From electrified jets to light-emitting polymer nanofibers: 2015 Results from the NANO-JETS ERC Project

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Developing the capability of electrospinning technologies in making nanofibers out of a large variety of compounds, including plastics, copolymers, biopolymers, and composites, is highly relevant to produce novel photonic materials [1]. Through this approach, solutions with significant presence of molecular entanglements are extruded by means of electrostatic fields, and micro- or nanofibers are collected on a metal plate as nonwoven mats, or on rotating collectors as uniaxially aligned arrays. The fiber morphology and diameter can be finely tailored, but this will need a tight control on the process parameters as well as an in-depth understanding of the multi-physics underneath (electrostatics, fluid dynamics, solvent evaporation kinetics, surface tension, etc.), which in turn may lead to the development of effective simulation tools for electrified jets. In 2015, the ERC NANO-JETS project (grant agreement 306357, http://www.nanojets.eu/) has been focused on the advanced analysis of the electrospinning fabrication procedures and parameters, through high-speed imaging and extensive simulation efforts, and on the design, realization and characterization of new photonic materials and systems based on the resulting light-emitting nanofibers.

Processed polymers included dye-doped poly(methyl methacrylate) [2,3] and polyacrylonitrile [4], polylactic acid [5], polyvinylidene-fluoride [6], polyvinyl-pyrrolidone (PVP) [7], and conjugated compounds such as poly[(9,9-dioctyl-fluorenyl-2,7-diyl)-alt-co-(1,4-benzo-[2,1',3]-thiadiazole)] and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] [8]. The effects of dissipative air drag in the initial stage of the process were analyzed and a numerical model was proposed to probe the dynamics of the electrified jets at different conditions of air drag force [9,10]. An open-source software, JETSPIN, was developed and made publicly available (GitHub repository, https://github.com/nanojets/jetspin/), allowing the electrospinning process to be simulated and possibly exploiting different computational architectures, ranging from single to parallel processor workstations [11]. In parallel, important contributions to the fundamental knowledge of the behavior of electrified jets were made possible collecting micrographs at 10,000 frames per second, which allowed the propagation velocity of instabilities and the jet angular fluctuations to be analyzed in depth (Fig. 1) [7]. This analysis can lead to finely controllable bending and solution stretching, and consequently to better designed fiber morphologies and structures. The

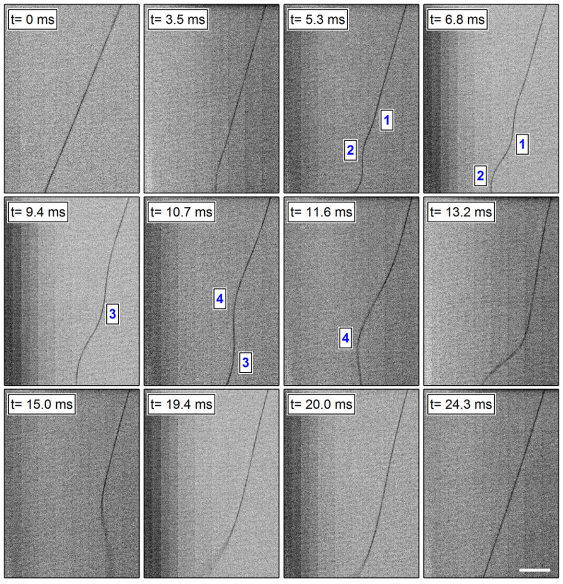

Figure 1. Photograph sequence of a typical instability cycle during electrospinning of a PVP solution. Numbers indicate the temporal evolution of each coil. Scale bar = 2 mm. Reproduced from Soft Matter, 2015, 11, 3424-31. DOI: 10.1039/c4sm02708f.

electrospinning of active organic materials was significantly improved by implementing the process in a controlled nitrogen atmosphere, which leads to the achievement of higher emission quantum yields of the resulting nanofibers due to the reduced incorporation of oxygen, as well as to significantly reduced optical losses along the fiber longitudinal axis due to the higher surface uniformity of filaments [8].

Applications in the field of photonics are numerous. A near-infrared polymer fiber amplifier with a working band of about 20 nm was obtained, showing amplified spontaneous emission with good gain coefficients and low levels of optical losses (a few cm^{-1}), suitable to be coupled with conventional fiber optics (Fig. 2) [2]. Also, ultraviolet light-emitting nanofibers were realized, which show optical gain and greatly enhanced anisotropic hydrophobicity compared to films [3]. The wetting behavior of these nanomaterials can be described by the onset of a composite state, in which directional fluid flow is enabled by arranging fibers in uniaxially aligned arrays. These features make these systems very well suited as excitation sources to be coupled with microfluidic devices, since the hydrophobic character reducing interfacial interactions with liquids can promote the occurrence of stable optical gain. Metal-enhanced fluorescence mechanisms enabled by Au nanocages were exploited to achieve a maximum enhancement up to 2-7 times with respect to the emission from pristine dyes embedded in electrospun nanofibers (at wavelengths 660-740 nm) [4]. Finally, the embedment of fluorescent capsules in electrospun polymers was explored as route to obtain ratiometric organic fibers for highly localized and reversible pH sensing based on proton-induced switching and on effective diffusional kinetic coupling between the sensing regions and the polymer matrix [5]. Due to their versatility and structural flexibility, these systems might enable a promising and robust platform for clinical diagnostics and for environmental sciences.

The results of the NANO-JETS project have been extensively disseminated through lectures, invited seminars, talks at national and international conferences, including, among others, the Discrete Simulation on Fluid Dynamics Conference, E-MRS, the Body Sensor Networks Conference, etc. The list of the publications generated by the project in 2015 is reported below. The NANO-JETS network of collaborations has been further widened with joint papers involving scientists at GeorgiaTech, at the Chinese Academy of Sciences, and at the Universities of Braunschweig, Chongqing, and Vienna. In compliance with the European Union guidelines and with the ERC grant agreement, all the project foreground publications are open-access online. Full versions of publications can be retrieved at the publishers websites, or in institutional repositories.

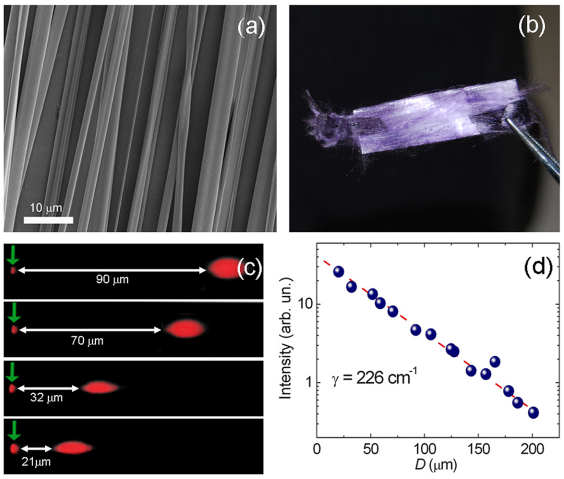

Figure 2. Scanning electron micrograph (a) and photograph (b) of near infrared light-emitting fibers. (c) Fluorescence micrographs of a fiber excited by a laser beam focused in spots at variable distances, D, from its tip (highlighted by vertical arrows). (d) Photoluminescence intensity vs. D (symbols) and best fit to an exponential decay (dashed line). γ: optical loss coefficient. Reproduced from ACS Appl. Mater. Interfaces, 2015, 7, 5213-18. DOI: 10.1021/am508046g. © 2015 American Chemical Society.

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