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Emission properties of electrospun polymeric nanofibres

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Summary. — The emission properties of polymer nanofibres fabricated by electrospinning are analysed. The nanofibres, made by conjugated polymers, display diameters of few hundreds of nanometers, depending on the process parameters, and exhibit photoluminescence tunable in the visible spectral range and polarized along the fibre axis. Nonradiative energy transfer in fibres made by blends of polymers and its exploitation for emission tuning are discussed.

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1. – Introduction

Nanomaterials and nanostructures are revolutionizing many scientific and technological fields, due to their unique physical properties arising from the nanoscale size and from the confinement effects on electronic, optical, and magnetic properties [1,2]. Nanomaterials can be synthesized and fabricated by both organic and inorganic materials and by their combination (hybrid nanomaterials), and can display diverse final shapes (dot, wire, tube, fibre, ...) [3]. The capability to synthesize hybrid nanomaterials has led, recently, to the realization of the smallest laser device composed by a metallic gold nanoparticle (diameter of about 14 nm), surrounded by a silica (44 nm) and an organic dye gain shell [4].

Among the different nanomaterials, polymeric nanofibres are attracting an increasing interest as innovative 1-dimensional (1D) nanomaterials, exhibiting peculiar, smart properties useful for many applications, including textiles, micro-electro mechanical systems (MEMS), sensing, artificial tissues and optoelectronic devices [5,6]. The interest on this class of materials relies on their physico-chemical properties, on their high surface to volume ratio and on the availability of a set of low-cost production techniques. Microfluidics [7], polymerization in nanoporous templates [8], dip-pen lithography [9],

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self-assembly [10], molding [11], and electrospinning [12] are some of the different technologies developed for the production of polymer nanofibres.

In particular, electrospinning is a simple, versatile and high-throughput technique allowing the continuous fabrication of both polymeric and inorganic nanofibres with diameters tunable in the range 10 nm–10 μ m [13]. The technique is similar to the mechanical drawing of fibres, the main difference being the use of electrostatic forces to stretch and elongate a viscous polymer solution. The electrostatic field is typically applied between the metallic needle of a syringe containing the polymer solution and a metallic collector. By increasing the applied voltage above a threshold value a continuous liquid jet is extruded from the needle. The liquid jet is continuously stretched during its time-of-flight toward the collector and the concomitant evaporation of the solvent allows the formation of tiny fibres with sub-micron diameter, generally collected as nonwoven mats. A unique feature of the electrospinning technology is the possibility to control the fibre diameter and the surface morphology by varying the processing variables, such as the applied voltage, the solution flow rate, the solution surface tension and concentration. These features and the possibility of processing numerous polymers, inorganics and composites account for the large number of applications that use electrospun nanofibres mats as key component [5]. For instance, nonwoven mats of electrospun nanofibres are finding application as filtration membrane [14,15], because of the high porosity of the fibres mats and the high surface to volume ratio, allowing an increased interaction between the filtrating component and the treated medium.

Among the different applications of the electrospun nanofibres, an emerging field is the fabrication of light-emitting nanofibres for photonics. There are two main methods to obtain light-emitting nanofibres: the first is based on the exploitation of optically inert polymers, such as poly (methyl methacrylate) (PMMA), doped with fluorescent small molecules (typically organic dyes) [16,17], whereas the second approach utilizes light-emitting conjugated polymers [18]. These polymers are a class of organic materials possessing the optoelectronic properties of semiconductors combined with the mechanical and structural properties of polymers. These materials, known also as organic semiconductors, are exploited as active components of light-emitting diodes (LED), solar cells, laser and field effect transistor devices [19]. Therefore, nanofibres made by these materials can constitute building blocks of miniaturized integrated photonic systems, where a single fibre can generate, guide and detect light. Electrospinning of conjugated polymer presents some difficulties due to their poor viscoelastic properties and solubility, drawbacks that can be overcome by properly varying the polymer solution, making it more processable [18]. In this way, fibres with sub-micron diameter can be produced, preserving the optoelectronic properties of the used conjugated polymers.

