. This could indicate the generation of some byproducts at low irradiation times which are then degraded or, probably, completely mineralized.

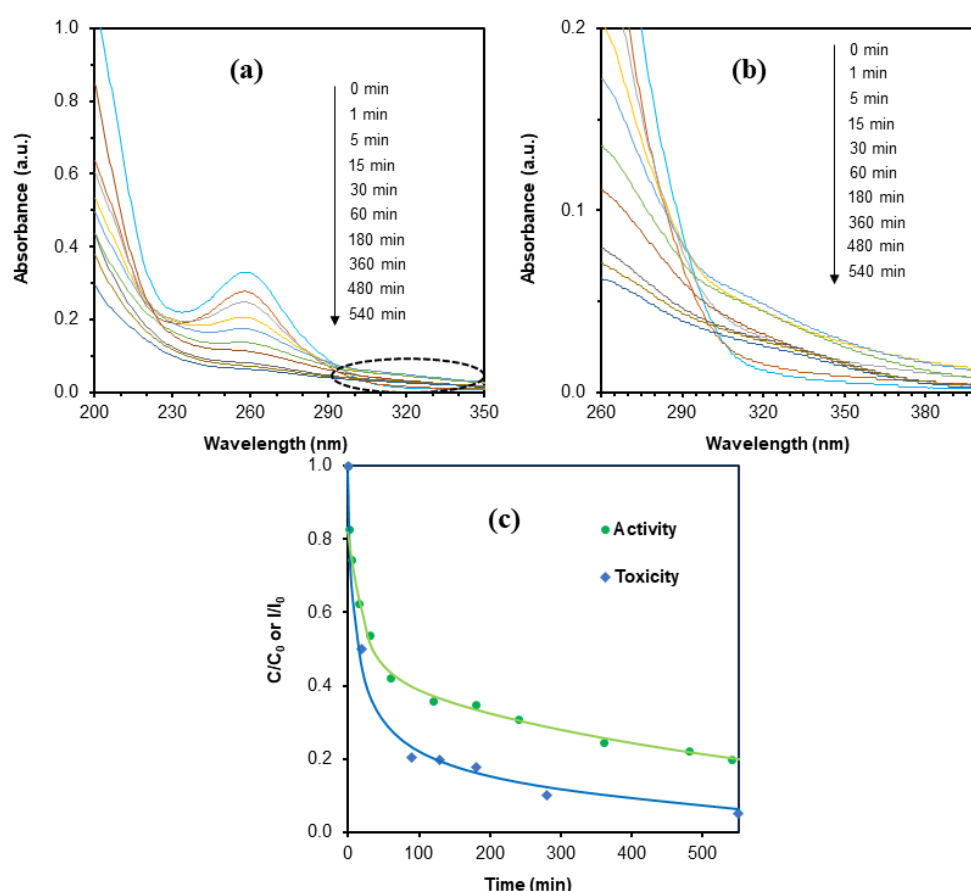


Figure 5.8. (a-b) Absorption spectra of the SMX solutions with different degradation time under blue-LED irradiation and (c) variation of the toxicity of solution treated for Ti70Zr30 photocatalyst.

Table 5.4. Comparison of the behavior of different Ti/Zr materials for photocatalytic degradation of dyes and drugs in water from literature.

Nature of Material	Nomenclature and optimum photocatalyst	Synthesis method / Organic Pollutant	Experimental conditions		Catalytic efficiency / Ref.
			Mass of catalyst, volume, initial concentration, pH (mg; mL; mg L ⁻¹)	Source Illumination (W)	Degradation ; time (%; min)
TiO ₂ /ZrO ₂ - CMCS (carboxy methyl chitosan)	T/Z-x x= content of titanium (%) (nTi:nZr = x:100) obtained by calcining	Microwave solvothermal / Rhodamine B	50; 100; 10; 10.3	UV-Light (CEL-LPH120)	90.5; 270 [73]
	T/Z-CMCS-x at 600 °C. T/Z-5				
TiO ₂ /ZrO ₂	TMZ-x (x=a, b, c, d, e) x=Zr/Ti molar ratio (3, 6, 9, 12, 15)	Hybrid solgel/Azo-dye, Ponceau BS	180; 180; 0.1 mM; Not shown	Medium pressure mercury lamp (125 W Philips)	99.3; 27 [36]
	TMZ-b Zr/Ti=6 %				
TiO ₂ /ZrO ₂	TiO₂-ZrO₂ x:y x:y=Ti:Zr % TiO₂-ZrO₂ 95:5	Sol-gel/ Metformin	500; 500; 10; 8	Mercury lamp (125 W)	70;180 [37]
TiO ₂ /ZrO ₂ derived from zirconium MOF	TiO₂/UiO-66	Solvothermal/ Rhodamine B	160; 200; 20; 9	LED lamp (100 w)	99; 180 [38]
Mesoporous TiO ₂ /ZrO ₂	sTiZrx-T Where s, x and T represents sol-gel method, mol% of Zr and calcination temperature.	Sol-gel/ Chloridazon	150; 50; 11; Not shown	Xenon lamp (150 W)	~55; 300 [39]
	sTiZr0.05-700				

Table 5.4 (Continued)

N-doped TiO ₂ /ZrO ₂ derived from Ti/Zr MOFs	N-TiO₂-ZrO₂-x x= content of zirconium (%) N-TiO₂-ZrO₂-5	Hydrothermal/ Methylene blue Hydrothermal/ Tetracycline Hydrothermal/ Phenol	10; 100; 20; Not shown	UV Lamp (500 W)	93.2; 80 86.3; 120 72.4; 120 [40]
Zr/TiO ₂	x mol.% Zr/TiO₂ x= content of zirconium (%) 2 mol % Zr/TiO ₂	Thermal hydrolysis/ Acid orange 7	50; 150; 3×10 ⁻⁵ mol/L; Not shown	UV Lamp (36 W)	99; 180 [41]
TiO ₂ /ZrO 2 NPs	Ti_xZr_y x and y wt.% of TiO ₂ and ZrO ₂ , respectively Ti70Zr30	Inverse microemulsio n/sulfamethox azole	100; 100; 5; 7	blue-LED lamp (100 W)	80.1; 540 This work

The toxicity of the treated water using Ti70Zr30 photocatalyst as photocatalyst was also studied, using the normalized biotest of luminescent inhibition of *Vibrio fischeri* bacteria. Data are plotted in **Figure 5.8c**.

Note that the toxicity of the water decreases, showing a closed behavior to the activity curve for the same irradiation times. This fact indicates that SMX is completely mineralized, reducing simultaneously the toxicity of the treated water, or the generated new byproducts are less toxic than the pristine SMX. Bibliographic results using materials with similar nature (ZrO₂-TiO₂ composites) were recorded in **Table 5.4** despite we rarely found Ti-Zr nanoparticles applied in drug degradation in water media.

It is observed that in most of the cases found, UV irradiation is required to obtain a high drug or dye degradation. In the present work, visible light is used obtaining

high degradation percent which is comparable with the bibliographic data using a less powerful light source ($\lambda=465$ nm).

5.4 CONCLUSIONS

$\text{TiO}_2\text{-ZrO}_2$ hybrid photocatalysts (Ti_xZr_y) were prepared, using a inverse microemulsion method, and efficiently tested in the degradation of sulfamethoxazole (SMX) in water under blue-LED irradiation. TEM images reveal that as the Zr content increases, the particle size decreases, obtaining narrower pore size distributions. The average particle size decreases from 26 nm and 4.9 nm for monometallic TiO_2 (Ti100) and ZrO_2 (Zr100), respectively to 3.4 nm for Ti30Zr70. The smaller the dp (determined by TEM), the greater the S_{BET} (specific surface area) becomes, indicating that nanoparticles expose a higher external surface area per unit volume. XRD findings reveal that at a low Zr content (Ti70Zr30, Ti50Zr50), zirconium titanates are formed, while at higher Zr concentrations ($\text{ZrO}_2 > 50$ wt. %), the predominant crystalline structure detected is cubic zirconia, despite monoclinic zirconia being the stable phase at temperatures below 1200 °C. The band gap decreases up to $E_g = 2.8$ eV by increasing the ZrO_2 content up to 50 % which can likely be attributed to the creation of a heterojunction between the zirconium titanate phases and the titania anatase phase.

Under blue-LED irradiation, the Ti70Zr30 photocatalyst achieved an impressive SMX degradation rate of up to 80.1 %, accompanied by a decrease in the toxicity of the treated water. This result can be attributed to the formation of zirconium titanates, as observed through XRD and XPS analyses, as well as the presence of a high active surface area.

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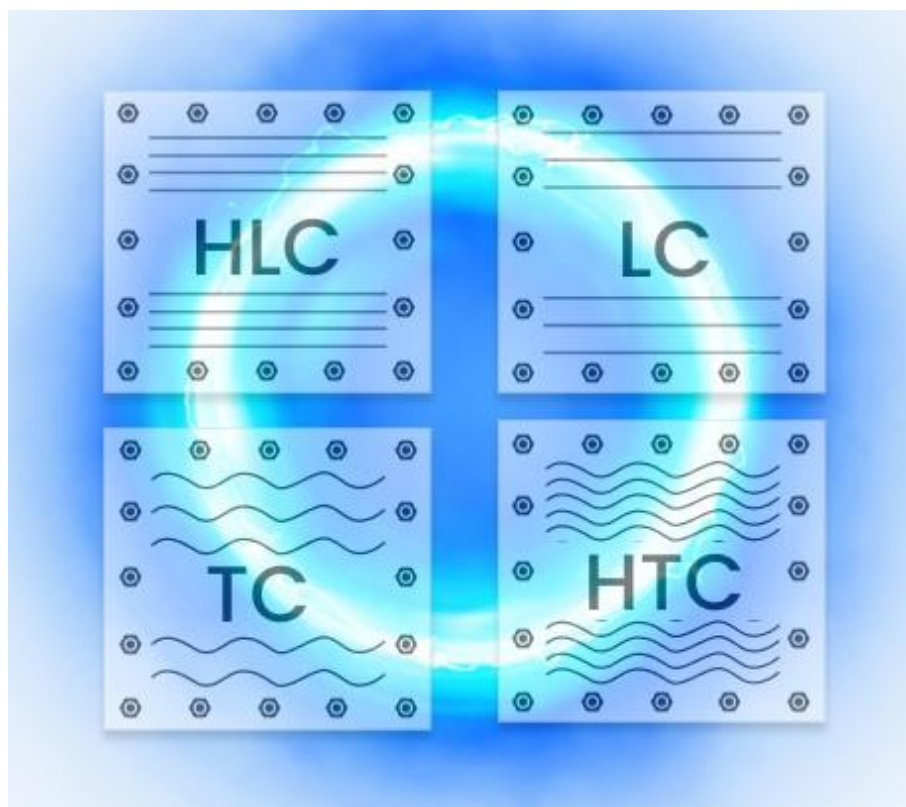
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**CHAPTER VI: DESIGN BY 3D PRINTING OF
PHOTOCATALYTICALLY ACTIVE
MICROREACTORS FOR THE REMOVAL OF
EMERGING POLLUTANTS**



