One-step fabrication of multifunctional core–shell fibers by co-electrospinning

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Abstract

In the present study multifunctional core–shell fiber mats were designed by co-electrospinning. These core–shell fiber mats have three different functionalities: they are magnetic and optically sensitive to pH and O_2. On the one hand, the shell is formed by a fluorescent pH-sensitive co-polymer which was previously synthesized and characterised by our research group. On the other hand, the core is a suspension formed by magnetic nanoparticles in a solution made up by a lipophilic indicator dye (oxygen indicator; PtOEP) and, poly methyl methacrylate, in THF. The magnetic nanoparticles were prepared by encapsulation of magnetite within a crosslinked polymeric matrix (MMA-co-EDMA).

The morphology of the well-organized core-shell fibers were characterized by SEM, TEM, and confocal laser microscopy. The luminescent properties of core-shell fiber mats were analyzed and they were successful used to monitoring simultaneously pH (from 6 to 8) and O_2, showing complete reversibility, high sensitivity (i.e. K_{sv}=7.07 bar^{-1} for determining O_2 in aqueous media), high magnetic susceptibility and short response times.

Keywords: co-electrospinning, multifunctional material, core-shell fibers, magnetic susceptibility, optical sensing, pH-monitoring; O_2-sensitive matrix.

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Introduction

Optical sensors represent an interesting alternative to electrochemical sensors for monitoring biological parameters such as oxygen and pH.[1] In contrast to their mainly electrochemical counterparts, optical sensors are easy to miniaturize, are cost-effective and they can be read-out without physical contact.[2]

pH and O_2 monitoring[3-5] are crucial on many (bio)chemical process. Real-time monitoring and imaging of these parameters in (bio)chemical samples are of high interest in bioengineering, life science[3] and for controlling bioprocesses in industry scale.[6, 7] Optical sensor particles represent a very useful tool for real-time monitoring of these parameters. Recently, the concept of optical sensor particles was enhanced by the incorporation of magnetic properties into their structure. This enables the operator to trap the sensors at a distinct spot and to guide them to a desired position within the measurement setup.[8]

During the last years the preparation of two-functionalised sensor nano- or micro-materials has been done in one-step.[9, 10] Usually, these two functionalities correspond to magnetic susceptibility and an optical sensing property i.e. pH or O_2. But, it is not possible to find any research in which these three functionalities (magnetic susceptibility and optical-sensing to O_2 and pH) were simultaneously incorporated into micro- or nano-sensing materials via a facile one-step. For a successfully conjugation of these three functionalities via a facile one-step, it is necessary to create two different chemical environments on the same material: a hydrophilic environment to pH indicator and a hydrophobic environment to O_2 indicator. The magnetic susceptibility could be incorporated in whatever of these environments. It depends of the chemical properties of the used magnetic materials.

Bearing in mind these requirements, it is possible to conclude that it is very difficult to achieve a multifunctional (magnetic, optical sensing to pH and to O_2) micro- or nano-material with satisfactory optical features via a facile one-step conventional techniques[10, 11] such as miniemulsion-evaporation, precipitation-evaporation, spray-dry, electrospray, emulsion-polymerization, solution-polymerization or miniemulsion-polymerization, among other.

One way to create two different environments in a micro- or nano-material is by co-electrospinning technique. This allows a strict control of the process parameters and thus the design of well-organized multifunctional materials.[12-15] The co-electrospinning technique allows one-step fabrication of micro- and nano-tubes or coaxial micro- and nano-fibers of different pairs of copolymers for different applications.[16] These are all structures with radial anisotropies. Very recently, co-electrospinning has been used to encapsulate labile materials other than polymers within fibers. For instance, Song *et al.*[17] used a stabilized emulsion of

FePt magnetic nanoparticles in hexane as the inner liquid and a melt of poly(e-caprolactone) (PCL) on the outside to encapsulate the nanoparticles inside nanofibers. Jiang *et al.*[18] used an aqueous melt of poly(ethylene oxide) (PEO) in which a protein (bovine serum albumin (BSA) and lysozyme) was dissolved as the inner fluid, with a melt of PCL on the outside. The result was coaxial nanofibers containing the protein in their core fiber.