In this communication, the main optical properties of electrospun polymer nanofibres are discussed. The emission tunable in the whole visible range (400–650 nm) is achieved, by exploiting conjugated polymers with different energy gaps. The photoluminescence (PL) of the fibres is comparable to the reference spincoated polymer film and the measured differences are attributable to the different packing of the polymer molecules in the fibres compared to thin films. Moreover, fibre emission is mainly polarized along the fibre axis, with polarization ratio up to 5, because of the preferential orientation of the polymer backbones induced by the high stretching of the polymer solution during the electrospinning process. Fibres can also be made by blends of conjugated polymers, where Förster nonradiative energy transfer is used to tailor the emission, by playing with the relative concentration of the blend components.

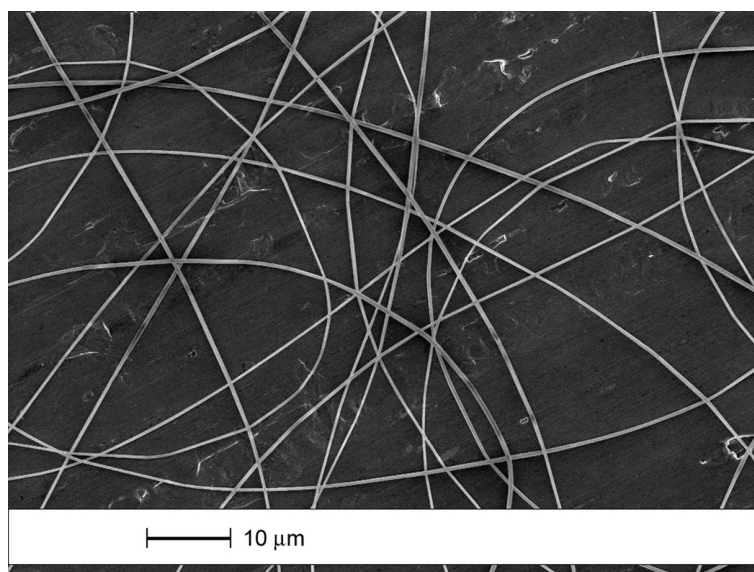


Fig. 1. – Scanning electron microscope image of a nanofibre mat deposited on Al foil. The fibres are made by PMMA doped with a NIR emitting polymethine dye. The fibres are electrospun at an applied voltage of 30 kV and a needle-collector distance of 25 cm.

2. – Methods

The electrospinning experimental apparatus has been reported elsewhere [16, 18]. Briefly, the electrospinning system is composed by a syringe pump (33 Dual Syringe Pump, Harvard Apparatus), feeding the polymer solution at constant rate (0.1–10 $\mu\text{l}/\text{min}$), a spinneret (a 18–27 gauge stainless-steel needle), a high-voltage power supply (10–30 kV) and grounded aluminum foils used as collectors (10 \times 10 cm^2).

Light-emitting nanofibres are fabricated both by doping PMMA with fluorescent and gain dyes [16, 17] and by using conjugated polymers with photoluminescence in the visible [18]. The former fibres are obtained by dissolving the fluorescent molecules (0.2–0.5 wt%) into a $1\text{--}3 \times 10^{-3}$ M chloroform solution of PMMA (Sigma-Aldrich). Figure 1 displays a typical scanning electron microscope (SEM) image of PMMA fibres doped with a polymethine dye emitting in the near infrared spectral range (800–950 nm).

Conjugated polymer nanofibres are realized by electrospinning a solution obtained by dissolving the polymers (American Dye Source Inc.) in a mixture of either chloroform or tetrahydrofuran and dimethylsulfoxide [18]. The use of such solvent combination allows the formation of fibres with almost uniform diameters. The fibres are typically electrospun at room temperature, with air humidity $< 40\%$.

The photoluminescent properties of the fibres are analysed by exciting the fibres with laser sources (wavelengths 325, 405 and 472 nm), by collecting the emission through an optical fibre and analysing the emission spectrum with a monochromator (iHR320, Jobin Yvon) equipped with a Charge Coupled Device (CCD) as detector. Fluorescent images of the fibres are measured by using a confocal microscope (FV1000, Olympus) and a 405 nm diode laser as excitation source.

