From electrified jets to light-emitting polymer nanofibers: 2016 Results from the NANO-JETS ERC Project

V. Resta,[1] V. Fasano,[1] M. Moffa,[2] G. Morello,[1] M. Montinaro,[1] A. Portone,[1] L. Romano,[1] M. Lauricella,[3] S. Succi,[3] A. Camposeo,[2] L. Persano,[2] and D. Pisignano[1,2]

[1]Dipartimento di Matematica e Fisica "Ennio De Giorgi", Università del Salento, Lecce - Italy

[2]NEST, Istituto Nanoscienze-CNR, Pisa - Italy

[3]CNR-Istituto per le Applicazioni del Calcolo "Mauro Picone", Rome - Italy

Disordered and non-woven networks of one-dimensional nanostructures (nanofibers) are enabling new applications in energy, structural, environmental, and bioengineering, such as sensors, transducers, and energy harvesters, due to their unique anisotropic properties. Electrospinning has been widely recognized as one of the most simple, quick, and inexpensive technologies to fabricate ultrafine polymeric fibers, including light-emitting and lasing nanofibers [1]. This technique allows one to manufacture nanofibers from a variety of materials, such as plastics, copolymers, and biopolymers. The used polymer solution is extruded by electrostatic fields and the produced filaments are collected on a metal plate as non-woven mats, or on rotating collectors as arrays of uniaxially aligned fibers. The resulting morphology of the deposited fibers can be controlled to reach diameters down to few tens of nm, through the chemical, geometrical, and electrical parameters of the process. The activities of the ERC NANO-JETS project (grant agreement 306357, www.nanojets.eu) during 2016 continued to produce new and unconventional classes of functional nanofibers with a focus on optics and photonics. Experimental research is currently spreading through Lecce (Department of Mathematics and Physics 'Ennio De Giorgi' at the University of Salento) and Pisa (CNR-Istituto Nanoscienze at NEST, Scuola Normale Superiore), with modelling performed at CNR-IAC in Rome.

The set of studied materials included poly(methyl methacrylate) (PMMA) decorated with gold nanorods [2], polyphenylenevinylene derivatives (MEH-PPV) [3], PMMA doped either with CdSeTe quantum dots (QDs) [4], or CdSe QDs or TiO2 nanoparticles [5], rhodamine 590 Chloride-doped poly(vinylpyrrolidone) (PVP), poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) and MEH-PPV/PVP [6], polystyrene doped with mechanically interlocked derivatives of

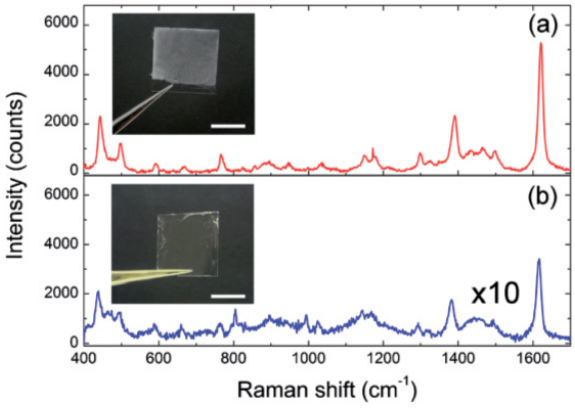

Figure 1. Raman spectra of methyl blue cast on a layer of PMMA nanofibers (a) and on a spin-coated PMMA film (b). The spectrum in b is multiplied by a factor 10 for better visualization. The spectra are collected by an integration time of 30 s. Fluorescence background has been subtracted. Insets: corresponding sample photographs. Scale bars: 1 cm. Reproduced from Analytical and Bioanalytical Chemistry, 408 (2016) 1357-1364. DOI: 10.1007/s00216-015-9226-9. © 2015 Springer-Verlag Berlin Heidelberg.

single walled carbon nanotubes [7], and poly(vinylidenefluoride-*co*-trifluoroethylene) [8].

