EMISSION PROPERTIES OF CONJUGATED POLYMERS AND NANOCOMPOSITE LIGHT-EMITTING NANOFIBERS

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Introduction

One dimensional (1D) polymer or nanocomposite nanostructures, such as elongated organic nanoparticles, nanowires and nanofibers, are attracting an increasing interest for many applications including nanophotonics, being strategic for the realization of sub-wavelength optical components. Upon nanofiber production, these elements can be effectively embedded in optoelectronic architectures, including field-effect transistors relying on 1D semiconductor channels, and nanophotonic circuits for generating, guiding and amplifying light.

In this framework, flexible, organic fibers, made by conjugated polymers, polymer blends, or incorporating other light-emitting molecules or active nanoparticles, are particularly appealing. These nanofibers show excellent emission properties in the visible and near infrared range, waveguiding characteristics, and potential for light amplification with the typical gain coefficients of light-emitting organic semiconductors. Polymer nanofibers can be fabricated by different approaches, including soft lithographies and polymerization methods, however the electrospinning is currently the unique technology with low cost and high throughput for producing these nanostructures [1].

A remarkable chemical flexibility is given by the fact that the addition of active components (i.e. nanoparticles or specific molecular species) to the electrospinning polymer solution allows one to obtain composite nanofibers with specific functionalities, such as photochromic behaviour, enhanced mechanical strength, improved biocompatibility, emission colour tunability. Electrospun nanofibers can also be assembled in ordered structures, tubular membranes, and aligned arrays. Here we report on the emission properties, including waveguiding and optical gain, of light-emitting nanofibers [2-6] fabricated by electrospinning of conjugated polymers and low-molar-mass molecules embedded in thermoplastic matrices, and discuss the wide potential applications of these novel materials for nanophotonic elements and optical circuits.

Experimental

Materials. We prepare our conjugated polymer-based and nanocomposites nanofibers by blending several light-emitting conjugated polymers and by embedding low-molar mass dye molecules into optically inert thermoplastic matrices such as poly(methylmethacrylate). The conjugated polymers, such as the poly[9,9-dioctylfluorenyl-2,7-diyl)-co-1,4-benzo-{2,1'-3}-thiadiazole)] and the poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) are purchased by American Dye Source (Canada), whereas the dye dopants, such as Coumarin, Rhodamine, Nile Blue A Perchlorate, and 2-(8-(4-p-Dimetyhlaminophenyl)-2,4-neopentylene-1,3,5,7-octatetraenyl)-3-methylbenzothiazolium Perchlorate, are purchased by Sigma-Aldrich. All the molecules are dissolved in 10^{-5}-10^{-3} M chloroform solutions.

Electrospinning. Our electrospinning set-up for the fabrication of light-emitting nanofibers is made by a syringe, a spinneret (a 18-23 gauge stainless steel needle), a high voltage power supply (10-30 kV), and a grounded aluminium foil used as collector (~10×10 cm^2). The collectors is mounted on an isolating stand at a variable distance from the needle (5-30 cm). The electrospinning experiments are carried out at room temperature, with air humidity between 30 and 50%.

Morphological and optical characterization. The morphological characterization of the nanofibers surfaces is carried out by tapping-mode atomic force microscopy in air, by using a Nanoscope III controller with a Digital Instruments Multimode head, and by scanning electron microscopy (SEM) by means of a Raith 150 electron beam system operating with an acceleration voltage in the range 5-20 kV and an aperture size of 20-30 μm. Furthermore, photoluminescence (PL) of the nanofibers is collected by depositing the fibers on quartz substrates, then exciting by a cw diode laser (405 nm) and collecting the spectra by a fiber-coupled monochromator and a CCD camera.

Results and discussion

Our electrospun nanofibers, made by conjugated and dye-doped polymers, exhibit diameter from a few hundreds down to a few tens of nm, depending on the electrospinning parameters (applied bias, solution concentration, injection rate, etc.). A non-woven mat of light-emitting fibers, imaged by scanning electron microscopy (SEM), is shown in Fig. 1. Furthermore, the fiber are found to exhibit a bright PL emission in the visible, from blue to red including white light, and in the near-infrared spectral range depending on the employed active material. In fact, the optical properties of the realized nanofibers can be controlled by employing calibrated blends of active polymers, exploiting the inter-species non-radiative energy transfer from a high-energy donor (*D*) to a low-energy acceptor compound (*A*). For a single donor-acceptor pair, the intermolecular $D \rightarrow A$ energy transfer rate, *K*, is given by:

$$K = \frac{1}{\tau_H}\frac{1}{R^6}\frac{3}{4\pi}\int \frac{c^4}{\omega^4 n^4} F_H(\omega)\sigma_D(\omega)d\omega = \frac{1}{\tau_H}\left(\frac{R_0}{R}\right)^6$$

where *n* is the refractive index, τ_H indicates the characteristic time of spontaneous emission from the host material, and R_0 is the Förster characteristic radius mainly determined by the spectral overlap between the donor emission spectrum, F_H, and the acceptor absorption, σ_D. In the fibers, the exact transfer rate depends on the distributions of *D* and *A* species inside the blends.

Fig. 2 displays a fluorescence micrograph of a red-emitting fiber (peak wavelength ≅ 660 nm, linewidth ≅ 110 nm), which shows uniform PL signal, thus indicating a homogeneous presence of chromophores along the fiber body.

Self-waveguiding of the PL is also found in the nanofibers, assisted by the higher refractive index (1-5-1.7) of the employed polymers with respect to the surrounding media. Typical optical loss

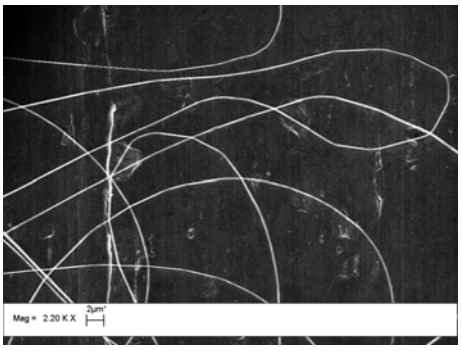

Fig. 1 SEM micrograph of infrared light-emitting nanofibers, as collected after electrospinning.

Fig. 2 Fluorescence image of fiber made by a red-emitting polymer. Fiber diameter ≅ 1 μm.

coefficients are down to the order of 10^{-1} cm^{-1}. We also find that fiber show good properties of optical gain under ns-pulsed optical excitation, and that individual fibers can operate as optical cavities, emitting laser light at visible wavelengths. Lasing performances achieved so far are of a few Å for linewidth above threshold (~ tens of μJ cm^{-2}).

Conclusions

We realize light-emitting nanofibers by electrospinning of conjugated polymers, blends, and dyes embedded in optically inert matrices. The fibers exhibit PL in the whole visible, and in the near-infrared, with emission and morphology depending on the active materials and processing parameters. These results are promising in view of the application to nanophotonics, including lasers, active waveguides, and devices relying on eventual electroluminescence properties, such as nano-scale light-emitting diodes and transistors.

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