1.3.29 Complex networks of organic nanowires: from coherent light emission to energy harvesting and biophysics

Organic nanowires are emerging as novel building blocks for photonic devices, energy nanogeneretors and smart substrates that can provide specific biophysical cues and direct stem-cell fate. We have investigated the properties of composite organic wires and filaments embedding various species of chromophores, including self-assembling rotaxane-type molecular systems, piezo-polymers and 2-dimensional materials. These composite materials are relevant for applications in optical amplifiers, lasers, chemical sensors, energy harvesting and tissue engineering.

Electrospinning is based on electrified jets of polymer solutions, which have to exhibit significant molecular entanglements, and it is nowadays the most promising method for producing organic nanofibers and nanowires due to its operational simplicity, low cost, and chemical versatility. Solutions are accelerated concomitantly to solvent evaporation, to deposit nanofiber-based coatings on solid surfaces, or to realize free-standing membranes. Active polymer nanofibers and nanowires, in the form of individual nanostructures or complex networks realized by such approach, exhibit better performances compared to conventional film-based materials and coatings [1]. Electrospinning is being developed in our group in order to realize new, active nanofibrous materials with applications in different scientific fields and technologies.

Figure 1a-d show an example of stimuli-responsive nanowires, realized by embedding a molecular motor in a polymer matrix [2]. Exposure to base and acid vapors induced the dethreading and rethreading of the molecular components in the solid wires (Fig. 1c-d). The light-induced photo-isomerization of the azobenzene molecules was also demonstrated in solid wires, making such composite systems responsive to both optical and chemical external stimuli. Interestingly, the dethreading of the axles from the rings enhanced significantly the Young's modulus of arrays made of aligned wires. These findings demonstrate the possibility of tailoring the macroscopic properties of such composite materials, by controlling the behavior of the molecular constituents at the nanoscale.

Another example of optically-active nanowires developed in our group is shown Fig. 1e-g, where near-infrared (NIR) emitting organic wires were realized by embedding light-emitting molecules in polymer fibers, obtaining optical gain up to 5 cm^{-1} [3]. The gain properties of macroscopic arrays made by many filaments can be tailored by controlling their assembly and mutual alignment. Recently, hybrid fibers and planar networks of polymer fibers with optical gain were realized which displayed lasing modes tailored by the topology of the fiber network [4-5].

The combination of electrospinning with nanopatterning technologies allows the generation of optically-pumped solid-state lasers, based on individual light-emitting nanofibers, which are textured by nanoimprint lithography [6]. Single-fiber distributed feedback lasers can be realized by Bragg gratings (with 400 nm - 600 nm period), imprinted directly onto the active nanowires. These devices show a threshold excitation fluence (750 μJ cm^{-2}) reduced by 40–50% with respect to nanopatterned, thin-film lasers made of the same molecular material, due to the higher field confinement which leads to correspondingly higher photonic density inside the active filaments (Fig. 2b) [6].