The effects of controlled gas flows on electrified jets with different conditions of air drag force were numerically analyzed aiming to improve the quality of the electrospinning products in terms of diameter dispersion [9]. The model, focusing on the bending instabilities onset of the jet, showed that a controlled gas counterflow allows a reduction of the average diameter of electrospun fibers. A refined description of the jet was obtained by an algorithm based on a uniform arc-length discretization of a fluid jet at constant time interval [10].

New applications have been proposed by functionalizing PMMA nanofibers with Au nanorods (NRs) for sensing based on surface enhanced Ra-

man scattering (SERS) [2]. The Raman spectra of methyl blue, used as molecular probe, were enhanced by about one order of magnitude compared to spin-cast films, especially due the increase of the surface area and light-scattering of the nanofiber arrays, as shown in Figure 1. Embedding individual quantum emitters in nanofibers improved the coupling efficiency of emitted single photons to waveguide modes, a possible key feature for future platforms for nanoscale quantum optics [4]. A quantum yield enhancement up to a factor of 2.5, with respect to free space, is expected when such a structure is further coupled to a metallic nanoparticle due to the additional plasmonic field enhancement [11]. Electrospinning was evidenced as a mean of forcing a preferred orientation of molecules with 3-dimensional nanocrystalline order, as opposed to films, which resulted in a 5-fold enhancement of the photoluminescence (PL) quantum yield of MEH-PPV and preferentially directed excitation toward chromophores oriented along the fiber axis. These aspects were studied by steady state and femtosecond time-resolved polarized spectroscopies, in view of enhancing performances of light harvesting architectures [3]. Figure 2 shows differences found for films and for fibers with relatively lower molecular order (LMO) and higher molecular order (HMO). Finally, new architectures were designed for single-fiber piezoelectric sensors based on suspended and higlhy flexible nanostructures [8], and for reinforced nanocomposites exhibiting Young's modulus and tensile strength improved by up to 200 per cent [7].

The results of the NANO-JETS project have been extensively disseminated through lectures, invited seminars, talks at national and international conferences, including, among others, Photonics West (SPIE), the 14th International Conference on Frontiers of Polymers and Advanced Materials, the Annual Nanophotonics International Conference of the Photonics and Bionanotechnology Association, and the International Conference of Electrospinning organized by the NANO-JETS team in Otranto. The list of the publications summarizing the 2016 research goals is shown below. The NANO-JETS network of collaborations was further strenghtened through other CNR Institutes (Institute of Chemical-Physics Processes, Institute of Cristallography), the Universities of Princeton, Illinois, Harvard, Northwestern, Harbin Engineering, King's College London, Italian Institute of Technology, IMDEA Nanoscience, Massachusetts Institute of Technology. In compliance with the European Union guidelines and with the ERC grant agreement, all the project foreground publications are

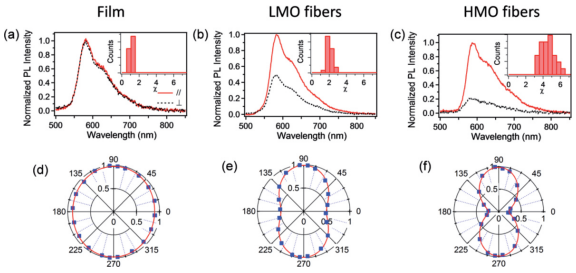

Figure 2. (a) PL spectral components of MEH-PPV films polarized either parallel with (red continuous lines) or perpendicular to (black dashed lines) the excitation laser polarization. (bc) PL spectra of MEH-PPV fibers polarized either parallel with (red continuous lines) or perpendicular to (black dashed lines) the fiber longitudinal axis. The insets show the distributions of the nanofiber polarization ratio, χ, obtained by measuring several individual MEH-PPV nanofibers, or different regions of the film. (df) Plot of the sample emission intensity vs the angle between the fiber and the polarization axis of the collection filter. The emission intensity maximum corresponds to the axis of polarization filter parallel with fiber length. Continuous lines are fits to the data by a cos^2 law. (a and d): films; (b and e) LMO fibers; (c and f) HMO fibers. Reproduced from Journal of the American Chemical Society, 138 (2016) 15497-15505. DOI: 10.1021/jacs.6b10761. © 2016 American Chemical Society.

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