Graphical Abstract

Abbreviations		
Parameter	Description	Units
ΔP	Pressure drop	kPa
LC	Linear microchannels	acronym
HLC	Linear microchannel with higher density	acronym
TC	Tortuous microchannels	acronym
HTC	Tortuous microchannel with higher density	acronym
V_T	Total Volume in microreactor	cm^3
V_C	Volume of one microchannel	mm^3
Q_T	Total recirculation flow rate to and from the microreactor	$\text{cm}^3 \text{ min}^{-1}$
μ	Dynamic viscosity of water	Kg (m.s)^{-1}
ρ	Density of water	Kg m^{-3}
k_I	Illuminated specific catalyst area	m^{-1}
SV	Surface-area-to-volume ratio	$\text{m}^2 \text{ m}^{-3}$
ρ_{cat}	Catalytic surface load	mg-cat cm^{-2}
t	Experimental time	min
d_{eff}	Effective hydraulic diameter	mm
d_h	Hydraulic diameter	mm
h	Microchannel height	mm
L	Microchannel length	mm
L_h	Hydrodynamic entrance length	mm
w	Microchannel width	mm
$\mathcal{Q}$	Cross-sectional area in a rectangular channel	mm^2
A_{cat}	Total catalyst surface	mm^2
C and C_A	Residual pollutant concentration at any time of irradiation	mg L^{-1}
C_0 and C_{A0}	Initial pollutant concentration	mg L^{-1}
C_n	Total number of channels	nondimensional
fN_{Re}	Friction constant	nondimensional
α	Geometrical aspect ratio	nondimensional
t_s	Estimated space time	s

6.1 ABSTRACT

3D printing, a rapid additive manufacturing technology, accelerates the design of novel, compact reactor systems by enabling testing of ideas and designs in days rather than weeks. Heterogeneous photocatalysis, offering an environmentally friendly solution by using light to mineralize contaminants, continues to attract significant attention. However, it is crucial to continue research in both areas to develop hybrid devices that combine 3D-printed microreactors and photocatalysts driven by sunlight to address the challenges of continuous flow for real applications in wastewater treatment plants.

Thus, the aim of this chapter is to present, for the first time, the strategy carried out to select the most suitable type of compact 3D-printed LED-microreactor based on two different parallel multichannel geometrical pathways (linear and tortuous channels) for liquid-phase reactions in recirculation flow mode. These have been designed to support photoactive nanoparticles developed to extend their solar light absorption capacity designs to eliminate emerging pollutants under simulated sunlight as innovative alternative to conventional slurry batch LED-reactors. Nanoparticles of photocatalysts capable of absorbing visible light were synthesized using hydrothermal and inverse microemulsion method. 3D-printed microreactors were fabricated using fused deposition modeling technology. Powder photocatalyst material was coated on the multichannel section of a 3D-printed polycarbonate matrix using an airbrushing process from a dispersion of photocatalyst in an acetone solution. The analysis of the results showed that the 3D-printed microreactor with a tortuous multichannel path exhibited the best performance in photodegradation of the emerging pollutant model using simulated sunlight through blue-LED

irradiation. These findings suggest that a recirculating 3D-printed LED microreactor with a coated sunlight-active photocatalyst, as a compact device, represents a novel technology potentially implementable in real continuous flow for eliminating pollutants in water and wastewater treatment plants.

Herein, we present the results for compact devices operated in continuous recirculation flow rates, featuring two parallel multichannel geometrical pathways (linear (LC) and tortuous channels (TC)), for the photodegradation of sulfamethoxazole (SMX) as model molecule of an emergent pollutant under simulated sunlight irradiation from blue-LED light. To extend the solar light absorption capacity, we used advanced semiconductors such as doped Ag-BiVO₄ calcined at 300 °C (Ag/BiV/300) and coupled TiO₂ and ZnO nanoparticles (TiZn-NPs), a potential heterojunction identified as the best-performing photocatalysts in slurry batch LED reactors throughout this thesis. These materials were anchored on the external surface of polycarbonate (PC) 3D-printed microreactors using an airbrushing technique.

Figure 6.1 illustrates the schematic flowchart of this chapter. The synthesis, doping, and characterization of photocatalysts, including the selection of doped Ag-BiVO₄ calcinated at 300 °C (labeled as Ag/BiV/300) as the first optimal photocatalyst for multichannel microreactor coatings, are detailed in [Chapters II](#) and [III](#). The flowchart concludes with the optimization system that integrates three key aspects: (i) the optimal geometry pathway in the 3D microreactor, (ii) the optimal recirculation flow rate, and (iii) two of the best-performing photocatalyst developed in this thesis for coating onto microchannels: (i) Ag/BiV/300 and (ii) TiZn-NPs.

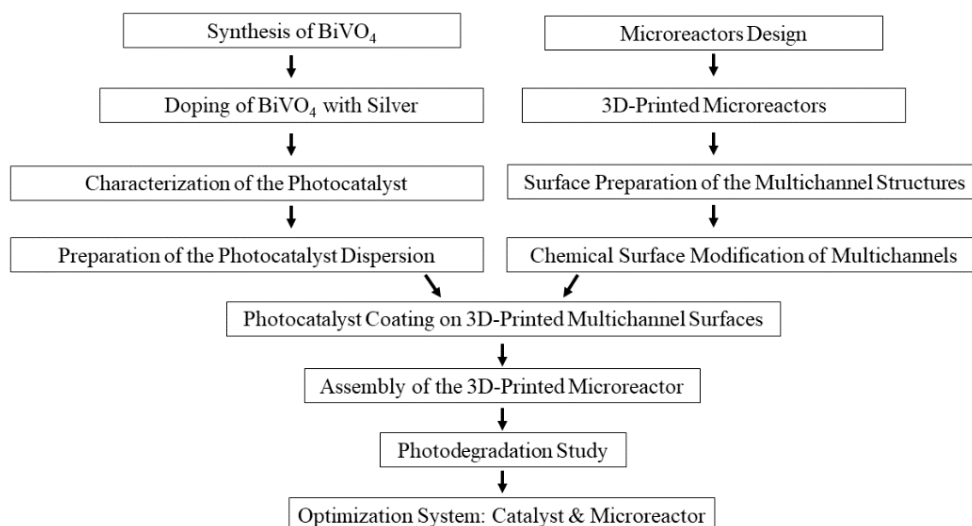


Figure 6.1. Flowchart structure.

6.2 EXPERIMENTAL

6.2.1 3D-Design Microreactors

The design of different microchannel pathways is based on width, height, dimensions channel quantity, and the path/length relationship, due that each curved segment gradually increasing the final length. In this work, we used Alibre Design software (Alibre, LLC) to design two distinct sets of microreactor configurations with different paths of rectangular channels arranged in parallel and packed in flat devices. These configurations induced either laminar or turbulent flow patterns during the interaction between the pollutant solution and the coated photocatalyst. One set featured linear microchannels (LC), while the other set had tortuous microchannels (TC). To study the effect of the number of microchannels on performance, the channel concentration was increased in each set, creating subsets with higher concentrations referred to as H. The nomenclature is: LC (linear

channel), TC (tortuous channel), HLC (higher linear channel), and HTC (higher tortuous channel) [1]. Schematic representations of four microchannel paths are shown in **Figure 6.2**.

During the design stage, several parameters were fixed: (i) to ensure the same residence time of liquid by microreactors device, the total volume (V_T) was set at 4.8 cm^3 ; (ii) the total length (L) of the multichannel sections was set at 60 mm; and (iii) the channel height (or depth) (h) was set at 2.0 mm. The cross-sectional areas (Ω) designed with a rectangular geometry for both linear and tortuous pathways were calculated using **Equation 6-1**. Where, w and h , mean width, and height of one microchannel.

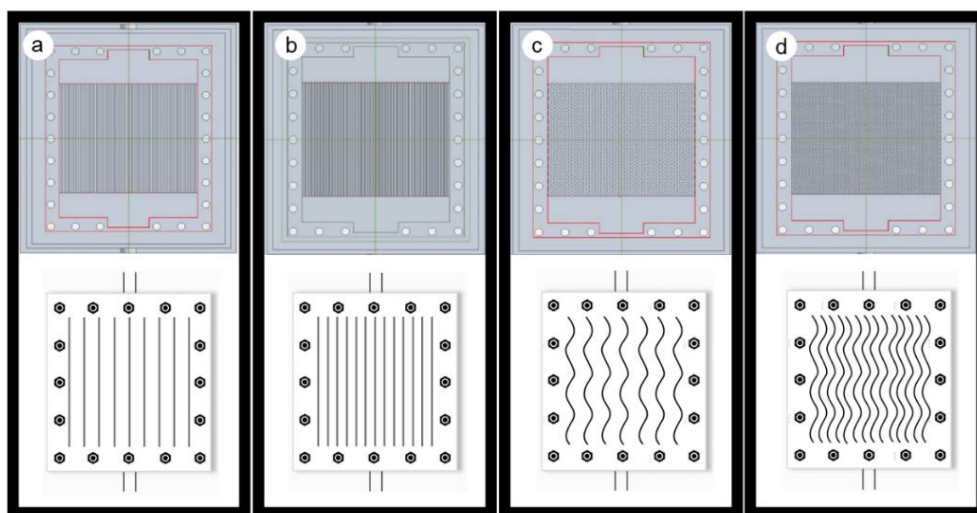


Figure 6.2. Top view images of lower structures of the microreactors containing the 3D micro-sized multichannel sections. Up: Alibre Design software, down: Schematic representation. (a) Linear Channel (LC), (b) High Linear Channel (HLC), (c) Tortuous Channel (TC), and (d) High Tortuous Channel (HTC).

$$\Omega = (w)(h)$$

Equation 6-1. Cross sectional area in a rectangular channel.

Table 6.1 presents the geometric parameters for each channel within the lower structures of the microreactors, corresponding to the multichannel sections, including the total number of parallel channels (C_n) for both sets and their respective subsets.

