

ELECTROSPUN CONJUGATED POLYMER NANOFIBERS AS MINIATURIZED LIGHT SOURCES: CONTROL OF MORPHOLOGY, OPTICAL PROPERTIES AND ASSEMBLY

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ABSTRACT

Light-emitting nanostructures made by conjugated polymers show interesting emission and electronic properties. In this work we report on novel approaches for the fabrication and control of light-emitting nanofibers by electrospinning. The shape, size and light-emitting properties of the fibers can be specifically tailored by acting on the composition of the solution used for the electrospinning process, an approach allowing for obtaining fibers ranging from micrometer-sized ribbons to almost cylindrical fibers with diameters down to few hundreds of nanometers. Moreover, following proper process optimization these fibers can also be precisely positioned in ordered arrays by near-field electrospinning, a method that exploits the stable region of the polymer jet. The possibility of precisely shaping the conjugated polymer fibers and of assembling the fiber in ordered arrays, combined with enhanced emission properties, opens interesting perspectives for developing novel emitting flexible nanomaterials suitable for light sourcing and optical sensing.

Keywords: nanofibers, conjugated polymers, electrospinning, photonic properties.

1. INTRODUCTION

The study of the interaction of light with nanostructures is enabling interesting and novel applications and devices, where new paradigms concerning the propagation of light are emerging [1]. Many metallic, dielectric and polymeric nanostructures are the subject of intense experimental efforts aimed at understanding the optical properties of such sub-wavelength systems, and the behavior of light impinging on them, with interesting interplays between scattering, waveguiding, absorption and emission phenomena [2, 3]. Among these systems, polymer nanostructures are still the less frequently investigated in terms of their photonic properties, even though they can be easily realized and tailored to specific applications due the availability of a large number of both bottom-up and top-down soft nano-manufacturing approaches [4]. Indeed, many fabrication techniques allow polymer nanostructures to be synthesized with almost arbitrarily shapes and size. In particular, nanowires and nanofibers made by conjugated polymers are among the most innovative nanostructures, often featuring enhanced optical and electronic properties [5]. However, the precise assembly and the achievement of a tight control of the shape of these nanostructures, as well as the reliability and uniformity of their optical properties, which are fundamental for investigating their interaction with light, are still an issue. In fact, many difficulties in shaping polymer nanostructures in a highly controlled way, and in handling them in order to carefully determine their mutual positions, are inherently related to the soft, deformable nature of these systems.

Polymer nanofibers and nanowires can be produced in a variety of ways, such as hard and soft template-assisted methods, self-assembly, and direct writing [6, 7]. A few of these techniques offer some degree of control on the ultimately resulting shape and assembly conditions of the individual nanostructures, however the amount of synthesized nanofibers is often low, which prevents production up-scaling and consequently limits practical applications. On the other hand, electrospinning (ES) [8] is based on drawing a polymer jet by an electrostatic field, allowing polymer (including conjugated polymer) nanostructures to be produced in good amount upon proper optimization of the process parameters [9].

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The typical diameter of resulting fibers can be well within the sub- μm range, and improved active (emission, lasing) and passive optical properties (waveguiding) have been demonstrated. These features are useful for many applications, such as miniaturized photonic devices and high-performance optical sensing [10]. Even more interesting is the internal nanostructure of the fibers [11]. Indeed, such internal nanostructure can include a denser core surrounded by a less dense shell of conjugated polymer materials, and the molecular orientation in these different regions may be different, thus allowing different light polarization states and different coupling conditions to be obtained for photons and embedded chromophore units [12]. Such peculiar molecular organization is created by the complex dynamics of the ES polymer jets, and it can be exploited for realizing novel nanomaterials which combine complementary functionalities in a single nanostructure. Indeed, electrified jets generally follow a straight trajectory in their early stage, and then develops several classes of instabilities, including whipping instabilities and bending instabilities which lead to a continuous decrease of the jet diameter. These effects cause a significant stretching of embedded macromolecules, and ultimately reflect in the diameter of deposited nanofibers. Hence, while these phenomena lead to intriguing size and internal orientational properties of polymer nanofibers, they also make very hard positioning individual nanostructures with good accuracy, and controlling the overall assembly of solid fibers (mostly deposited in a random way on planar collecting surfaces). Furthermore, processing conjugated polymers by ES techniques is generally much more difficult compared to optically inert, plastic materials, due to the significantly lower degree of molecular entanglement, frequently poor solubility, etc. For all these reasons, controlling the morphology, and the assembly and optical properties of conjugated polymer nanofibers needs a careful optimization of the process conditions and of the involved solution and spinning parameters, namely the fine tailoring of the ES needle-collector distances, solution conductivity and concentration, applied voltage bias, and so on.