Therefore a potential way to introduce via a facile one-step the three functionalities commented before on a micro- or nano-material could be by co-electrospinning of two adequate pairs of copolymers. In this work we use co-electrospinning of two copolymers to design multifunctional (magnetic susceptibility, optical sensitivity to O_2 and pH) core-shell fibers via one-step; a fluorescent pH-sensitive copolymer (NP1(X)) was used as the outer fluid, and a suspension formed by polymethyl methacrylate (PMMA) melt magnetic nanoparticles and O_2 indicator (PtOEP) was used as the inner fluid. Thus, the core is magnetic and optically sensitivity to O_2 and the shell is pH-sensitive.

NP1(X) was previously synthesised and characterized by our research group[19] for producing pH-sensitive nanofibers by electrospinning.

Materials and methods

Chemicals

Methyl methacrylate (MMA; Aldrich; 99%) and ethylenglycol dimethacrylate (EDMA; Aldrich; 80%) were passed through a column filled with neutral alumina prior to use. Azobisisobutyronitrile (AIBN; Fluka; 98%), N,N-dimethylformamide (DMF; Scharlau, reagent grade), tetrahydrofuran (THF; Aldrich; 99%) , Pt(II) octaethylporphine (PtOEP), poly(vinyl pyrrolidone) (PVP; Acros Organics, weight-average molecular weight, Mw = 1300000) and polymethyl methacrylate (PMMA; Aldrich, weight-average molecular weight, Mw = 350000) were used as received. NP1(X) (M_w; 104.517 Dalton, M_w/M_n; 1.4, Intrinsic viscosity (IV); 0.28 dLg^{-1}, pKa; 7.6) was synthesised and characterized following the literature.[19]

Magnetic hybrid nanoparticles encapsulated by EDMA/MMA (EDMA/MMA-Fe_3O_4-OA-NP). Magnetite coated with oleic acid (lipophilic magnetic nanoparticles) was prepared by the conventional method.[11] Then, 2 g of lipophilic magnetic nanoparticles were dispersed in 5 mL of n-heptane and added to 400 mL of Milli-Q water containing 250 mg of SDS. The ice-cooled mixture was sonicated for 20 min in a high-energy sonifier (BRANSON, S-450D) at 70% amplitude for 20 min. The resulting mini-emulsion was transferred slowly (under mechanical stirring) to a double-necked flask containing 1.5 mL of 30 wt % MMA, 70 wt % EDMA. The mixture was stirred for 2 h at room temperature. Next, 180 mg of potassium peroxodisulfate (KPS) was added to start the polymerization, and the reaction system was heated to 65ºC under a gentle stream of nitrogen. After a polymerization time of 24 h, the resulting product was washed six times with Milli-Q water, five times with acetone, and five times with THF in order to eliminate surfactant and unreacted compounds. After washed the particles were dispersed in THF. The final concentration of magnetic nanoparticles in THF was of 16 mg/ml.

Instruments

The characterisation of EDMA/MMA/-Fe_3O_4-OA-NP and core-shell fibers was developed by TEM (Zeiss DSM 950), HRSEM (LEO, Carl Zeiss, GEMINI-1530) and by confocal fluorescence microscopy (Leica DMI6000). The luminescent characterization of core-shell fibers was carried out with a luminescent spectrometer Varian Cary Eclipse. A PC-controlled system was designed to control the gas composition. For gas mixing, two mass flow controllers of Type 1179 from MKS Instruments (Andover, MA, USA) were used.

Fabrication and characterization of multifunctional core-shell fibers

Co-electrospinning solutions

To make the core-shell fibers by co-electrospinning one external solution and two different internal suspensions were used. Table 1 shows the nomenclature and the composition of internal suspensions and the external solution. The percentages shown in the Table 1 were calculated as weigh percentage (g of solute per 100 g of solution).