Table 6.1. Design parameters for each individual channel and surface characteristics. The mass of photocatalyst (W_{cat}) coated on a PC substrate was 105 ± 10 mg.

Geometrical paths multichannel	Number of channels (C_n)	Width (w)	Volume (V_c)	Catalyst surface (A_{cat})	Surface load (ρ_{cat})
		μm	mm^3	mm^2	mg cm^{-2}
LC	40	1000	120	300	35
HLC	66	600	72	276	38
TC	25	1000	188.5	471	22.3
HTC	42	600	113.1	434	24.2

In **Table 6.1** the total catalyst surface, A_{cat} , which corresponds to the total surface area along one channel coated with the photocatalyst, is obtained using **Equation 6-2**. These calculations exclude the upper side of the microchannel, which remains uncoated because it corresponds to the top cover of the microreactor. The catalytic surface load, ρ_{cat} , was derived from **Equation 6-3** [2–4].

$$A_{cat} = (2h + w)L$$

Equation 6-2. Total catalyst surface.

$$\rho_{cat} = \frac{W_{cat}}{A_{cat}}$$

Equation 6-3. Catalytic surface load.

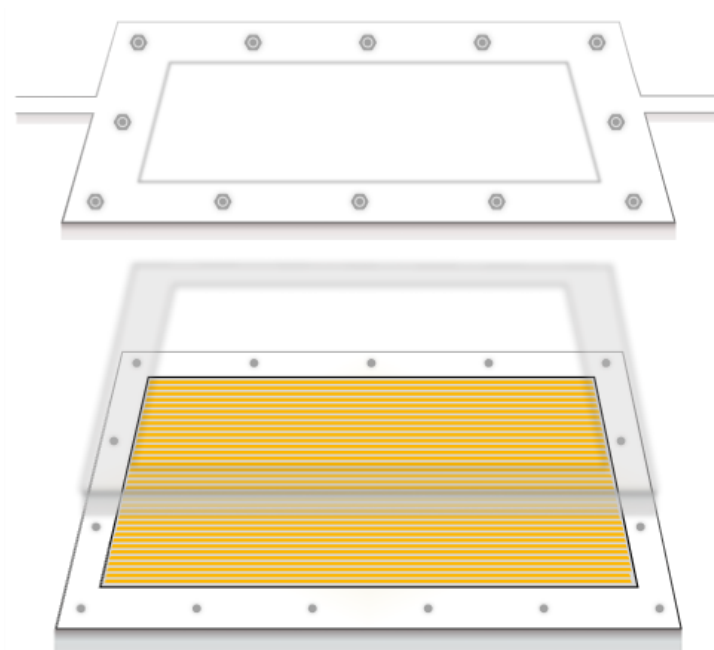


Figure 6.3. Schematic image of the 3D-printed microreactor before assembly. Bottom: Lower microreactor structure ideally coated with the photocatalyst onto multichannels. Middle: Elastic rubber piece for hermetical seal. Up: Top cover microreactor structure without coating.

The complete-body 3D-printed microreactor consisted of three key components: one part containing the multichannel section with four distinct geometrical paths forming the lower microreactor structure for coating (see **Figure 6.3**), another containing the top cover microreactor structure with liquid inlet and outlet tubes. The third component, made of elastic rubber, was designed to ensure a hermetic seal between the lower and top cover microreactor structures.

6.2.2 3D-Printing Microreactors

The International Organization for Standardization (ISO) defines 3D printing, an additive manufacturing (AM) technology, as “a process of joining materials to make objects from three-dimensional (3D) model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies” [5,6].

After the designs, the fabrication microreactors process started by converting the 3D CAD geometry to a standard tessellation language (STL) file. By slicing the STL file, the 3D model is transformed into 2D information, which will be reproduced layer by layer by the 3D printer using fused deposition modeling (FDM), among additive technologies, is the simplest and most cost-effective 3D printing technique [7]. This method extrudes a filament of thermoplastic material through a heated nozzle, creating 2D cross-sections that are assembled layer by layer to fabricate desired three-dimensional (3D) structures as functional products with previously unthinkable features, thereby revolutionizing materials science [8–10].

The microreactor was printed in a commercial Ultimaker 3D printer, model S3 using Ultimaker Cura 5.6.0 software, equipped with a 1.75 mm diameter filament

and a 0.4 mm diameter nozzle to extrude the desired material, as shown in **Figure 6.4**. Previously, the printing parameters were studied and adjusted.

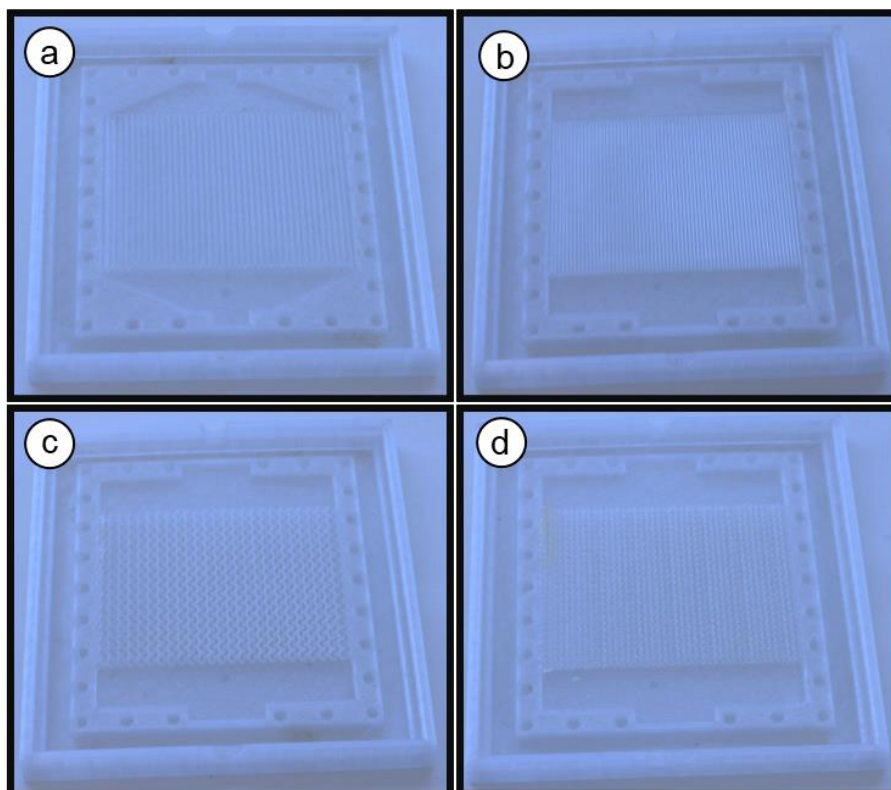


Figure 6.4. 3D printed lower microreactor structures. Shown the geometrical paths in multichannel sections (a) Linear Channel (LC), (b) High Linear Channel (HLC), (c) Tortuous Channel (TC), and (d) High Tortuous Channel (HTC).

The lower structure (**Figure 6.4**) and top cover pieces of the microreactors were 3D-printed in polycarbonate plastic (PC), a translucent polymer material chosen for its excellent optical clarity and high toughness to facilitate light transmission from the blue-LED source to the immobilized photocatalyst on the surface of the

multichannel section. The elastic rubber piece for hermetic sealing was printed in thermoplastic polyurethane (TPU). After extrusion of the polymeric PC or TPU, the pieces were printed layer by layer and allowed to cool to room temperature.

6.2.3 Surface Preparation of the Multichannel Structures

Once the microreactors were printed, any excess or residual polymeric material, including PC retained inside the microchannels, was removed by washing each microreactor piece with DDW and soap without using alcohol. The cleaned lower microreactor structure containing the multichannel section was then dried at 20 °C for 10 min using an infrared light lamp positioned 30 cm above. After the lamp was turned off, the pieces were allowed to naturally reach room temperature, a condition selected based on previous works with PC by other authors [11,12].

6.2.4 Chemical Surface Modification of Multichannels

Subsequently, the section containing the multichannels underwent controlled chemical surface modification to increase its roughness and facilitate the adhesion of the photocatalyst powder. The piece was held vertically, and a 50 % aqueous solution of acetone was allowed to flow slowly through the microchannels until flooding the internal surface, inducing recrystallization, and increasing the original roughness of the PC.

This procedure was repeated two more times, followed by washing (DDW and soap) and drying (infrared light lamp) the piece as in the previous step [13,14]. Finally, the piece prepared for coating the advanced semiconductors was hermetically stored in suitable plastic bags.

6.2.5 Preparation of the Photocatalyst Dispersion

To achieve homogeneous immobilization on the PC matrix, the photocatalyst powder sample was initially triturated using an agate mortar to minimize its size. The dispersion solution was prepared by mixing 1.0 g of the fine powder photocatalyst with 20 cm³ of pure acetone, ethanol (96 %), and Millipore water in a ratio of 2:1:1. The prepared dispersion was stirred magnetically for 10 min at 220 rpm and then subjected to a 30 min sonication process to achieve a homogeneous dispersion. This was performed using a glass vessel covered with a black cloth to avoid interactions with ambient or artificial light sources. This dispersion was directly used for spraying onto the multichannel sections without any further modifications.

6.2.6 Photocatalyst Coating on 3D-Printed Multichannel Surfaces

The advanced photocatalyst samples were exclusively deposited on the inner surface of the multichannel using an airbrush spray gun, following our novel procedure. Therefore, it is important to highlight that only the two side walls (height, h) and the bottom (width, w) of the microchannel were coated with the photocatalyst powder because the upper face of each microchannel corresponds to both the top cover microreactor structure and the cover of the microchannels. During application, the double-action trigger of the airbrush allowed the controlled release of the photocatalyst through a 0.5 mm diameter nozzle while simultaneously maintaining compressed air at 4 bars.

This experimental procedure ensured precise control over the quantity and thickness of the deposited powder sample, achieving a uniform layer on the inner

surface of each channel. Subsequently, the freshly sprayed multichannel section coated with the photocatalytic powder underwent the same drying procedure as in the previous steps. The microreactor was allowed to cool to room temperature under natural conditions. Next, the dried surface of the multichannel was washed with DDW to remove and recover loose photocatalytic material that had not adhered to the PC surface, followed by a new drying process. The homogeneity of the inner surface containing the immobilized photocatalysts was evaluated using a stereoscope or microscopy (see **Figure 6.5**).