Here we report on the emission, uniformity and polarization properties of electrospun nanofibers and of their arrays, which are made by various species of conjugated polymers. The shape and morphology of light-emitting conjugated polymer fibers are studied by varying the ES parameters, and include both cylindrical and ribbon-like structures with generally smooth surface. Structures with size down to about 100 nm are produced, with tailored shapes. Furthermore, ordered arrays of fibers are developed by near-field electrospinning (NF-ES) [13] which enables the precise positioning of individual light-emitting nanostructures, with micrometer spatial resolution. Indeed, NF-ES is based on using a small separation distance from the extruding capillary tip and the collecting surface onto which nanofibers are deposited, thus exploiting a region of electrified jets in which instability are not yet developed and where the fluid trajectory is still straight. This allows a high positioning precision to be obtained for light-emitting nanofibers, although special care is needed to achieve sub- μm wire diameters. Also with NF-ES, we obtain fiber diameters down to 100 nm, which allows sub-wavelength, active and flexible waveguides to be produced by conjugated polymers. Indeed, NF-ES has been widely used with poly-(ethylene oxide) (PEO) [13, 14], piezoelectric materials such as poly(vinylidene fluoride) [15], and for building free-standing three-dimensional microstructures through controlled polymer solution jet coiling [16], whereas the application with light-emitting conjugated polymers is still largely unexplored. The wide application of this method to light-emitting conjugated polymers, and the future further improvement of positioning accuracy and fiber diameter control may lead to the realization of novel structures for miniaturized photonics, including organic photonic crystals based on organic nanofibers.

2. METHODS

Fibers of conjugated polymers are obtained by ES, using different solvents and concentrations [12, 17]. All the here used pristine materials are commercially available. For far-field ES, an apparatus composed by a syringe pump (Harvard Apparatus), a high voltage power supply (Gamma High Voltage Research) and a grounded or negatively-biased collector is used. Both planar surfaces and rotating disks are employed for fiber collection, to investigate the resulting polarization properties of light emitted by nanofibers. The values of typical applied voltage bias are above 10 kV. NF-ES experiments are performed by using a home-made system, that includes a syringe equipped with a 26 gauge needle and a tungsten tip with μm -diameter, a high voltage power supply (Innotec) and a grounded collector mounted on a x - y - z translation stage. Such a stage allows the light-emitting nanofibers to be deposited in specific positions. The stage translate with a controllable velocity, which is up to several tens of cm/s, and the exact architecture (i.e., coils, other bent motifs, straight lines etc.) of deposited nanofibers is strictly dependent on such velocity. Here the conjugated polymers can be blended with PEO, which favors the formation of uniform fibers due to the more advantageous viscoelastic properties of the resulting blend solution. Furthermore, a voltage bias much lower than in conventional ES is used for NF-ES (< 2 kV), which is made possible by the reduced needle-collector distance. The morphology and the light-emission properties of the resulting nanofibers, at both array and individual nanostructure-scale, are investigated by scanning electron

microscopy (SEM) and by confocal laser scanning microscopy, respectively. For confocal microscopy, we use a system composed by an inverted microscope (Eclipse Ti, Nikon) and a laser confocal scan head (A1R MP, Nikon). The samples are excited by an Ar⁺ laser ($\lambda_{exc}=488$ nm) and the intensity of the emission is measured by using a spectral detection unit equipped with a multi-anode photomultiplier (Nikon). This allows spatially-resolved spectra to be collected.