Experimental set up to produce the co-electrospinning

For co-electrospinning of the different samples[20, 21] the liquid flow-rates formed by outer and inner solutions were independently impulse by two syringe pumps (Cole Parmer 74900 Series). The syringes used are Teflon Becton & Dickinson of 5 and 2 cm^3, respectively. The outer and inner solutions were impulsed through of Teflon capillary tube until a concentric couple of stainless steel capillary tubes (injector). The outer and inner diameters of stainless steel capillary tubes were: external tube Φ_{ext}/Φ_{int}=1.7/1.4 mm, internal tube Φ_{ext}/Φ_{int}=1/0.7 mm. To apply the electric field, two high voltage power supplies were used (Gamma High Voltage ES30P and Bertan 205B-10R) to establish a potential difference between the injector and the collector, which was a flat metallic plate of 20x30cm located 23.5 cm apart from the injector.

One of the power supplies was connected to the injector in positive polarity (V_i) with respect to ground, while the second power supply was hooked to the collector and run in negative polarity (V_c) with respect to ground. Table 2 shows the different flow-rates and voltages to make the co-electrospinning. The selected flow-rates and voltages within this configuration allowed the collection of dry fibers mats. The process was run for about 2.5 h to collect about 20 cm diameter rounded mats of core-shell fibers. Then, they were dried in a vacuum at 85 ºC to a constant weight.

Characterization of multifunctional core-shell fiber mats

The morphological characterisation of core-shell fibers mats was done by TEM and laser confocal fluorescent microscopy. To analyze the fiber mats by laser confocal microscopy, the emission spectra of each indicator were previously recorded by using different excitation lasers. The adequate excitation wavelengths to produce the simultaneous emission of both indicators (NP1(X) and PtOEP) were 488 and 530 nm, respectively. It is necessary to remark that the 488 nm laser has lower intensity than the 530 nm one.

The magnetic susceptibility of the core-shell fiber mats were measured with a Manics DSM-8 magnetometer.

For the luminescent characterization a piece of the fiber mat was fixed in a glass plate of 36 mm of diameter. Then, it was placed into a home-made flow-cell which was connected to a FIA system (see Electronic Supporting Information, ESI, Fig. ESI-1). Different buffer solutions (phosphate-citrate-borate, ionic strength adjusted to 80 mM with NaCl, and a constant concentration of O_2) with pH values of 4, 6 and 8 were passed through the cell and the fluorescence spectrum of the core-shell fiber mats at the excitation and emission wavelengths of the NP1(X) ($\lambda_{exc}/\lambda_{em}$=480/520 nm) were recovered. In addition, the phosphorescent spectra of the core-shell fiber mats at the excitation and emission wavelength of the O_2 indicator ($\lambda_{exc}/\lambda_{em}$=380/650 nm) were also recorder for each pH at different O_2 concentration.

The different O_2 concentrations were established by bubbling into the buffer solution a gas flow (100 mL mim^{-1}) with four different percentages of O_2 balanced in N_2: 0, 10, 20 and 100% O_2.

The pH calibration also was done by using a 1.5 mm diameter optical fiber probe (Varian Iberica, Spain) coupled with a special magnetic separator with an optimized geometry as described elsewhere*[22]* (see ESI, Fig. ESI-2). Briefly, the separators consisted of four block magnets arranged like a star around the optical fiber with their like poles pointing against each other. The optical fiber probe was connected to the luminescence spectrometer (Varian

Eclipse) by using a Varian fiber adapter. To measure with this set up the samples were prepared by adding 2.0 mg of core-shell fiber mats into a conventional quartz cuvette which contained 2 mL of the pH buffer solution. The cuvette was shaken for 10 s prior to each measurement. The magnetic separator collected the piece of mat on the tip of the optical fiber probe and, therefore, the luminescence intensity to each pH value was read out.

Results and discussion

One-step fabrication of multifunctional core-shell fiber mats

In order to design a three-functional (magnetic and optical sensing to pH and O_2) core-sell fibers, two copolymers with different polarity were assembled by co-electrospinning. The proposed structure for these fibers consists on the incorporation of magnetical and optical O_2-sensitive properties into de core and optical pH-sensitive properties in the shell.