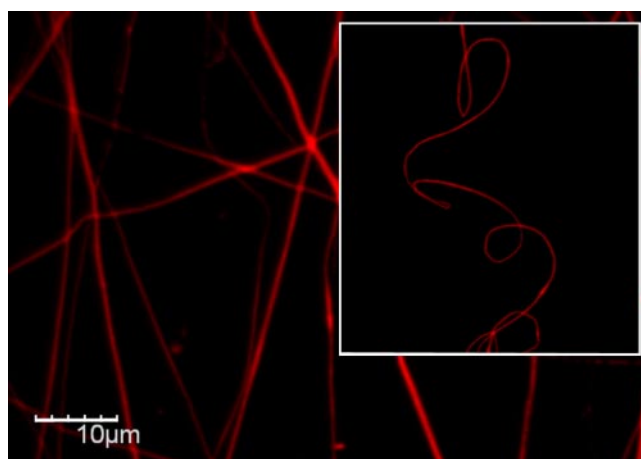


Fig. 2. – Confocal microscope fluorescence images of MEH-PPV nanofibres. The fibres are electrospun at an applied voltage of 10 kV and a needle-collector distance of 12 cm.

3. – Results and discussion

In fig. 2 confocal fluorescence images of a mat of conjugated polymer nanofibres are displayed. The investigation of the morphological properties of conjugated polymer nanofibres through SEM and atomic force microscopy evidences almost uniform diameters, with a minimum observed diameter of 75 nm [18]. The average diameter can be tuned from 200 nm to 400 nm by changing the applied voltage and the needle-collector distance: smaller fibres are obtained by increasing the applied voltage and the needle-collector distance [18]. These findings are in accordance with the models, predicting a fibre diameter: $d \propto (\phi/I)^{2/3}$, where ϕ is the solution flow rate and I is the needle-collector current [20].

Typical emission spectra of conjugated polymer nanofibres are displayed in fig. 3. The emission spectrum of the poly [(9,9– dioctylfluorenyl–2,7–diyl)–co–(1,4–benzo–{2,1',3}–thiadiazole)] (F8BT), fig. 3A), is peaked at 537 nm and has a full width at half maximum (FWHM) of about 65 nm, whereas the emission spectrum of the poly

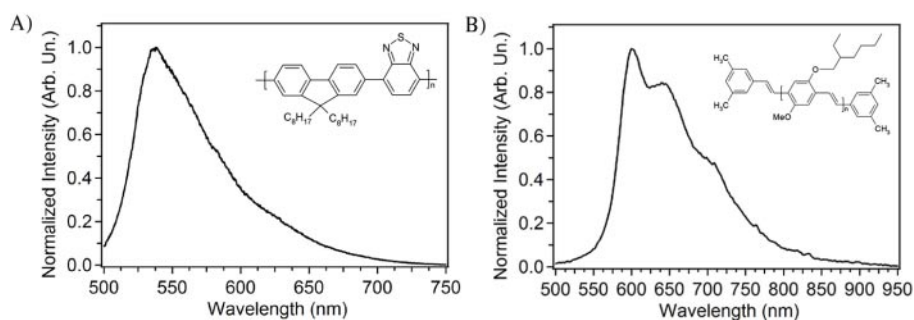


Fig. 3. – Photoluminescence spectra of F8BT A) and MEH-PPV B) nanofibres. In the insets the molecular structures are displayed, respectively.

[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) is peaked at 600 nm and has a FWHM of about 110 nm (fig. 3B)). The shapes of the emission spectra are comparable to the photoluminescence of the used polymers, confirming that the electrospinning process preserves the optical properties of the polymers. Nevertheless, some differences are sometimes observed by comparing the emission spectra of the fibres with reference films, spincast from the same solution. Most of the samples display a blueshift of the emission, up to 5 nm for MEH-PPV [21], an effect related to the suppression of energy migration toward low-energy chromophores. Emission in conjugated polymer is a complex phenomenon since the conjugated polymers are molecular systems composed by chromophores with slightly different energy gaps. The optical or electrical pumping excites the different sub-units (chromophores), creating excitons, that migrate toward the lowest-energy sites, mainly by nonradiative energy transfer processes, like the Förster energy transfer [22]. This exciton migration is favored by the spatial proximity of the chromophores, because of the dependence of the nonradiative energy transfer rate on the relative distance between the interacting systems (see the following). Therefore, a different packing of the polymer molecules can strongly modify the exciton migration process [23] and can give rise to blue- or red-shifted emission. The reported blue shift of the emission in the fibres compared to spin cast films is, therefore, related to the different molecular packing in the fibres compared to the films.