We then focus on the polarization of photoluminescence (PL), comparing different fiber production methods. The polarization properties of the electrospun, active fibers are investigated by a micro-PL set-up. The system is composed by a diode laser (excitation wavelength, $\lambda_{exc}=408$ nm) coupled to an inverted microscope (IX71, Nikon). In order to excite the PL, the laser beam is focused onto individual fibers through the microscope objective. The emission spectra are collected by exciting the fibers through a linearly polarized laser beam (spot diameter of a few tens of μm). The beam is incident onto the fiber sample, which is deposited on a quartz substrate, along the direction normal to the substrate surface. The polarization of the excitation laser beam is aligned parallel to the fiber longitudinal axis. The nanofiber PL signal is then coupled into an optical fiber and analyzed using a monochromator (Jobin Yvon, iHR320) equipped with a CCD detector (Jobin Yvon, Symphony). Suitable polarization filters are used for characterizing the polarization state of the sample emission.

3. RESULTS AND DISCUSSION

Figure 1a-c shows some examples of SEM images of electrospun fibers made by different conjugated polymer species. In all cases, good amounts of bright light-emitting nanofibers are produced, in dense mats. Fibers shown in Fig. 1a have diameters in the range of 1-3 μm , and a prevalent ribbon shape. This is mainly attributed to the used solvent, CHCl_3 , which is characterized by a fast evaporation rate. For this reason, the solvent favors the formation of a solid skin