To incorporate magnetic properties in the core, we selected a suspension of lipophyllic magnetic nanoparticles formed by magnetite covered with oleic acid (γ-Fe_3O_4-OA) in PMMA/THF as inner suspension of the co-electrospinning. The stability of the suspension of these nanoparticles in PMMA/THF is not good enough for developing the co-electrospinning because γ-Fe_3O_4-OA decants in a short period of time. Thus γ-Fe_3O_4-OA was encapsulated in a MMA-co-EDMA polymeric matrix in order to increase their stability in PMMA/THF. MMA-co-EDMA polymeric matrix was selected because it is chemically similar to PMMA, which is the polymer used for the inner suspension, and thus the chemical affinity between magnetic nanoparticles and PMMA melt is maximized. EDMA/MMA-Fe_3O_4-OA-NP provides a high stable inner suspension which allows a compound cone in steady state during long time (more than 4 hours). Fig. 1 shows the HRSEM and TEM pictures of EDMA/MMA-Fe_3O_4-OA-NP.

The oxygen-sensing properties were incorporated by dissolving PtOEP in the inner suspension. It was selected because it has good optical properties,*[23]* adequate sensitivity to O_2*[10, 24]* and appropriate polarity to be solubilised in PMMA/THF.

To functionalise the fibers with a pH-sensitive optical material, we selected the pH-sensitive co-polymer melt previously developed by our research group*[19]* (NP1(X); M_w; 104.517 Dalton, M_w/M_n; 1.4, Intrinsic viscosity (IV); 0.28 dLg^{-1}, pKa; 7.6) as outer fluid. To produce a stable and continuous co-electrospinning procedure, we used a high percentage of polymer (30 wt % to NP1(X)) in the outer fluid, in order to increase the coupling between polymeric chains during the co-electrospinning procedure, helping to solidify the electrified jet near his generation. A sufficiently high viscosity of the outer fluid is essential to develop a compound cone in steady state. Thus, in our case it was necessary to increase the viscosity of the outer fluid by addiction of 1.4 % (w/w) PVP (M_w; 1300000).

Apart from the requirements regarding the physical properties of the fluids, for a given setup and fluid pair there exists a parametrical range of operation in which the compound cone and so the compound fibers are produced. In this work, to develop a compound cone in steady state we have found a range, without in depth exploration of the limits, in which we can easily operate. Fig. 2 shows the Taylor cone for two voltage difference between the injector and the collector (ESI shows Fig. 2 in colour, see Fig ESI-3) maintaining constant the flow-rates (outer and inner flow-rates were selected as 1.0 and 0.1 mL h^{-1}, respectively). It shows that an increase of the voltage difference provides a bigger Taylor cone. The selected voltages (Fig. 2A: Injector voltage; 9 kV, and collector voltage; 0.7 kV) allow obtain a homogeneous compound cone in steady state, during long time. For a fixed voltage difference between the spinneret and the collector, the operative range depends on the flow-rates of both fluids. Typically, the inner fluid flow rate, Q_{in}, may be set at K times the outer fluid flow rate, Q_{out}. K varies roughly between 0.1 and 0.5 mL h^{-1} in our case and Q_{out} remains constant in 1 mL h^{-1}.

Fig. 2 shows qualitatively how the compound cone develops as K increases from 0.1 for Q_{out} = 1 mL h^{-1}. When K is increased the compound meniscus grows (Fig. 2C and D) until the flow inside the meniscus starts mixing both fluids ($K \approx 0.7$). For other values of Q_{out}, the phenomenology as K varies similar. The diameter of the core and thus, the amount of magnetic nanoparticles in the core of the fibers, is increasing when K is also increased from 0.1 to 0.5 mL h^{-1} (see Fig. 3). Due to this fact, the magnetic susceptibility of the fibers is also increased when K is increased (see Fig. 4). To sum up, the selected outer and inner flow-rates were 1.0 and 0.5 mL h^{-1}, respectively. Under these conditions homogeneous compound cone in steady state can be obtained during long time.