The continuous stretching and elongation of the polymer solution during the electrospinning process induce also an alignment of the polymer backbones along the fibre axis, with an impact on the molecular packing in the final solid-state fibres. As a consequence, nanofibre emission is mainly polarized along the fibre axis, with a polarization ratio (the ratio between the intensity of photoluminescence polarized along the fibre axis and the intensity of the emission polarized perpendicular to the fibre axis) up to 5 for MEH-PPV fibres [24].

Tunability of the emission is an important property for the exploitation of the conjugated polymer nanofibres as sub-micron, polarized light sources. The measured small emission shifts are not exploitable for emission tuning, that can be mainly achieved in the visible range by using the different conjugated polymers, so far, synthesized, having emission in the range 400–750 nm. An alternative approach is represented by the use of polymer blends as base materials. Polymeric blends are composite systems where two or more conjugated polymers are mixed with variable relative content. In these systems, energy transfer by dipole-dipole coupling (Förster transfer [22]), from the polymer with higher energy gap (donor) to the polymer with smaller energy gap (acceptor) can occur if the emission spectrum of the donor polymer overlaps with the absorption spectrum of the acceptor, and the dipoles are sufficiently close to each other. For isolated single molecules at a distance R , the Förster transfer rate, (K_{FT}), is given by [22]

$$(1) \quad K_{FT} = \frac{1}{\tau} \left(\frac{R_0}{R} \right)^6,$$

where τ is the radiative luminescence lifetime of the donor molecule and R_0 is the Förster radius, given by

$$(2) \quad R_0^6 = 0.5291 \frac{k^2 \eta_D}{n^4 N_{AV}} \int_0^\infty f_D(\tilde{\nu}) \varepsilon_A(\tilde{\nu}) \frac{d\tilde{\nu}}{\tilde{\nu}^4}.$$

In the above expression, η_D indicates the native emission efficiency of the donor molecule, n is the refractive index of the material, $N_{AV} = 6.022 \times 10^{23}$ is Avogadro's number, f_D is the normalized emission spectrum of the donor in the absence of acceptor molecules, ε_A is the molar decadic extinction coefficient of the acceptor, $\tilde{\nu}$ is the frequency wave number and k^2 is a factor related to the orientation of the donor and the acceptor dipole moments [25, 26]. For conjugated polymer blends, typical values of R_0 are of few nanometers.

For fibres made by conjugated polymers, the transfer rate has a modified expression, that takes into account the dipole interaction between different molecules distributed over the fibre volume. For fibres with diameters of hundreds of nanometers the expression of transfer rate is similar to the one obtained for thin films, predicting a Förster transfer rate proportional to the the acceptor/donor relative molar concentration (Φ) [27]. Therefore, the nanofibre emission can be tailored by using blends of polymers and simply controlling the donor/acceptor relative concentration. By this approach polymer nanofibres emitting white light have been realized by blending a blue-emitting conjugated polymer (donor) and a red-emitting one (acceptor), with an acceptor/donor molar concentration of $\Phi = 10^{-2}$ [28].

4. – Conclusions

In summary, light-emitting polymer nanofibres can be fabricated by electrospinning organic semiconductors. The conjugated polymer nanofibres display emission tunable in the visible range and emission polarized along the fibre axis. Single light-emitting nanofibres constitute novel build-blocks for microscale integrated photonics and can be used as microscale laser sources [17], as polarized light sources in lab-on-a-chip devices [29] and as active channel in field effect transistors [24]. The possibility of manipulating single polymeric fibres [30] opens the way for the assembly of complex photonic circuits where a single fibre can operate as source, waveguide and detector.

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