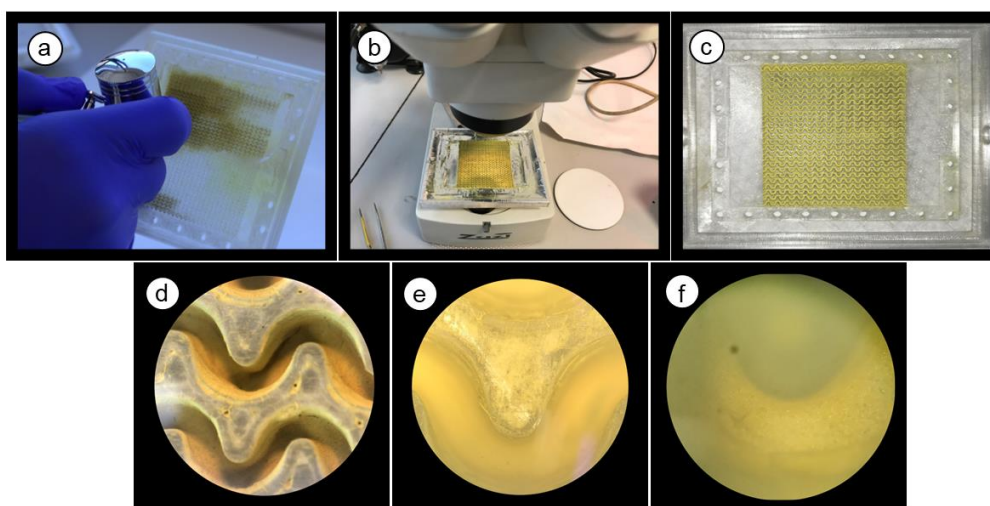


Figure 6.5. Photocatalyst coating quality for immobilized Ag/BiV/300 photocatalyst. (a) Airbrush spray process on HTC, (b) Evaluation of coating by stereoscopic equipment, (c) Lower microreactor structure of TC after coating. Microscopy image for TC configuration, (d) Top view of the multichannel at 10X magnification, (e) Upper face of the microchannel without coating of photocatalyst at 100X magnification and (f) Inside of the microchannel with coating of photocatalyst at 100X magnification.

The spraying process for coating, washing with DDW, and drying was repeated until the desired homogeneity was achieved to obtain a uniform layer of the immobilized photocatalyst inside the channel. Finally, the amount of fine powder photocatalyst loaded onto the surface was determined by weighing the dried lower microreactor structure before and after deposition, resulting in 105 ± 10 mg. This quantity was the same as that used in the photocatalytic test conducted with a slurry batch LED-reactor.

6.2.7 Assembly of the 3D-printed LED-microreactor

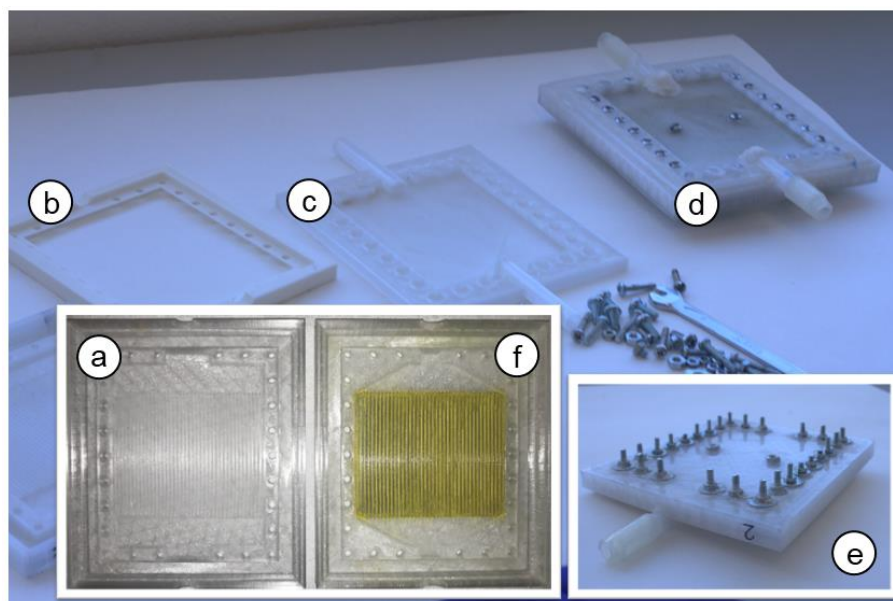


Figure 6.6. Assembly process of the 3D-printed microreactor: (a) Polycarbonate lower microreactor structure for the linear channel (LC) before coating, (b) Elastic rubber piece printed in TPU used for hermetic sealing, and (c) Top cover microreactor polycarbonate structure containing the liquid inlet and outlet tubes. The microreactor assembly is shown in (d) top image and (e) bottom image (f)

Comparison of the lower microreactor structure before and after photocatalyst coating for LC configuration.

For the microreactor assembly after the photocatalyst coating process, the three 3D-printed pieces (shown in **Figure 6.3**) were joined and secured using 22 galvanized screws (4.0 x 10 mm) with roundhead hex nuts and washers, as described in **Figure 6.6**. The following assembly, all contact surfaces among the three pieces and screws of the microreactor were sealed using epoxy glue.

6.3 PHOTODEGRADATION STUDY

To facilitate and ensure a correct comparison among reaction setups, including slurry batch LED-reactors with dispersed photocatalysts ([Chapters III to V](#)) and 3D-printed LED-microreactors coated with photocatalysts in recirculation flow mode, tests were conducted under the same technical and operational conditions, such as: (i) 100 cm³ of the pollutant model (SMX) at a concentration of 5 mg L⁻¹, (ii) LED source (100 W, 465 nm, 4080 lm W⁻¹) and fan configuration providing 0.80 mW cm⁻², (iii) experiment duration (540 min), (iv) aliquot volume (1.5 cm³), (v) the same amount of photocatalyst (105 ± 10 mg) novelty coated on a PC substrate, (vi) neutral pH, and (vii) ambient temperature and pressure.

These photocatalytic reactions were conducted in a batch recirculation mode, which is often referred to as a continuous-flow recirculation mode [15], where the recirculation mechanism homogenizes the system. In this mode, a fixed volume of the SMX solution is circulated through the 3D microreactor device and mixing tank, both maintained under constant stirring for multiple passes. This process helps to reduce the diffusional resistance of the film and facilitates the reaction [3,15]. This

operation mode ensures the detection of minimal changes in the pollutant concentration due to cumulative variation over multiple passes of the pollutant solution through the 3D microreactor device.

The experimental setup for photodegradation studies which comprise five essential components, is illustrated **Figure 6.7**.

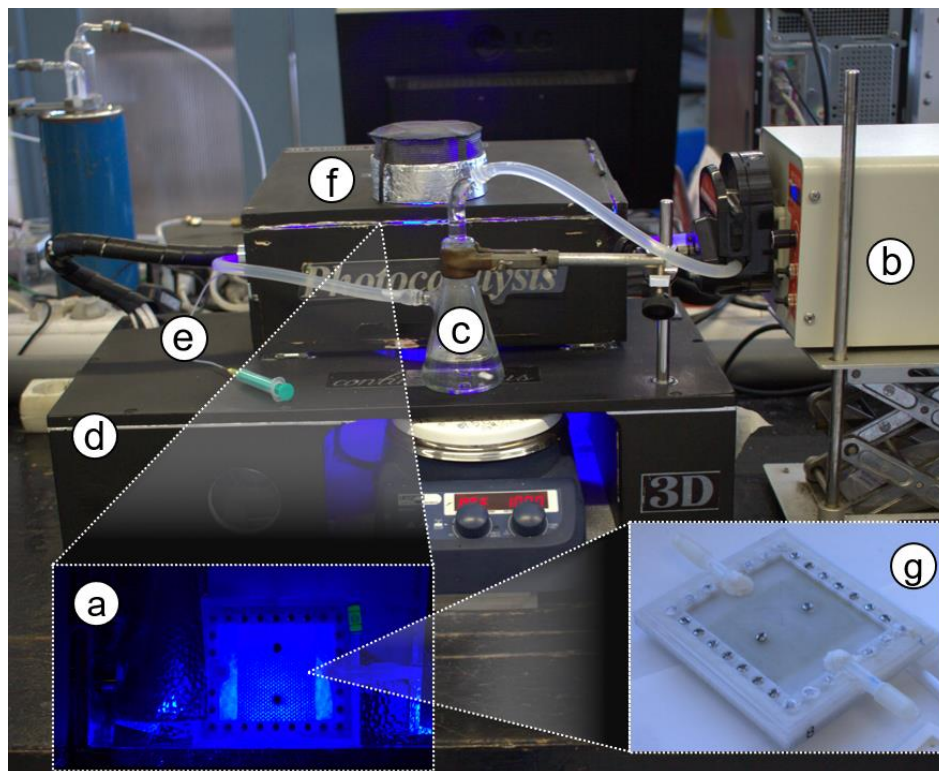


Figure 6.7. Components of the recirculating photocatalytic 3D microreactor device: (a) Top view of the 3D-printed LED-microreactor with coated photocatalyst in LED-on mode, (b) Peristaltic pump, (c) Mixing tank, (d) Custom-built photocatalytic device box, (e) Syringe sampler, (f) Top foldable wall containing

5x10 LED bulbs and a fan for cooling, and (g) 3D Microreactor after hydraulic optimization, ready to start the photodegradation study.

The first component is a 3D-printed LED-microreactor with a coating of 105 ± 10 mg of photocatalyst on its microchannels section (**Figure 6.7a** and **6.7g**). The second component (**Figure 6.7b**) is a peristaltic pump responsible for recirculating the contaminant to ensure multiple passes of the contaminant solution and controlling the flow. This pump is connected to both the microreactor and the mixing tank, enabling the outlet stream from the mixing tank to serve as the inlet liquid to the microreactor, and vice versa. The mixing tank is the third element in the setup and serves dual purposes: (i) it acts as a simulated wastewater tank in a hypothetical treatment plant and (ii) also functions as a supply reservoir for the contaminant solution. This is equipped with a magnetic stirring device operating at 220 rpm, as shown in **Figure 6.7c**.

The fourth component is a custom-built device containing two 50 W blue-LED lamps emitting light at 465 nm, with a total electric power of approximately 100 W and a luminous efficacy of 4080 lm W^{-1} , as it can be observed in **Figure 6.7d** from blue light. It contains a syringe sampler positioned at the microreactor stream outlet for sample collection at different reaction times (**Figure 6.7e**). The fifth and final component is a fan to maintain a homogeneous interior temperature (30°C) as shown in **Figure 6.7f**. To evaluate the photoactive properties of the immobilized photocatalysts, the 3D-printed LED-microreactor was positioned horizontally between both blue-LED lamps at a 3.0 cm.