Fig. 3 shows SEM and TEM pictures of the C1, C2 and C2-O_2 core-shell fibers (see Tables 1 and 2 for the chemical composition of the fiber mats). It shows a regular and homogeneous formation of the fibers, during the co-electrospinning procedure, in all the cases (see figures 3A, 3B and 3C). Fig. 3 also shows how in all the cases, the EDMA/MMA-Fe_3O_4-OA-NP are homogeneously distributed along the core fiber (see figures 3D, 3E and 3F). The addiction of 0.2 % of the O_2 indicator (PtOEP) into the inner suspension did not affect to the co-electrospinning process, and thus the morphology of the core-shell fibers did not change (see Fig. 3D).

Fig. 4 shows the magnetic susceptibility of these fiber mats. It shows that the magnetic susceptibility of the mats is notably increased when the percentage of EDMA/MMA-Fe_3O_4-OA-NP in the inner fluid is increased. So, C1, which contains a 4% w/w of EDMA/MMA-Fe_3O_4-OA-NP, has a saturation magnetization of 0.90 emu g^{-1}, while C2 and C2-O_2, which contain 17% w/w of EDMA/MMA-Fe_3O_4-OA-NP, show a saturation magnetizations of 1.60 and 1.50 emu g^{-1}, respectively.

Confocal laser microscopy was used for analysing the distribution of PtOEP and NP1(X) (see Fig. 5). Fig. 5A shows a picture of the fluorescent emission of the C2-O_2 using only one excitation wavelength (488 nm). At this excitation wavelength, only the emission of NP1(X) was observed. When both 488 and 530 nm lasers were used, the emission of both NP1(X) and PtOEP were simultaneously observed (see Fig. 5C). It shows a narrow red emission through the entire core fiber due to the PtOEP emission. Thus we can conclude that PtOEP was homogeneously distributed through the internal core fiber.

The homogeneous distribution of PtOEP through the core fiber is achieved by the different polarity of the external solution and internal suspension used to make the co-electrospinning. The PtOEP indicator is highly hydrophobic, thus the diffusion of PtOEP from fiber core to the fiber shell is minimized.

Characterization of the optical sensing properties of C2-O_2 to pH and O_2

To characterise the pH-optical properties the core-shell fibers mats C2 and C2-O_2 were treated as it was commented in the experimental section. The fluorescent emission spectra were recorder at different pH values when the samples were excited at 480 nm, which is the maximum excitation wavelength of NP1(X)*[19]* (see Fig. 6A). It shows that C2 is more luminescent than C2-O_2 and that the luminescence of both mats increases when the pH value is also increased. In addition, Fig. 6A also shows an emission at 650 nm for C2-O_2 which is not observed for C2 mats. Fig. 6B shows a magnification of this part of the spectra.

This emission has been attributed to the presence of PtOEP. It can be produced by a fluorescence resonance energy transfer (FRET) from NP1(X) to PtOEP because the emission spectrum of NP1(X) overlaps with the excitation spectra of PtOEP (see Fig. ESI-4).

In order to demonstrate that the emission at 650 nm corresponds to the O_2-sensnitve dye, the fluorescent emission spectra of C2-O_2 at pH=8 were recorded when the mats were exposed to different O_2 concentration levels. The excitation wavelength used was 480 nm. Fig. 6C shows that the intensity of this band is decreased when the O_2 concentration is increased. Therefore, it is possible to conclude that FRET process between NP1(X) and PtOEP occurs.

Since FRET physically originates from the weak electromagnetic coupling of two dipoles, the length scale for detection in FRET-based methods is limited by the nature of the dipole–dipole interaction.[25] The most relevant parameter of this interaction is the dipole-dipole separation distance, which is typically limited to <100 Å (corresponding to 10 nm).[24] Therefore, in our case, FRET can be only produced in the interface between the core and shell of the fiber because it is the only places in which both luminophores can be close each other.

Fig. 6D shows the pH calibration of C2 and C2-O_2 mats, in an adequate pH range (6-8) for most biological systems (around the pK_a of NP1(X))[19]. It is possible to conclude that C2 mat is more sensitive to pH than C2-O_2. It could be attributed to the FRET phenomenon observed in C2-O_2. The efficiency of FRET in C2-O2 could be related with the pH because when the pH is increased the shell is deprotonated and therefore the charge of the shell is also increases. It means that the shell is swelled and therefore the diffusion of OH^- into the shell is increased, providing the deprotonation of the molecules located in the core-shell interface which provides an increase of the efficiency of FRET. To sum up, the FRET phenomenon is depending of the pH of the media; at basic pHs the FRET is more efficient than at acid pHs. It could explain why the sensitivity to pH of C2 is higher than the sensitivity of C2-O_2.

