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Active polymer nanofibers for photonics, electronics, energy generation and micromechanics

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ABSTRACT

Active polymer nanofibers for opto- and nano-electronics benefit from low cost and versatile fabrication processes and exhibit an unequaled flexibility in terms of chemical composition, physical properties and achievable functionality. For these reasons, they have rapidly emerged as powerful tool for nanotechnologies and as building blocks of a wide range of devices. Both bottom up and top down nanofabrication concepts were developed to produce nanofibers made of conjugated or other functional polymers and blends. This article summarizes and reviews the chemico-physical and functional requirements for polymer nanofibers to be used in opto- and nanoelectronics, as well as recent advances in various promising device architectures, such as light emitting and photovoltaic devices, photodetectors, field-effect transistors, piezo- and thermoelectric generators, and actuators. The outlook of functional polymer nanofibers and of devices based on them is also outlined and discussed.

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1. Introduction

Synthetic and processing technologies to produce, functionalize and assemble polymer nanofibers and materials and devices based on them have achieved enormous advances in the last decade [1–3]. Indeed, the use of polymer nanofibers for an enormous variety of applications grounds on solid motivations due to their ultra-high surface-to-volume ratio, morphological and optical anisotropy, unique mechanical characteristics [4], and other physico-chemical properties, such as charge transport, thermal conductivity [5], and molecular adsorption capability, which can be significantly enhanced compared to bulk, film-forming, or macroscopic fiber-based materials. These features make polymer nanofibers interesting for all those technological fields where a very large surface is needed in order to allow nanostructures to interact effectively with external liquid or gas media. Applications include the realization of sensors and bio-sensors, the development of most efficient materials for catalysis, filtration, biotechnology, regenerative medicine and tissue engineering. In all these fields, technologies to realize nanofiber-based materials have already reached commercialization, with a lot of dedicated start-up companies [6]. As a matter of fact, some industrial, goods-producing segments, such as those addressing the commercialization of dedicated equipment and of products whose added value is directly provided by nanofibers, are gaining increasing visibility on the market. This is making the field one of the most vibrant in the broad framework of nanotechnologies, due to the actual perspectives of socio-economic impact.

In other areas of applications, polymer nanofibers are still relatively immature as newly developed material. However, a few of these fields, such as nanophotonics and nanoelectronics, are tremendously intriguing from a scientific and technological viewpoint. Here, future, novel materials and devices have being seeded over the last few years, by realizing nanofibers made of optically and electronically active molecules. The classes of materials utilizable to this aim are well-known. On one side, one can consider conjugated polymers, i.e. macromolecules presenting unpaired (π) electrons. These polymers can exhibit electrical conductivity, together with an either one-dimensional or two-dimensional topological structures, as well as various other peculiar physical properties which make them excellent materials for many applications in optoelectronics, nanophotonics and nanoelectronics [7]. Such features comprise semiconducting behavior, wide tuneability of the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), and at least partially controllable supramolecular ordering and anisotropy of the resulting optical and electronic properties. Nowadays it has become clear that active nanofibers can be realized with conjugated polymers, following a number of complementary fabrication approaches (Table 1). Examples include many derivatives of poly(*p*-phenylene vinylene) (PPV) [8–31], polythiophenes including especially poly(3-alkylthiophene)s (P3ATs) [9,12,20,32–51], poly(fluorene)s [9,14,21,52–62], various side-chain grafted poly(arylene ethynylene)s [63], polyacetylenes [64–66], etc. The molecular structures of a few of these polymers, relevant in this framework, are shown in Fig. 1.

A different possibility relies on preparing nanocomposite nanofibers, namely blending polymers (even optically and electrically inert) with molecular dopants or nanocrystals as active building-blocks. This strategy is often preferred when the preparation of nanofibers requires good viscoelastic or thermoplastic behavior from the used polymer solutions or matrices [9,16,47,48,67–72], which conjugated polymers and low-molar-mass molecules do not normally provide. The range of applications where active nanofibers made of conjugated polymers or nanocomposites are exploited is continuously increasing, and include so far organic light-emitting devices (OLEDs), solid-state lasers, sub-wavelength waveguides and other nanophotonic components, photovoltaic cells, transistors and phototransistors, rectifying junctions, logic gates and nonvolatile flash memories.

Furthermore, even some insulating polymers can be of great interest as materials allowing active nanofibers to be fabricated. This is case, for instance, of poly(vinylidene fluoride) (PVDF) and its derivatives. In the last few years, these polymers were employed to produce piezoelectric nanofibers for energy harvesting through nanogenerators and for pressure sensing and accelerometry. Recently, not only piezo-polymers, but also conductive polymer materials and fibers with good thermoelectric properties have begun to be used for the realization of miniaturized components for energy generation, a perspective of remarkable interest for the development of distributed sources of renewable electricity recovering waste heat. Finally, the production of actuators exploiting the elongated and robust geometry of polymer nanofibers is another intriguing prospect, enabling the development of novel, effective and cheap elements for robotics and biotechnologies operating at different length-scales.

This review presents active polymer nanofibers for application in nanophotonics and nanoelectronics, summarizing the main technologies reported to date and allowing these nanostructures to be fabricated, and the main fields of use and proposed device platforms for the