Following this setup, firstly cleaning and leaching test involved recirculating 100 cm^3 of DDW at a fixed flow rate for 12 h was carried out. This process aimed

to remove any organic and inorganic impurities adsorbed on the photocatalyst surface and assess the potential loss of coating material that was not firmly attached to the microchannel surfaces. During the test, hydraulic connections between essential components were checked, and reaction conditions were optimized. After completion these tests, no measurable amount of photocatalyst was detected during DDW recirculation.

Secondly, before the photodegradation tests, 100 cm³ of the SMX pollutant solution at a concentration of 5 mg L⁻¹ was prepared. This value was determined from the SMX adsorption isotherms on the materials and adjusted to pH 7.0 using NaCl and HCl solutions (0.01 N). These conditions matched those used in the slurry batch LED-reactor tests. The SMX solution was then loaded into the recirculation tank and injected into the microreactor using a peristaltic pump.

In each experimental run, the recirculation flow rate (low flow rate of 5 cm³ min⁻¹ and high flow rate of 30 cm³ min⁻¹) to and from the microreactor was fixed. The effluent from the microreactor was returned to the mixing tank by initiating the flow-recirculation mode for 12 h in LED-off mode before exposure to irradiation. This procedure assessed changes in pH, pollutant solution concentration, and leaching of the photocatalyst, none of which were detected.

6.4 RESULTS AND DISCUSSION

6.4.1 Immobilization of the Photocatalysts

Figure 6.8 shows the methodology employed to coat the photocatalyst inside the microchannels in the PC structure. In **Figure 6.8a**, the printing equipment is displayed, and the inserted image provides a 100x micrograph of the original PC

surface, emphasizing the characteristic crystallinity resulting from the natural curing process during 3D printing.

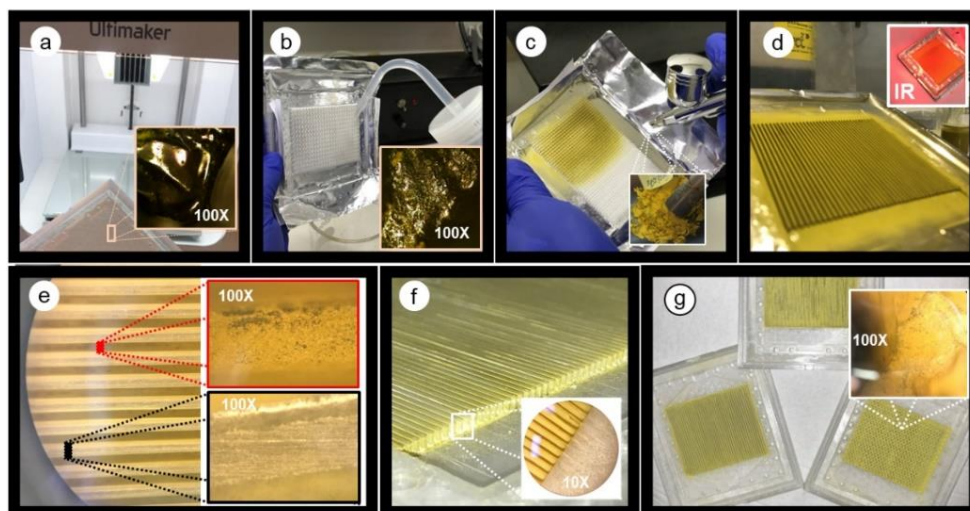


Figure 6.8. Immobilization process of photocatalysts into PC microchannels. (a) Manufacturing through 3D printing. Inserted image: Surface evaluation after printing. (b) Cleaning process with 50 % acetone. Inserted image: Increase roughness surface after chemical treatment. (c) Atomization application using airbrush. Inserted image: Characterization of ground powder material. (d) Homogenization stage. Inserted image: Drying with infrared light. (e) Microscopic analysis at 100X. Upper inserted image: 100X magnification of the interior of channels with adhered photocatalyst. Lower inserted image: 100X magnification of the clean upper surface of channels without adhered photocatalyst. (f) Microreactor after immobilization process. Inserted image: 10X magnification of the channel edge. (g) Microreactors with different designs of channels. Inserted image: 100X magnification of the inner of channels with adhered photocatalyst, especially in tortuous channels.

To remove possible blockages in the channels and any PC agglomerations that may have occurred during the 3D printing process, a washing procedure with water and soap was performed, followed by treatment with 50 % acetone, as depicted in **Figure 6.8b**. The increase in the roughness of the original plastic was assessed using a microscope (see image inserted in **Figure 6.8b**).

A comparison of the inserted images in **Figure 6.8a**, and **8b** confirms the increased roughness on the surface due to the chemical treatment with acetone. This modified surface was used to immobilize the powdered nanoparticles.

Figure 6.8c illustrates the process of coating the PC microchannels. The image inserted in **Figure 6.8c** shows the powdered nanoparticles of Ag/BiV/300 before mixing with acetone, ethanol, and DDW solution. The dispersion immobilization was performed using an airbrush spray gun, as shown in **Figure 6.8c**. The microreactor, freshly sprayed with the photocatalytic powder, was dried under red irradiation during 30 min (refer to the image inserted in **Figure 6.8d**). The homogeneity of the surface was assessed using a stereoscope or microscope to ensure a deposition of 105 ± 10 mg of photocatalyst. To ensure the effective immobilization of the particles on the PC substrate, several washes with DDW and subsequent spray applications of the photocatalyst dispersion were performed.

Figure 6.8e shows the microchannel after the immobilization of the photocatalyst. The homogeneity of the coating inside the microchannel is depicted in the top image inserted in **Figure 6.8e**. Meanwhile, the bottom image inserted shows a surface free of photocatalyst, which is in contact with the top piece of the microreactor containing the fluid inlet and outlet pathways.

The precise immobilization on the shore of the microchannels in the section for liquid inlet is depicted in the images of **Figure 6.8f**. Finally, **Figure 6.8g** shows the different geometries after the deposition for the previous reactor assembly. The distribution of the nanoparticles on the PC surface as well as the degree of coverage were similar for four multichannel designs. This pointed to a nearly identical reproduction of the layer structure on the substrate to the PC surface by sprayed process. The image inserted in **Figure 6.8g** displays the textural homogeneous deposition of the photocatalyst in the specific case for HTC multichannel.

6.4.2 Chemical Surface Modification

Figure 6.9 illustrates schematically the detailed procedure for coating photocatalyst on PC surface. **Figure 6.9a** and **Figure 6.9b**, shows the surface after an acetone treatment, acting as a pore-creating agent for the adsorption process (see **Figure 6.9c**). Acetone can increase the surface roughness to facilitate a partial embedded effect provoking the permanent immobilization of the nanoparticles. Additionally, this enhances the resistance against the mechanical action caused by the recirculating liquid containing the emerging pollutant. Therefore, the exposed surface of the nanoparticles will work in the photodegradation reaction properly, as illustrate in **Figure 6.9d**.

The good adhesion of the photocatalyst layers is evidenced by two means: (i) micrograph images (see **Figure 6.5** and **Figure 6.8**) showing the covered area with photocatalysts partially embedded on the surface of the PC matrix, as illustrated in **Figure 6.9d** and (ii) tests for the mechanical stability of the coatings conducted in the assembled microreactor by recirculation flow at a maximum flow rate of $200 \text{ cm}^3 \text{ min}^{-1}$ for 12 h.

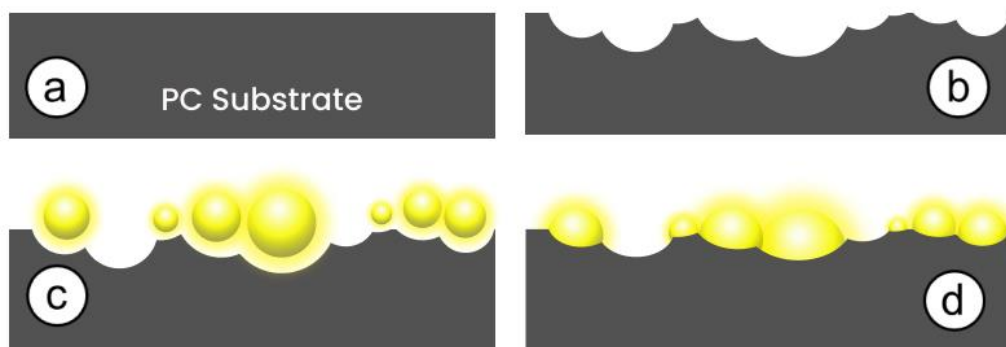


Figure 6.9. Schematic representation of the textual modification process during the coating of Ag/BiV/300 photocatalyst on 3D-printed polycarbonate: (a) depicts the original surface after natural curing of the 3D printing process, (b) shows the roughness on the polycarbonate surface resulting from the chemical modification with acetone, (c) illustrates the adsorption of photocatalyst, and (d) shows the permanent immobilisation of the photocatalyst achieved by partial embedding.

After these tests, the weight loss was negligible and could not be quantified, indicating no leaching of the photoactive material. In addition, a maximum flow rate of $200 \text{ cm}^3 \text{ min}^{-1}$ was used to determine the recirculation flow rates for the photodegradation study, with 5 and $30 \text{ cm}^3 \text{ min}^{-1}$ selected to provide a wider operational range.

6.4.3 Hydrodynamic Results

Combining 3D printing technology with microreactor design can broaden the chemical engineering potentials [16]. The small channels offer advantages such as improved mixing and heat transfer, small sample sizes, and safer and more controlled operation, among others. [17,18]. However, the flow condition in

microchannels is mainly laminar, with fluid moving in parallel streams with little disruption between layers [19,20].

One strategy to disrupt laminar flow in microreactors is chaotic advection, which induces spontaneous flow instabilities by separating boundary layers and creating recirculating or transversal flows, opening new avenues for research in microfluidics [21]. To enhance mass transfer in microreactor technology, sections containing multichannels or turbulence promoters can be inserted into the fluid flow pathway

The precise characterization of the hydrodynamic flow provides information about the axial dispersion and overall pollutant degradation inside the 3D-printed microreactor. To achieve disturbed flow and enhance mass transfer, different microchannel pathways based on path width, height, length, and channel quantity were assessed. Parameters such as pressure drop and Reynolds number were determined following the methodology described in the literature [17,18].