Anyway, due to the very good properties (high brightness, high sensitivity to pH changes, around its pKa value, etc.)[19] of NP1(X), the lost in the sensitivity to pH is not significant, and C2-O_2 keep very good features to optical pH-monitoring.

The pH calibration and the pH reversibility were also studied by using a 1.5 mm optical fiber coupled into magnetic collector.[11] Fig. 7 shows the variation of the luminescence intensity of C2-O_2 mat after magnetic collection (see Fig. ESI-3 for the set-up used).

We would like to remark that 2 mg of C2-O_2 mat can be efficiently collected with a magnet providing a sensing spot inside the cell which allows optical pH readout from the outside.

To demonstrate that the core-shell fiber responds to O_2 and to analyse the influence of the pH in the determination of oxygen, the luminescence intensity of C2-O_2 mat were recorded at different O_2 concentrations and at different pH values (see Fig. 8). It shows that C2-O_2 mat is sensitive to oxygen and, in addition, the sensitivity to O_2 is not influenced by the pH of the media.

To determine the sensitivity to oxygen, the reversibility and the response times in gas phase and in solution at pH=8 of C2-O_2 mat, the variation of the luminescence intensity versus concentration of oxygen were recorded to obtain the Stern-Volmer plots. Fig. 9 shows the oxygen sensitivity and reversibility of C2-O_2 in gas phase and in solution at pH=8, respectively. The sensitivity to O_2 of C2-O_2 mat were K_{sv}=3.88 bar^{-1} in gas phase and K_{sv}=7.07 bar^{-1} in solution; and the t_{90} response times were determined as t_{90}=15s from O to 5% O_2 and t_{90}=12s from 5 to 0% O_2 in both cases gas phase and aqueous media.

The reversibility and the almost linear correlation between I_0/I versus pO_2 in both cases are useful for practical applications. High signal intensities are important for oxygen imaging. Moreover, the high brightness of the incorporated O_2 indicator (PtOEP) overcomes the problem of the highly light-absorbing EDMA/MMA/-Fe_3O_4-OA-NP.

Conclusions

In this work we present a new multifunctional advanced material. This material is based in the utilization of electrified coaxial jets for the design via facile one-step of three-functional and well-organized core-shell fibers. Also, we have demonstrated that the co-electrospinning is a powerful tool to design three-functional core-shell fibers with controlled distributions of axial anisotropies in composition, via a facile one-step, with high production and effective cost. The multifunctional advanced material development in this work is based on the encapsulation by co-electrospinning of a hydrophobic suspensions formed by PMMA melt, magnetic nanoparticles (EDMA/MMA/-Fe_3O_4-OA-NP) and a hydrophobic luminescent oxygen indicator (PtOEP) into a pH-fluorescent sensing copolymer (NP1(X)) previously synthesized by our research group. We successfully demonstrated that these core-shell fiber mats are magnetic and they have a well-organised structure which allows simultaneously, the optical monitoring of pH and O_2 *in-situ* and at real-time. In addition, the magnetic susceptibility of the core-shell fibers can be tuned by changing the percentage of EDMA/MMA/-Fe_3O_4-OA-NP in the inner suspensions.

Due to the versatility of the co-electrospinning technique, the new advanced materials development in this work can be easily modified to match other requirements for a wide range of scientific and clinical applications. To our knowledge, this is the first time that magnetic and optical O_2- and pH-sensitive properties were successful conjugated on the same micro- or nano-material via a facile one-step with high production an effective cost.

Acknowledgments

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Fig. 1. HRSEM picture (A) and TEM picture (B) of EDMA/MMA-Fe_3O_4-OA-NP.