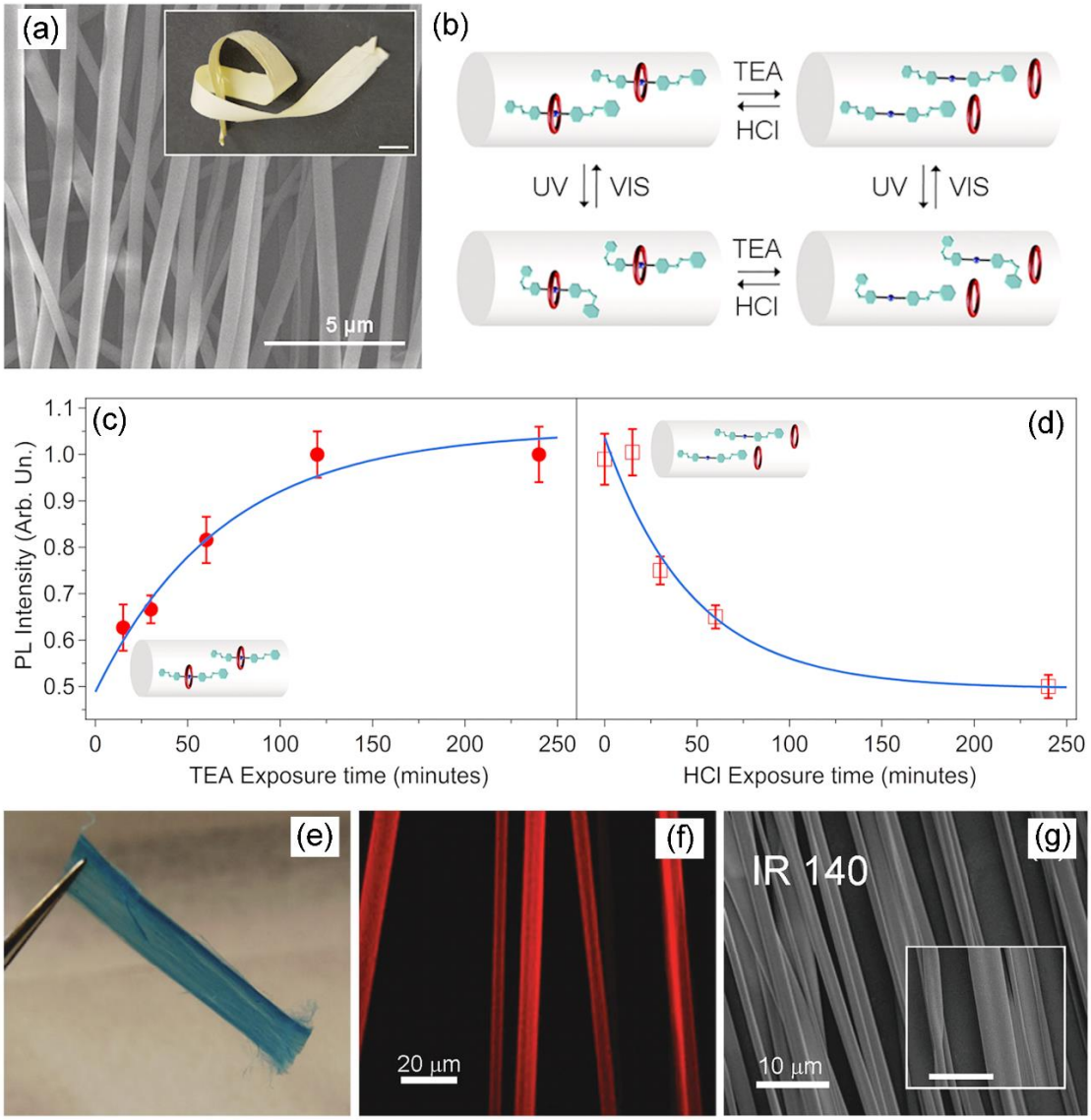

Figure 1. (a) SEM micrographs of polymer filaments doped with rotaxane-type molecular systems. Inset: photograph of an array made of such wires. Scale bar = 1 cm. (b) Schematics of the photo-isomerization processes of the azobenzene end-units of the axle and of the chemically-induced dethreading/rethreading processes of the axle and ring molecular components. Photo-isomerization processes occur upon exposure to ultraviolet (UV) and visible (Vis) light, whereas the dethreading/rethreading processes are induced by exposure to base/acid vapors (triethylamine, TEA, and HCl, respectively). (c)-(d) Photoluminescence (PL) intensity of polymer nanowires doped with molecular motors vs. base (c) and acid (d) vapors exposure times. These data evidence the reversible dethreading/rethreading processes that the axle and ring molecular components undergo inside polymer wires, upon chemical stimulation. Adapted from Ref. [2]. © 2014 American Chemical Society. (e) Photograph and (f) fluorescence confocal micrograph of an array of polymer wires doped with a NIR-emitting dye. (g) Scanning electron microscopy (SEM) images of polymer wires doped with a NIR-emitting dye. Inset scale bar = 10 µm. Adapted with permission from [3]. Copyright © 2014 WILEY-VCH Verlag GmbH & Co.

Analogously, electrospun piezoelectric nanofibers outperform thin films, in terms of self-poling capability and conformability to many surfaces. Aligned arrays of these nanofibers (Fig. 2c, d) in mutual contact exhibit improved voltage output due to electromechanical coupling of multiple filaments, together with large areas (up to tens of cm^2) and light weight, and they can be repeatedly bent and twisted

without fracture [7]. These features make functional polymer nanofibers very appealing for application in the fields of nanogenerators, self-powered systems, including implantable bioelectronics, smart wearables and body sensor networks, and ambient-assisted living.