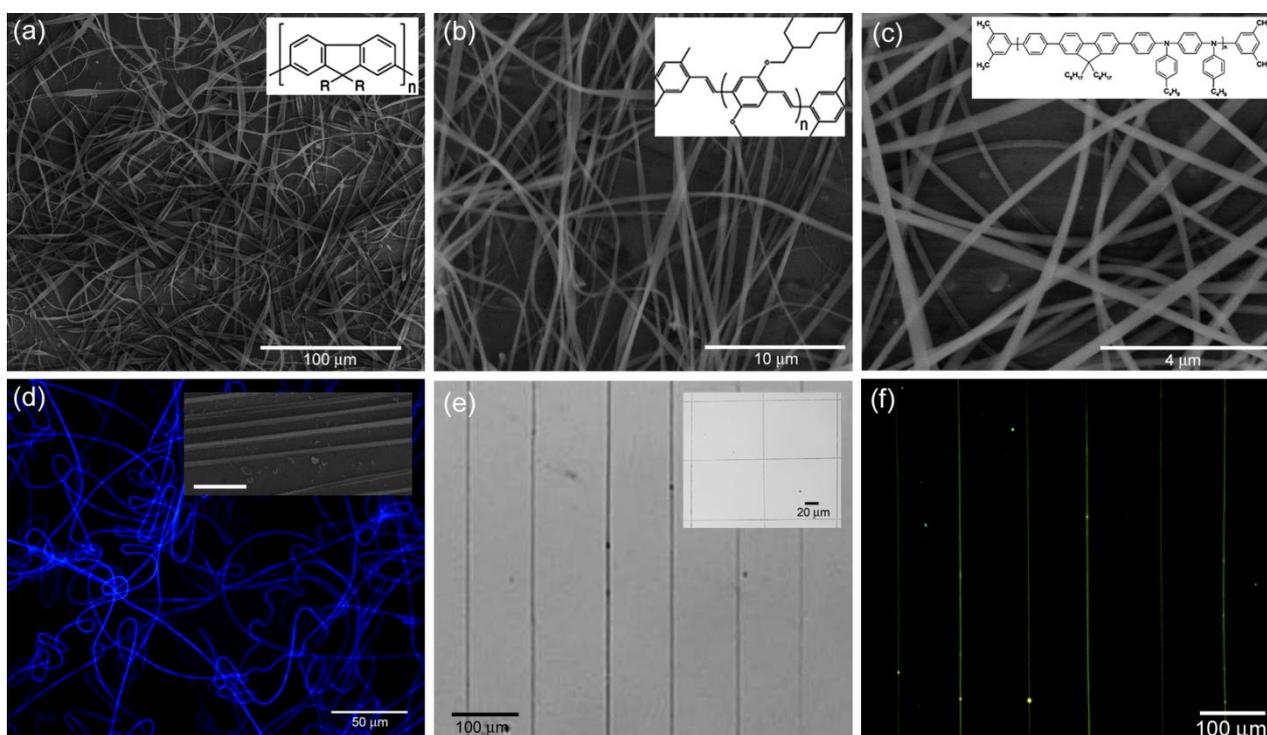


Figure 1. (a)-(c) SEM images of conjugated polymer electrospun nanofibers. Fibers are made by: (a) poly(9,9-di-*n*-octylfluorenyl-2,7-diyl), (b) poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-vinylene] (MEH-PPV) and (c) poly[(9,9-dioctylfluorenyl-2,7-diyl)-*co*-(*N,N'*-diphenyl)-*N,N'*-di(*p*-butyl-phenyl)-1,4-diamino-benzene] (PFO-PBAB). The molecular structures of the polymers are shown in the respective insets. In the inset of (a) R=CH₂(CH₂)₆CH₃. (d) Fluorescence micrograph of PFO-PBAB conjugated polymer nanofibers. Inset: SEM image of uniaxially aligned electrospun nanofibers. Scale bar: 25 μm . (e) Optical microscopy image and (f) corresponding fluorescence micrograph of an array of conjugated polymer nanofibers made by NF-ES. Inset of (e): optical micrograph of an array of crossed nanofibers.

during the polymer jet propagation, followed by a collapse of the structure after evaporation of the solvent from the inner jet [18].

Adding to the conjugated polymer solution a solvent with a slower evaporation rate (such as dimethyl sulfoxide) is found to be effective for stabilizing the electrospun jets and ultimately reducing the diameter of the fibers in the submicron range, as shown in Fig. 1b. Here, we show light-emitting electrospun fibers with average diameter of about 500 nm. In this case, the ribbon shape may still be observed, and associated to flattening and relaxation processes involving individual nanofibers and likely occurring when the jet impinges onto the collecting surface. Furthermore, the size of these polymer nanostructures can be remarkably reduced by the addition of organic salts, that increase the charge density and the elongation forces experienced by the jet during ES. This approach allows light-emitting electrospun nanofibers to be realized with size in the range 100-200 nm (Fig. 1c). The fibers display a bright emission, which is generally uniform along their length and in different regions of deposited mats, as shown in Fig. 1d. Moreover, for many nanophotonic applications, it is important to deposit the nanostructures in pre-determined patterns. For electrospun nanofibers produced in the far-field ES regime, the instabilities characterizing the jet propagation generally prevent the possibility of forming ordered structures and the fibers are typically collected as samples of randomly oriented objects (Fig.s 1a-c). Arrays of uniaxially-oriented active nanofibers can be realized by using a rotating collector (inset of Fig. 1d), but without careful control on the position of each individual nanostructure. Instead, samples made of precisely positioned, parallel or perpendicular fluorescent fibers, can be realized by NF-ES (Fig.s 1e-f). Fig. 1e and 1f show parallel light-emitted fibers with a regular spacing of about 100 μm , whereas the inset in the figure displays a geometry with crossed fibers. This approach, exploiting the stable region of the ES jet as mentioned above, is therefore highly versatile and allows arrays of polymer nanofibers with almost arbitrarily patterns to be realized. The linear density of beads or defects of light-emitting nanofibers produced in this way is below 10^4 m^{-1} . Hence, the photonic properties of light-emitting fibers made of conjugated polymers and precisely organized at super-nanostructure scale can be investigated.