The Geometrical aspect ratio (α , $0 < \alpha < 1$) friction constant ($f.Re$), hydraulic diameter (dh), and effective hydraulic diameter ($deff$) were calculated using the **Equation 6-4** to **Equation 6-7** according literature [22].

$$\alpha = \frac{w}{h}$$

Equation 6-4. Geometrical aspect ratio.

$$f N_{Re} = 96(1 - 1.3553\alpha + 1.9467\alpha^2 - 1.7012\alpha^3 + 0.9564\alpha^4 - 0.2537\alpha^5)$$

Equation 6-5. Friction constant.

$$d_h = \frac{4A}{P} = \frac{4(w)(h)}{2(w+h)} = \frac{2(w)(h)}{w+h} = \frac{2w}{(\alpha+1)}$$

Equation 6-6. Hydraulic diameter of the channel. Where A and P , are cross-sectional area and wetted perimeter, respectively.

$$d_{eff} = \left(\frac{64}{f N_{Re}} \right) d_h$$

Equation 6-7. Effective hydraulic diameter for laminar flow regimes.

Hydraulic characteristics for each microchannel as function of recirculation flowrate are presented in **Table 6.2** below. The axial mean velocity of fluid (u) is estimated as the ratio of flowrate (Q_T) to the channel cross-section area (Ω), using the **Equation 6-8**.

$$u = \frac{Q_T}{(\Omega)(C_n)}$$

Equation 6-8. Axial mean velocity.

$$N_{Re} = \frac{(\rho)(u)(d_{eff})}{\mu}$$

Equation 6-9. Reynolds number.

$$\Delta P = \frac{96}{N_{Re}} \frac{(\rho)(u^2)}{2} \frac{L}{2h}$$

Equation 6-10. Pressure drops in microchannels.

Table 6.2. Hydraulic characteristics for each microchannel as function of recirculation flowrate.

Geometrical paths multichannel	Flow rate (Q_T)	Axial mean velocity (u)	Reynolds number (N_{Re})	Pressure drop (Δp) (10^{-3})
	$\text{cm}^3 \text{min}^{-1}$	mm s^{-1}		kPa
LC	5.0	1.04	1.78	1.75
HLC		1.05	1.11	2.87
TC		1.67	2.85	6.56
HTC		1.65	1.74	10.59
LC	30	6.25	10.69	10.47
HLC		6.31	6.64	17.21
TC		10.00	17.11	39.39
HTC		9.92	10.44	63.54

For water: $\rho=995.71 \text{ Kg m}^{-3}$, $\mu=0.000798 \text{ Kg (m.s)}^{-1}$ at 30°C

Reynolds number (N_{Re}) is an important non-dimensional number involved in the fluid flow study. It reflects the ratio of inertial with respect to viscous forces, and its definition appears in **Equation 6-9**. Where μ the dynamic viscosity, ρ the density. Dynamic viscosity and density values were set $0.000798 \text{ kg (m s)}^{-1}$ and, 10^3 kg m^{-3} , respectively. The pressure drop (Δp) were determined from to **Equation 6-10**. From **Table 6.2** we can observe that all flows show Reynolds number corresponding to laminar type flows.

6.4.4 Photodegradation Results using 3D printed devices

These photocatalytic materials can degrade organic compounds typically via heterogeneous systems composed of two types of reactors: (i) finely dispersed

powered in liquid phase (i.e. slurry reactors). [23,24], and (ii) immobilized form on porous structures (i.e. fixed-film reactor) [23,25]. Slurry reactors require photocatalyst recovery, which adds to the overall cost of water treatment. In fixed-film reactors, photocatalyst recovery is not an issue; however, these systems often exhibit low efficiencies due to limited photocatalyst surface area and mass transfer issues [26]. One highlighted strategy to address these challenges involves the use of foams and microreactors with active photocatalytic phases coated on its surfaces [27–29].

Figure 6.10 illustrates the setup for the photodegradation tests using a homemade recirculating 3D-printed LED-microreactor device coated with powdered photocatalyst. After coating, the photocatalyst adhered onto microchannel surface inside 3D-microreactor forming the 3D&Ag/BiV/300 or 3D&TiZn-NPs compact devices. The operational conditions were maintained as those in the slurry batch LED-reactor tests described earlier in [section 6.3](#).

After assessing changes in pH, pollutant solution concentration, and leaching of the photocatalyst, and using the same pollutant solution prepared in the previous step (see [section 6.3](#)), the photodegradation experiment was initiated by switching to LED-on mode, maintaining the selected flow rate and operating conditions described earlier. The procedure for determining the outlet concentration of the pollutant is described in Chapter II, [Section 2.3.3](#), to calculate the photodegradation percentage at different times

The photodegradation of SMX was investigated across varying linear and tortuous geometric channel paths inside the microreactor, considering different pathway and multichannel concentrations and flow rates. Microchannel length,

amount of coated photocatalyst, pollutant concentration, and incident light intensity were kept constant in all cases.

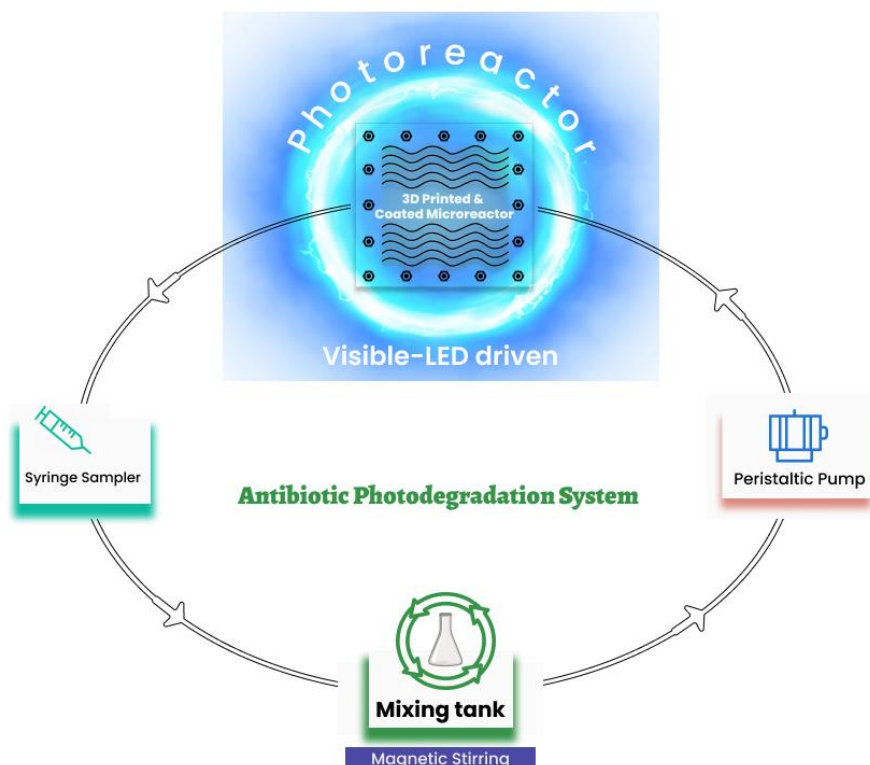


Figure 6.10. Schematic representation of experimental procedure to SMX photodegradation study through a recirculating photocatalytic microreactor device. Schematic representation showing the 3D-printed & coated photocatalyst microreactor, peristaltic pump, syringe sampler, and mixing tank.

During the photodegradation tests at the selected flow rate, normal hydrodynamic functionality of the microreactor was observed, thereby avoiding

water leakage from both the assembled 3D-printed LED-microreactor and the hydraulic connections among the essential device components.

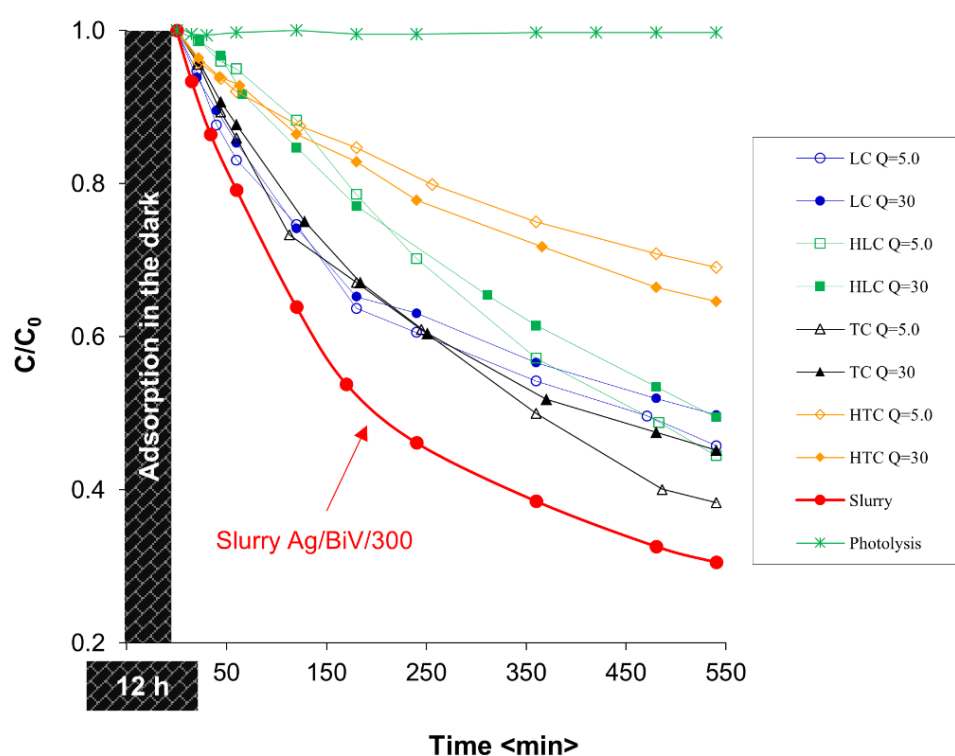


Figure 6.11. Photodegradation results for SMX degradation using 3D-printed LED-microreactors coated with Ag/BiV/300 photocatalysts on both lower and higher concentrations of linear and tortuous multichannels under simulated sunlight irradiation at $Q_T = 5$ and $30 \text{ cm}^3 \text{ min}^{-1}$. Tendency from the slurry batch LED-reactor and photolysis conducted under the same technical and operational conditions are shown for comparison.