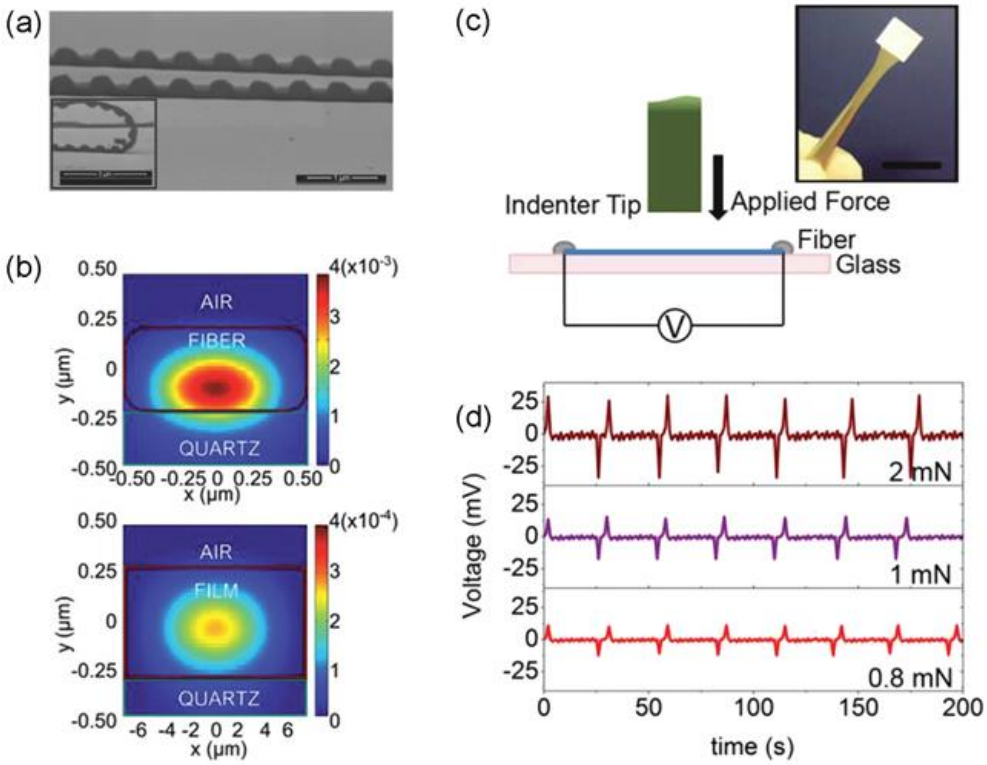

Figure 2. (a) Scanning electron micrograph of nanopatterned polymer fibers for lasing. Inset: bent patterned fibers. (b) Modeling of light propagating in the distributed feedback lasers. The maps show the normalized, real part of the Poynting vector component along the sample in-plane, longitudinal direction, calculated on a cross-section of a patterned fiber (top) and film (bottom), respectively. For the fiber, fields are much more confined in the transversal direction (see the different horizontal scales for the two maps). The fundamental transverse electric (TE) is calculated by Finite-Difference Time-Domain (FDTD) simulations. Adapted with permission from [6]. Copyright © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Scheme of a developed set-up for force-indentation measurements on piezoelectric electrospun nanofibers (photograph in the inset). (d) Measured output voltages under various, repeatedly applied stresses. Adapted with permission from [7]. Copyright © 2014 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Organic nanowire and their networks can be also specifically functionalized for realizing novel classes of smart substrates able to provide specific biophysical cues and direct the stem cell fate [8-9]. We developed a hybrid approach in which polymer nanofibers of polycaprolactone (PCL) realized by electrospinning are surface functionalized with graphene oxide (GO) by means of a layer-by-layer method schematized in Fig. 3a.

Fibrous scaffolds are particularly interesting for tissue engineering applications, as their nanofilaments structurally mimic the hierarchical organization of the natural extracellular matrix. We realized four types of PCL scaffolds: fibers with random and aligned orientation functionalized with GO and fibers with random and aligned orientation which undergo the same layer-by-layer processing except for the treatment with GO (Fig. 3b and 3c respectively). The employed method

guarantees uniform and homogeneous GO adsorption on the fiber surface, and the overall functionalization significantly affect the surface wettability by increasing the hydrophilicity of PCL. Such effect is fundamental for an efficient cell–substrate interaction.