Although electrospun conjugated polymer fibers are usually quite uniform along their length as stated above, minor dishomogeneities and defects may be present due to the complex configurational dynamics of macromolecules in electrified jets [11, 12], to possible axisymmetric instabilities of the jets, etc., and to the consequent, different aggregation states of the same molecules in the solid-state. These dishomogeneities may impact on optical properties, and especially on PL spectral features. For instance, Figure 2 shows typical emission properties of MEH-PPV nanofibers, investigated by confocal microscopy and spectroscopy. In particular, we collect the emission spectra from different regions of the sample, in order to assess the uniformity of the emission throughout the produced fibers. The size of each excited region is of the order of $5 \times 5 \mu\text{m}^2$. The resulting spatially-resolved spectra highlight minor differences among the spectra collected from the different regions (Fig. 2b), with a variation of the order of 10% of the intensity ratio between the highest energy vibronic replica (at about 585 nm) and the vibronic replica at 635 nm. This is in turn

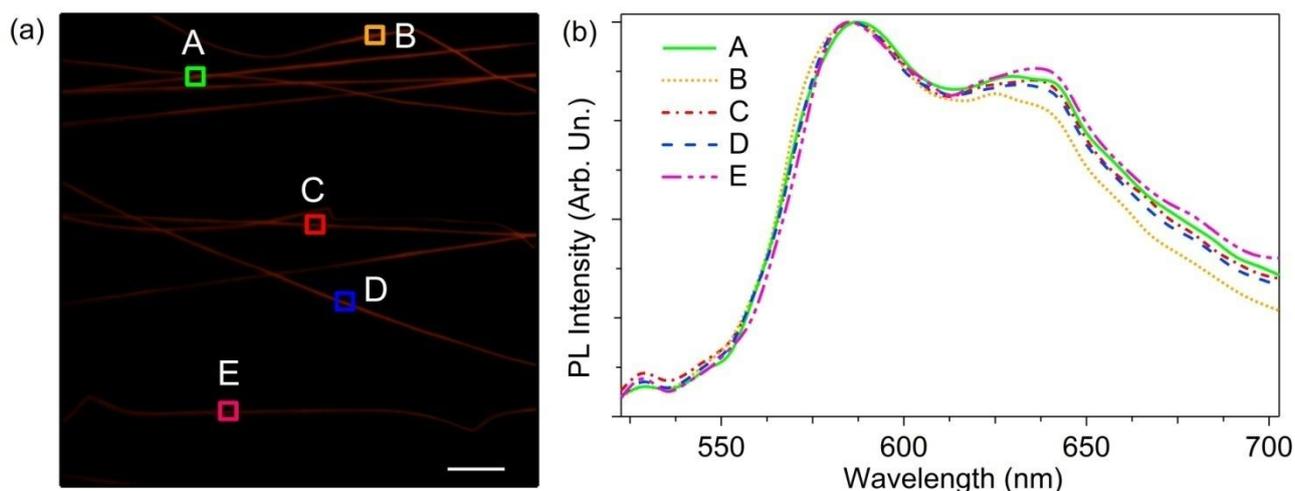


Figure 2. (a) Confocal fluorescence image of MEH-PPV fibers, produced by far-field ES. Scale bar: 20 μm . (b) Spatially-resolved PL spectra, acquired in different regions of the nanofiber sample. The displayed spectra are collected in the regions labeled as A, B, C, D, E, respectively, in the fluorescence micrograph (a). Each emission spectrum is normalized to its maximum value.

reflected in slight different of the full width at half maximum of the emission spectra. The observed variation of the vibronic structure is indicative of small local differences in the formation of interchain species, aggregates and packing of the MEH-PPV macromolecules, which is known to affect the shape of the emission spectra [19].

We also investigate the polarization properties of the nanofibers PL. Figure 3 shows typical PL spectra from MEH-PPV electrospun nanofibers, evidencing emission polarized mainly along the fiber longitudinal axis. This occurs as a consequence of the orientation of the conjugated polymer macromolecules along the fiber axis, induced by the high stretching of the solution jet during the ES process [20]. The degree of the PL polarization depends on many factors related both to the solution properties (concentration and used solvents) and to other ES variables such as the applied electric field, the flow rate and the fiber collecting system (i.e. static, or rotating collector). For conjugated polymers we find that the solvent quality and the solution concentration may significantly affect the resulting polarization properties of the emission. In particular, reducing the solution concentration generally leads to an improvement of the polarization degree of the emission. Figure 4 shows the spectral features of the polarization ratio, which is defined as follows:

$$R_{PL} = I_{//} / I_{\perp} \quad (1)$$

where $I_{//}$ and I_{\perp} are the intensities of the emission with polarization parallel and perpendicular to the fiber axis, respectively.