Figure 6.11 presents the photodegradation profiles using a recirculating 3D-printed LED-microreactor device coated with powdered Ag/BiV/300 photocatalyst (3D&Ag/BiV/300). One set of results is for photolysis, and the other is for the same photocatalyst powder used in a slurry batch LED-reactor for comparison (studied earlier in [Chapter III](#)). All results are summarized in **Table 6.3**

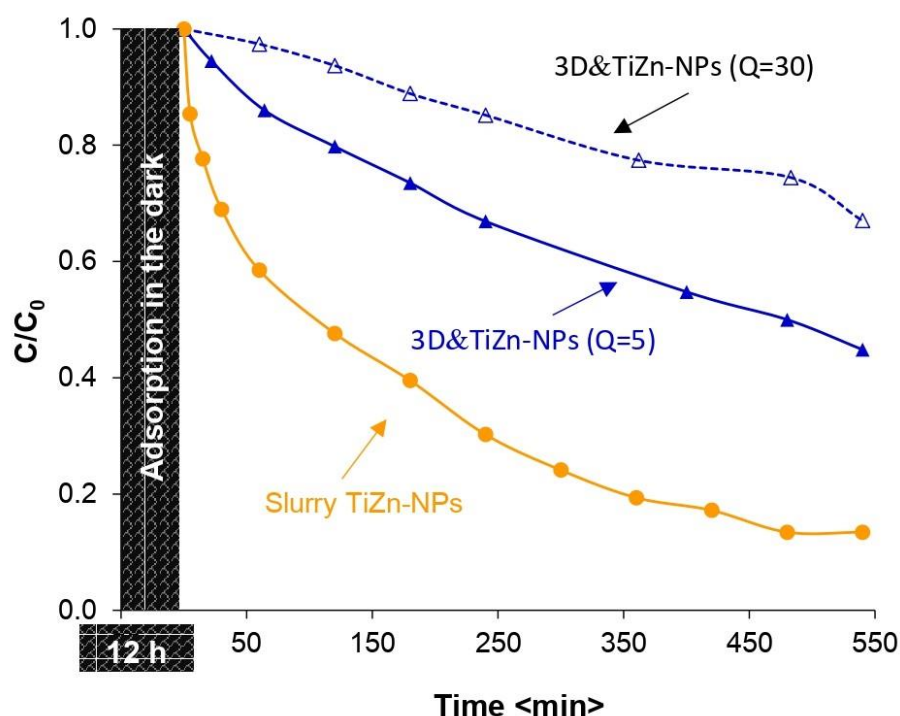


Figure 6.12. Photodegradation results for SMX degradation using 3D-printed LED-microreactors coated with TiZn-NPs on lower concentrations of tortuous multichannels (TC) under simulated sunlight irradiation at $Q_T = 5$ and $30 \text{ cm}^3 \text{ min}^{-1}$. Tendency from the slurry batch LED-reactor conducted under the same technical and operational conditions are shown for comparison.

On the other hand, **Figure 6.12** depicted the photodegradation results obtained with 3D&TiZn-NPs devices. Using a recirculation flow rate of $5 \text{ cm}^3 \text{ min}^{-1}$ the highest photodegradation efficiency was achieved: 55.1 %. However, at $30 \text{ cm}^3 \text{ min}^{-1}$, the photodegradation efficiency decreased to 33 %.

Table 6.3. % of SMX photodegradation results after 540 min of reaction time using the 3D-printed LED-microreactors devices: 3D&Ag/BiV/300 and 3D&TiZn-NPs.

Geometrical paths multichannel	$Q_T = 5 \text{ cm}^3 \text{ min}^{-1}$		$Q_T = 30 \text{ cm}^3 \text{ min}^{-1}$	
	% SMX degradation	Symbol	% SMX degradation	Symbol
3D&Ag/BiV/300*				
LC	54.2	○	50.2	●
HLC	55.5	□	50.5	■
TC	61.6	△	54.8	▲
HTC	30.9	◇	35.4	◆
3D&TiZn-NPs**				
TC	55.1	▲	33.0	△

*69.7 % and **86.6 % using slurry batch LED-reactor

The behaviour of the compact photocatalytic devices 3D&Ag/BiV/300 and 3D&TiZn-NPs are very promising for SMX degradation even in comparison to the slurry type reactor. It should be noted that the anchoring of the photocatalytic phase onto the microchannels produce a loosing of nanoparticles exposed surface, which justify the different reached SMX degradation, but the advantage of theses packed devices are very important as it has been highlighted in previous Sections, and these works very well. All of these results will be discussed in depth in the following Sections.

6.4.5 The Geometry Effect

Figure 6.11 depicts the profiles and **Table 6.3** shows the photodegradation results for SMX degradation using blue-LED light irradiation for 540 min as a function of both the geometry paths of multichannels and the recirculation flow rate, one at a low rate of $5 \text{ cm}^3 \text{ min}^{-1}$ and another at $30 \text{ cm}^3 \text{ min}^{-1}$. The overall trend in photodegradation indicates that the increase in the concentration of multichannels (HTC and HLC) in either linear or tortuous geometrical paths leads to apparent contradictory effects.

At the minimal flow rate ($5 \text{ cm}^3 \text{ min}^{-1}$), the tortuous geometrical path with a lower concentration of multichannels (TC) exhibited the highest effectiveness, achieving a photodegradation performance of up to 61.6 %. Following this, the linear geometrical path with a higher concentration of multichannels (HLC) achieved 55.5 %. Therefore, the order of photodegradation efficiency was $\text{TC} > \text{HLC} > \text{LC} > \text{HTC}$. At the high flow rate ($30 \text{ cm}^3 \text{ min}^{-1}$), the order of photodegradation efficiency was the same as at the low flow rate, with $\text{TC} > \text{HLC} > \text{LC} > \text{HTC}$. However, at the high flow rate, the highest effectiveness was slightly lower, achieving a photodegradation performance of 54.8 %, a decrease of 6.8 % compared to the low flow rate.

In the linear geometrical path, photodegradation efficiency increases from 54.2 % to 55.5 % for LC and HLC at a low flow rate, while at a high flow rate, the increase is slight from 50.2 % to 50.5 % for LC to HLC. In the tortuous geometrical path, efficiency drops from 61.6 % to 30.9 % and from 54.8 % to 35.4 % for TC to HTC at flow rates of 5 and $30 \text{ cm}^3 \text{ min}^{-1}$, respectively.

This simultaneous slight increase and significant decrease could be attributed to diffusional limitations caused by the surface tension of water within the multichannel. In this latter case, a combined effect between the increase in the concentration of multiple parallel channel arrangements supporting the photocatalyst and an intrinsic reduction in the width of the multichannels induces a more significant pressure drop, as seen in **Table 6.2**.

Additionally, it is important to consider that this performance difference could be attributed not only to the parallel multichannel path but also to the illumination efficiency [30]. It should be noted that the catalytic phase deposition by airbrushing on TC and specially HTC channels has one important handicap: these types of channels have many sharp bends where the catalyst can be extra-deposited. Moreover, the thickness of the catalyst layer may not be as uniform as on the lineal type microchannels, which would provoke a decrease of photocatalytic efficiency. Even more, in the case of HTC devices some of the microchannels could be blocked after the catalyst deposition by the above-mentioned reason. This homemade catalysts-deposition technique must obviously be optimized for future scaling, but the fact that the hydrodynamics of the fluid induced by the geometrical path significantly influences the degradation of SMX pollutant, has been shown.

6.4.6 The Recirculation Flow Rate Effect

Examining the effects of two recirculation flow rates allowed us to study their impact on the photodegradation of SMX. It was found that the most effective recirculation flow rate was $5 \text{ cm}^3 \text{ min}^{-1}$. In major of cases, the degradation percentages showed better performance compared to the test conducted at $30 \text{ cm}^3 \text{ min}^{-1}$ with the same geometrical path. The only exception was observed in the HTC

test, where the degradation rate was 30.9 %, slight lower than the rate observed at $30 \text{ cm}^3 \text{ min}^{-1}$, which was 35.4 %. The slowest flow rate of $5 \text{ cm}^3 \text{ min}^{-1}$ probably enhances the intimate contact between the pollutant solution and the photocatalyst coating. In any case, 3D-printed LED microreactors coated with photoactive phases in recirculation flow is a configuration that would be able to produce comparable results to those of slurry batch LED reactors.

6.4.7 Cycles of Microreactor Reuse

To evaluate the potential for microreactor reuse under the same operational conditions, the linear geometrical path with minimal concentration of multichannels (LC) was selected. This choice was made due to both its minimal 3D printing time and ease of coating with the photoactive phase.

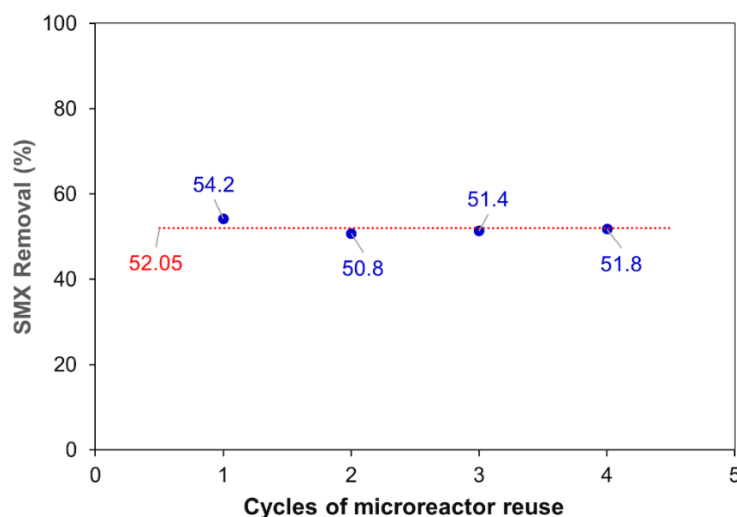


Figure 6.13. Cycles of 540 min of reuse of microreactor with linear geometrical path and minimal concentration of multichannels.

Our findings demonstrate that the fabricated 3D microreactors offer promising advantages, with an average efficiency of 52.05 % observed after four cycles of 540 min of reuse as shown in **Figure 6.13**, remained functional after each reuse step.

These results provide foundational insights demonstrating the feasibility of utilizing novel 3D printing technology to create photocatalytically active microreactors for wastewater treatment plants. These microreactors can effectively facilitate the photocatalytic removal of emerging pollutants under real conditions, operating at suitable flow rates for practical applications, including large-scale fabrication.

6.5 CONCLUSIONS

Microreactors with various geometrical paths of multichannels was designed and 3D printed using additive technology with polycarbonate material. The design includes two distinct arrangements: linear and tortuous parallel multichannels. Modifications were implemented to vary the flow regime conditions, resulting in two new subsets with lower and higher microchannel densities.