Finally, we cultured primary neurospheres from DPSCs on the fibrous surfaces and assessed the substrates biocompatibility thus revealing no remarkable cytotoxic effects. In addition, the fiber orientation was found to influence the cell morphology through a cytoskeletal reorganization and a superior cell elongation on aligned fibers scaffolds when compared to the random oriented ones. Through the evaluation of the expression of several differentiation markers, we found that the different scaffolds selectively direct the fate of neurospheres toward four different lineages, such as osteoblastic, glial, fibroblastic, and neuronal as schematized in Fig. 3d. The confocal imaging of specific markers confirms these findings (Fig. 3e). Overall, the combination of wetting properties, protein adsorption capacity and effects on cell morphology of the substrate is able to specifically directs the cell commitment without the use of exogenous factors thus unveiling new potentialities for cellular programming.

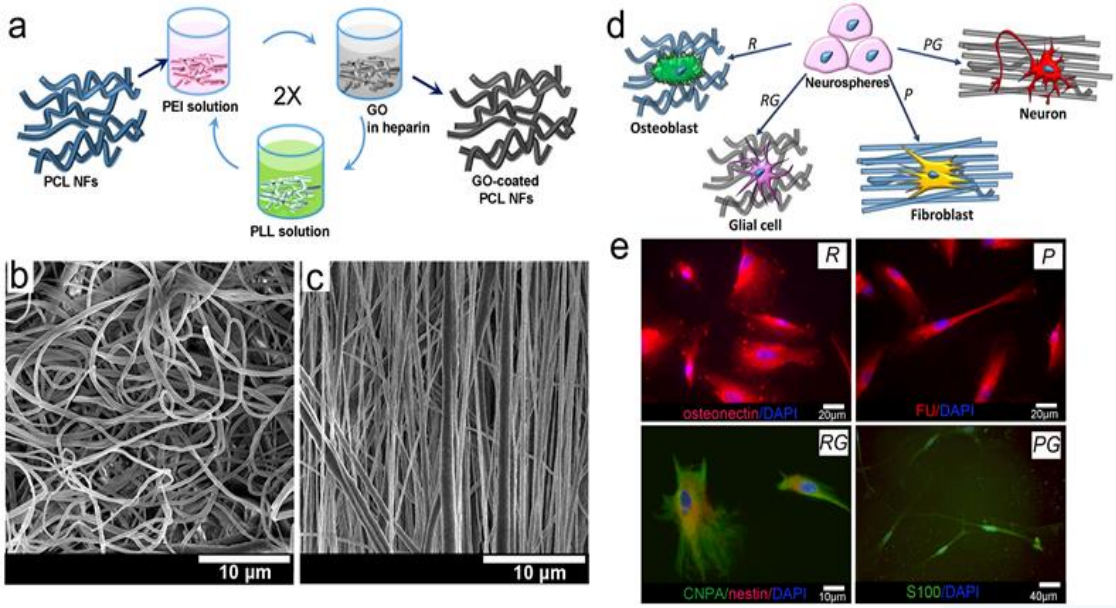

Figure 3. (a) Schematics of the stepwise coating of nanofibers by GO. Briefly, the surface of the scaffolds was activated by soaking in polyethyleneimine dissolved in PBS, then fibers were immersed into heparin with GO, followed by soaking in poly-l-lysine. After every step, fibers were washed in PBS. The immersion, washing, and soaking steps were repeated two times. (b,c) SEM images of random (b) and aligned (c) fibers. (d) Schematics of the different cell commitment: neurospheres from DPSCs show a differentiation propensity for osteoblastic, glial, fibroblastic, and neuronal cells on random fibers (R), random GO-coated fibers (RG), uniaxially aligned fibers (P) and uniaxially aligned GO-coated fibers (PG), respectively. (e) Immunofluorescence staining against osteonectin (red)/DAPI (blue), CNPase (green)/nestin (red)/DAPI (blue), FU (red)/DAPI (blue), and S100 (green)/DAPI (blue) respectively on neurosphere grown on substrate R, RG, P, and PG fibers. Adapted with permission from [9]. Copyright © 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

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