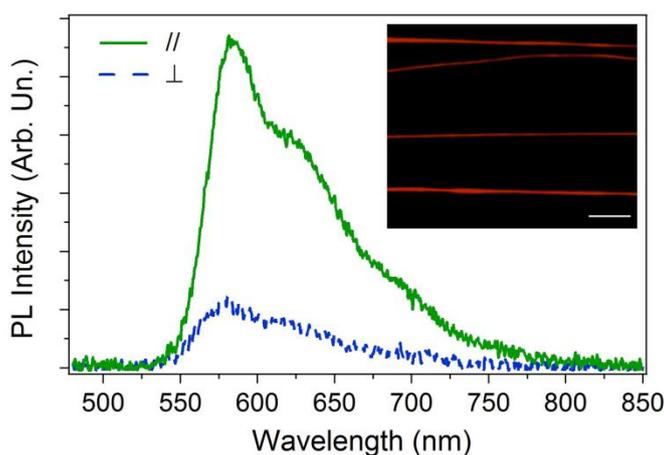


Figure 3. PL spectra of MEH-PPV electrospun nanofibers with emission polarization parallel (green continuous line) and perpendicular (blue dashed line) to the fiber axis. Inset: Confocal fluorescence image of a region of an array of MEH-PPV uniaxially aligned fibers, used for the emission polarization analysis. Scale bar: 20 μm .

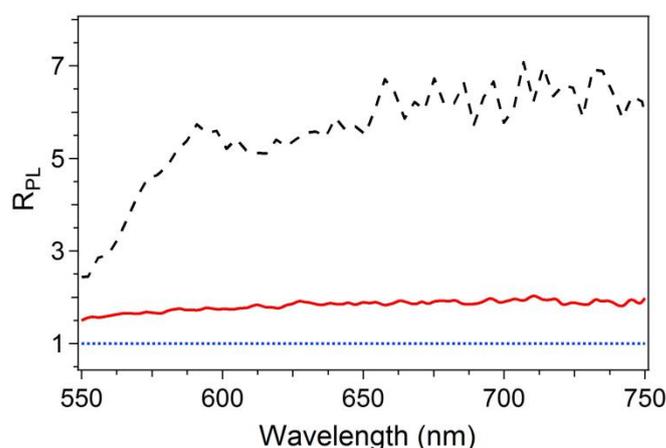


Figure 4. Wavelength dependence of the PL polarization ratio, R_{PL} , for MEH-PPV fibers obtained by a far-field ES system (black, dashed line) and by the NF-ES method (red, continuous line). The horizontal dotted line highlights the reference unity value corresponding to unpolarized emission.

In Fig. 4, R_{PL} is displayed for MEH-PPV fibers realized by using either a standard, far-field ES system (black dashed line) or the developed NF-ES set-up (red continuous line), respectively. R_{PL} reaches values up to 7 for fibers spun onto a rotating collector (with angular velocity of 4000 rpm) in far-field ES, whereas lower values (around 2) are obtained by NF-ES. Here, the effects which may limit the alignment of the conjugated polymer macromolecules are related to phase separation occurring between the PEO matrix and the active MEH-PPV polymer, as observed in similar systems [21], to the use of poor solvents, which are known to disfavor conjugated polymer chain alignment compared to good solvents [22], and to the generally reduced molecular stretching in NF-ES.

4. CONCLUSIONS

In summary, individual fibers and macroscopic arrays of light-emitting, conjugated polymer nanofibers have been produced, and characterized by means of complementary ES technologies. The experimental approaches here developed for various active materials allow the individual nanofiber shape and size to be controlled, as well as the geometry of the resulting macroscopic assembly to be tailored. A good uniformity is obtained for emission spectral properties along the fiber length, and from different regions of deposited mats. In particular, the resulting polarization properties of light emitted from nanofibers is found to depend significantly on the production process. These polymer nanostructures are useful for investigating light propagation and diffusion in both individual nanostructures and macroscopic samples with variable geometries and morphology. Future applications will include nanofiber-based organic photonic crystal structures and optical sensors.

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