A home-designed airbrush deposition method was developed and employed to achieve the incorporation (anchoring) of the photocatalytic phase onto microchannels of 3D polycarbonate microreactors. Microscopy analysis confirmed that the distribution the photocatalytic nanoparticles across the surface was random, with varying degrees of coverage, predominantly appearing as agglomerated particles. These investigations into synthesis, immobilization, and photocatalysis can serve as a basis for the development of an innovative process for reusing photocatalysts for the elimination of emergent pollutants.

The behaviour of the compact photocatalytic devices 3D&Ag/BiV/300 and 3D&TiZn-NPs are very promising for SMX degradation even in comparison to the slurry type reactor.

The results indicated that tortuous path led to an improvement in photocatalytic performance compared to linear channels low density configuration, achieving degradation efficiencies of 61.1 % and 55.5 %, respectively. This improvement was attributed to the increased flow regimen, which facilitated random interactions between the emergent pollutant solution and the photocatalyst coated onto the microchannels.

In devices type HLC and HTC that have the narrowest channels, the airbrushing deposition of the photocatalytic phases carried out could provoke the formation of some non-uniform photocatalytic microchannels making difficult the comparison of the catalytic results with the LC and TC type devices.

Photocatalytic 3D-printed LED-microreactor devices have been successfully developed for degradation of water pollutants. These devices have shown very good performance, stability.

The Photocatalytic 3D-printed LED-microreactor devices have shown reusability capacity at least in four reaction cycles of 540 hours each.

The potential replacement of traditional manufacturing methods by 3D printing in applied catalysis opens significant opportunities for fabricating novel microreactor structures. Combined with nanotechnology in the design of photocatalytic materials, these technologies can enhance our ability to mitigate

environmental problems. Consequently, research focused on 3D printing to build functional photoreaction systems coupled with photocatalytic materials, which can eliminate emerging pollutants, continues to attract significant attention in both industrial and academic areas.

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CAPITULO VII: CONCLUSIONES GENERALES

CAPÍTULOS I Y II.

Se ha realizado una exhaustiva revisión del estado del arte relacionado con la tecnología de impresión 3D aplicada al desarrollo de foto-reactores compactos.

Se han establecido nuevos métodos de síntesis, basados en procesos de emulsión inversa y solvotermales, para desarrollar fases foto-catalíticas basadas tanto en vanadatos de bismuto, como en óxidos bimetálicos (con Ti, Zr, Ce y Zn), con estructuras y características físico químicas adecuadas para funcionar bajo luz solar.

También se definieron métodos de síntesis de catalizadores a escala nanométrica, integrables con sistemas de reacción compactos y funcionales, fabricados mediante tecnologías aditivas de impresión 3D, que modelan y optimizan las condiciones de reacción basadas en fases fotoactivas de materiales semiconductores.

CAPÍTULO III.

Fotocatalizadores basados en vanadato de bismuto fueron sintetizados mediante un método solvothermal, y sus propiedades fisicoquímicas fueron ajustadas mediante tratamientos de calcinación a diferentes temperaturas. Se determinó que 300 °C es la temperatura óptima para maximizar la fase monoclinica (*m-s*), la más activa en fotocatalisis.

También se desarrollaron vanadatos de bismuto dopados con plata como calcinando posteriormente a la temperatura óptima establecida. Estos fotocatalizadores mantuvieron la estructura cristalina monoclinica deseada.

Los fotocatalizadores mostraron saltos de banda prohibida entre 2.37 y 2.49 eV, siendo 2.47 eV para el material dopado y calcinado a 300 °C.

El efecto de la temperatura de calcinación y la adición del dopante se evaluó en la degradación de sulfametoxazol en disolución acuosa usando luz LED azul en un reactor por lotes a pH neutro. Así, se logró un 46 % de degradación con la muestra sin dopar tratada a 300 °C, mientras que a la misma temperatura, la adición del dopante aumentó la degradación hasta 69.7 % (un 23.7 % adicional).

La estabilización de la fase monoclinica y la presencia de nanopartículas de plata son probablemente responsables del incremento de la fotoactividad debido a la transferencia facilitada por el metal puede reducir la recombinación de pares electrón-hueco, y así estabilizar los sitios activos.

El modelo de Langmuir-Hinshelwood-Hougen-Watson se aplicó a la degradación del SMX, indicando que la reacción superficial es el paso determinante en la velocidad de reacción. El parámetro cinético ($A = K_A/K_{sr}$), diferente de cero, sugiere que la transferencia de masa desde la solución a la superficie del catalizador influye especialmente en la fotodegradación.

CAPÍTULO IV.

Fotocatalizadores de semiconductores acoplados, basados en nanopartículas de óxidos bimetálicos (Ti/Zr, Ti/Zn y Ti/Ce) se sintetizaron exitosamente mediante el método de microemulsión inversa.

Las nanopartículas con Ti/Zn (TiZn-NPs) y TiZr (TiZr-NPs) mostraron el patrón de difracción típico de la fase anatasa del dióxido de titanio, sugiriendo la interacción de los óxidos de zinc y zirconio en la fase anatasa.

Las nanopartículas de Ce/Zr (CeZr-NPs) exhibieron un desplazamiento en los picos de difracción respecto a los óxidos monometálicos, indicando una síntesis exitosa.

Las nanopartículas de Ti/Ce (TiCe-NPs) mostraron tanto las fases mixtas como las fases puras de los dióxidos de titanio y cerio. Sin embargo, las partículas de Zr/Zn y Ce/Zn mostraron solo los picos característicos de los óxidos metálicos individuales.

Como tendencias generales de distribución de la composición encontradas en este tipo de óxidos bimetálicos podemos concluir que los átomos de Ti tienden a estar bien presentes en la parte externa de las nanopartículas mientras que el Zn suele situarse principalmente en el interior de las mismas.

Las propiedades texturales más desarrolladas correspondieron con las muestras TiZn-NPs y TiZr-NPs.

Los catalizadores mostraron diferentes capacidades para la degradación de sulfametoxazol, dónde todas las fases desarrolladas con nanopartículas que

contuvieran titanio fueron claramente fotoactivas, destacando por muy encima del resto las TiZn-NPs y TiZr-NPs.

Se ha demostrado por tanto que la combinación adecuada de semiconductores acoplados, en una misma estructura cristalina, permite aprovechar las ventajas de ambos y mejorar la eficiencia fotocatalítica, siempre que en las estructuras cristalinas desarrolladas se puedan generar vacantes de oxígeno, así como mantener baja la capacidad de quimisorción de éste.

CAPÍTULO V.

Se desarrollaron fotocatalizadores híbridos $\text{TiO}_2\text{-ZrO}_2$ (Ti_xZr_y) utilizando el método de microemulsión inversa y se probaron eficientemente en la degradación de sulfametoxazol (SMX) en agua bajo irradiación de LED azul.

En esta serie de fotocatalizadores, a medida que aumenta el contenido de Zr, el tamaño de partícula disminuye y se obtienen distribuciones de tamaño de poro más estrechas.

Cuanto más pequeño es el tamaño de partícula de las fases, se obtienen mayores valores de superficie específica, lo que indica que las nanopartículas exponen una mayor superficie externa por unidad de volumen.

Químicamente destacar que a bajos contenidos de Zr ($\text{Ti}_{70}\text{Zr}_{30}$, $\text{Ti}_{50}\text{Zr}_{50}$), se forman titanatos de zirconio, mientras que a concentraciones más altas de Zr ($\text{ZrO}_2 > 50\%$ en peso), la estructura cristalina predominante detectada es zirconia cúbica, a pesar de que la zirconia monoclinica es la fase estable a temperaturas inferiores a $1200\text{ }^\circ\text{C}$.

El salto de banda prohibida disminuye hasta 2.8 eV al aumentar el contenido de ZrO_2 hasta 50 %, lo que probablemente se puede atribuir a la creación de una hetero unión entre las fases de titanato de zirconio y la fase de anatasa de titania.

Bajo irradiación de LED azul, y en las condiciones experimentales utilizadas, el fotocatalizador $\text{Ti}_{70}\text{Zr}_{30}$ es capaz de alcanzar el 80.1 % de degradación de SMX.

CAPÍTULO VI.

Se diseñaron e imprimieron cuatro tipos de microrreactores en 3D mediante tecnología aditiva con policarbonato. El diseño incluye dos disposiciones distintas: multicanales paralelos lineales y tortuosos, así como dos densidades de canal diferentes, unos más anchos (baja densidad) y los otros más estrechos (alta densidad).

Se desarrolló y empleó un método aerográfico de deposición de nanopartículas fotoactivas, de diseño propio, para lograr la incorporación (anclaje) de la fase fotocatalítica en los microcanales de los dispositivos compactos fabricados por impresión 3D, dando lugar en conjunto a los microrreactores propiamente dichos.

El comportamiento de los dispositivos compactos $3\text{D}\&\text{Ag}/\text{BiV}/300$ y $3\text{D}\&\text{TiZn-NPs}$ en la degradación de SMX en disolución acuosa, ha sido exitoso, siendo comparable con reactores de suspensión (slurry) en igualdad de condiciones experimentales. Estos dispositivos han demostrado ser estables durante al menos 4 ciclos de reuso de 540 horas cada uno.

El dispositivo con canales tortuosos tuvo mejor comportamiento fotocatalítico que el de canales lineales, ambos en configuración de baja densidad alcanzando

eficiencias de degradación de SMX del 61.1 % y el 55.5 %, respectivamente. Esta mejora se atribuyó al aumento del régimen de flujo laminar, que facilitó las interacciones aleatorias entre la solución contaminante emergente y el fotocatalizador anclado en los microcanales.

La deposición de las fases activas en canales suficientemente estrechos (alta densidad) podría tener un límite funcional. Es decir, los canales suficientemente estrechos pueden bloquearse durante la deposición aerográfica de la fase activa.

La impresión 3D aplicada a la catálisis, en sustitución o mejora de métodos o técnicas de fabricación más tradicionales, abre importantes oportunidades para el diseño e implementación de nuevas estructuras monolíticas de microrreactores. Combinando el diseño a escala nanotecnológica de materiales fotocatalíticos, con estos nuevos dispositivos-3D se puede mejorar nuestra capacidad para afrontar y mitigar los problemas medioambientales.

La investigación que incluye la impresión 3D para construir sistemas de fotorreacción funcionales, acoplados a nanomateriales fotocatalíticos, que pueden eliminar contaminantes emergentes, sigue estando en primera línea de la investigación tanto en el ámbito industrial, como en el académico.