Fig. 2. Taylor cone geometries for two voltage differences between the injector and the collector maintain constant the flow-rates (outer and inner flow-rates, selected were 1.0 and 0.1 mL h–1 respectively, the voltage difference of A is higher than B), and evolution of the Taylor cone geometry for a outer flow-rate of 1 mL h^{-1} and a inner flow-rate of C) 0.1 mL h$^{–1}$ and D) 0.5 mL h$^{–1}$.

Faltan las fotos de SEM ; A, B y C.

Fig. 3. SEM and TEM pictures: A, B and C show the SEM pictures of C1, C2 and C2-O_2 core-shell fibers mat, respectively. D, E and F show TEM pictures of C1, C2 and C2-O_2 core-shell fibers mat, respectively.

Fig. 4. Magnetization curves at room temperature of C1 (grey line), C2 (black solid line) and $C2\text{-}O_2$ (black dashed line).

Fig. 5. Confocal microscopy pictures of C2-O_2 A) when the sample is excited at 488nm; B) magnification of one fiber of the Fig. 5A; C) when the same fiber of Fig 5B is simultaneously excited at 488 and 530 nm.

Fig. 6. A) Fluorescence spectra of C2 and C2-O_2 at several pH values, λ_{exc} = 480 nm, slit widths$_{exc/em}$ =5/5 nm and detector voltage of 530V. B) Magnification of the emission band observed in Fig 6A at 650 nm. C). Luminescence quenching observed for C2-O_2 mat at pH=8 with the O_2 (λ_{exc} = 380, slit width$_{exc/em}$ =10/10 nm, detector voltage 650V; td = 120 ms, tg = 5 ms); D) pH calibrations of C2 and C2-O_2 arround the pKa of NP1(X).

Fig. 7. pH monitoring and reversibility of C2-O_2 using the magnetic set-up.

Fig. 8 Variation of the luminescence intensity of C2-O_2 with the concentration of O_2 at different pH values ($\lambda_{exc}/\lambda_{em}$ = 380/650 nm, slit width $_{exc/em}$ =10/10 nm, detector voltage 650V; t_d = 120 ms, t_g = 5 ms).

Fig. 9. Variation of the luminescence intensity of C2-O2 with the concentration of Oxygen balanced with N2 A) in gas phase and C) in a pH=8 aqueous solution; and the Stern–Volmer plots of C2-O_2 in B) gas phase and C) in solution. (($\lambda_{exc}/\lambda_{em}$ = 380/650 nm, slit width $_{exc/em}$ =10/10 nm, detector voltage 650V; t_d = 120 ms, t_g = 5 ms).

Table 1. Nomenclature and composition of internal suspensions and external solutions.

Solutions	DMF[a]	THF[a]	NP1(X)[a]	PMMA[a]	PVP[a]	PtOEP[a]	EDMA/MMA-Fe_3O_4-OA-NP[a]
E1	70.4	0	28.2	0	1.4	0	0
IA-b	0	84.7	0	12.7	0	0	2.54[b]
IB-b	0	84.7	0	13.3	0	0	0.6[c]
IA-bO_2	0	84.7	0	12.7	0	0.2	2.54[b]

[a] Calculated as weigh percentage (g of solute in 100 g of solution)

[b] It corresponds to a weigh percentage of 17 % without taken into account the solvent.

[c] It corresponds to a weigh percentage of 4.5 % without taken into account the solvent.

Table 2 Experimental parameters to make co-electrospinning of the different core-shell fiber mats.

Core-shell fibers mats	External solution	Internal suspension	External flow-rate ($mL\cdot h^{-1}$)	Internal Flow-rate ($mL\cdot h^{-1}$)	Injector voltage (kV)	Collector voltage (kV)	Distance between electrodes (cm)	Size of Deposition[a] (cm)
C1	E1	IB-b	1.0	0.5	9.7	0.7	23.5	23x17
C2	E1	IA-b	1.0	0.5	9.7	0.7	23.5	23x17.5
C2-O_2	E1	IA-bO_2	1.0	0.5	9.7	0.7	23.5	22.5x17.5

[a] The dimensions are corresponded with the major and minor diagonal of an ellipse.