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Semiconducting nanofibers in photoelectrochemistry

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ABSTRACT

Nanostructured semiconducting materials show intriguing properties not possessed by their macroscopic counterparts. First of all they exhibit high surface area to volume ratio, which offers interesting possibilities in several applications, as the improved and increased solar light adsorption in photoelectrochemistry and photocatalysis. Low charge–carrier mobility and high charge recombination rates are the key limiting factors in solar energy conversion systems. New extraordinary opportunities arise by the exploitation of nanomaterials. Indeed, learning to fine tune the behavior of nanoscale semiconductors and to integrate them in real devices have become one the main topics in the energy-related fields. Significant work has been especially done demonstrating that innovative photovoltaic architectures, and well-performing photoelectrochemical systems can be designed by the proper integration of nanostructured semiconducting metal oxides.

In this scenario nanofibers by electrospinning have attracted great interest, since they can be obtained by a relative simple and low-cost process, if compared to other technologies used for the fabrication of nanostructures. Moreover electrospinning offers several possibilities and strategies to design nanofiber-based nanostructures with different arrangement, well-controlled composition and morphology.

1. Introduction

Energy production, use and supply will be among the priority societal challenges of the next decades[1]. Since energy is lifeblood of our everyday activities, new effective strategies must be developed in order to reduce our dependence on fossil fuels. Indeed, traditional fossil fuel-based energy sources significantly contribute to greenhouse gas emissions (GHG) that must be reduced for climate change mitigation [2,3] The development of efficient technologies able to exploit the potential of renewable sources will play a crucial role towards more sustainable energetic systems [4,5]. In this view, during the last decade significant attention has raised on semiconducting metal oxides that have demonstrated to be effective functional materials to design well-performing renewable energy systems [6–8]. Nanostructured metal oxides (as TiO_2, ZnO, CuO and SnO_2 just to mention some of them) have been explored intensively in a wide range of applications, showing excellent catalytic, optical and electrical properties that lead to a wide range of applications [9–13]. A strong correlation has been demonstrated between their morphology and their final properties. Thereby making possible to identify precise strategies for properties tuning by nano-shape control [14–17]. Several nanostructures have been proposed and investigated over years in several areas, as nanotubes [18,19], nanobelts [20], flower-like [21,22], nanoparticles [23,24] and nanofibers [25].

Nanofibers by electrospinning can be thought to as the conjunction point between the nanoscale world and the macroscopic one, thanks to the diameters of the fibers, in the range of some tens of nanometers, and their length that can easily reach some kilometers.

Electrospinning is an electrohydrodynamic technique that utilizes electrostatic forces to produce polymer-based fibers with diameters ranging from few nanometers up to several micrometers [26–29]. During the process an electrostatic field is applied between a small size needle and a grounded substrate (or collector) to drive the assembly of nanofiber mats. The process is based on the principle that strong repulsive electrical forces can overcome the surface tension in a charged polymeric jet [30,31]. In contrast with fibers obtained with conventional spinning methods, such as wet, dry, melt and gel spinning, nanofibers by electrospinning show very interesting morphological characteristics, like high surface area to volume ratio, small size pores guaranteeing high porosity. Polymeric solutions of both natural and synthetic polymers can be processed giving high surface area mats. Interestingly, the final nanofibers can be based not only on polymers, but through proper chemical and thermal processing, also on metals, metal oxides, ceramics, and different classes of composites, e.g.

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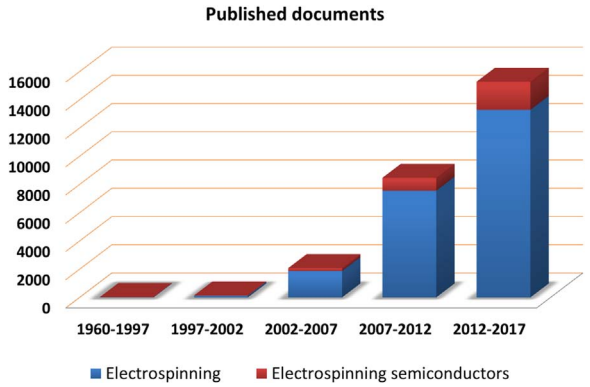

Fig. 1. In blue the number of documents published in the field of electrospinning are shown. In red the works referring to electrospinning of semiconductors are highlighted. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

organic/organic, organic/inorganic and inorganic/inorganic [32,33].

Having so unique features, electrospun nanofibers have attracted great attention over years, as demonstrated in Fig. 1 by the dramatic increase of the number of related publications. During the last decade, electrospun nanofibers have significantly broaden their application areas, covering almost all scientific fields [32]: from energy storage and production [25,34-36], from biomedical sciences as drug delivery and tissue regeneration [36–39] to sensing devices [40–42] and catalysis [43–45]. In Fig. 1 the number of publications in the area of electrospinning applied to semiconductors is also analyzed, showing increasing interest on this class of nanostructures.

The present review focuses its attention on semiconducting nanofibers by electrospinning, surveying first the development of different nanofiber-based nanostructures that have fabricated over years and their application in energy-related areas.

2. Principles of electrospinning technology

The Electrospinning process constitutes the unique technique for the production of nanofibers with diameters in the range between few nanometers and some microns.

The process is based on a self-assembly process driven by the Columbic interaction between charged elements of the polymeric fluids, allowing the formation of nanofibers; this process is in strong contrast to conventional fibers producing techniques. The transition from a microscopic fluid element, such as the droplet formed at the beginning of the process, to a solid nanofiber is ensured by a series of jet instability. All the jet instabilities give rise to an extremely high extensional deformation and simultaneously they induce the strain rates during fiber formation; all these physical aspects enhance, among other effect, a high orientation order in the nanofibers, improving the mechanical properties. Electrospinning process is applied predominantly to polymer-based material including both natural and synthetic polymers; however, it is also possible to obtain metallic, ceramic and carbon nanofibers starting from an electrospun polymeric solution by means of successive treatment, such as calcination, pyrolysis and so on. The schematic setup of electrospinning is based on three major components [46], as represented in the Fig. 2(a): i. an high-voltage power supply, ii. a spinneret, which constitutes one of the two electrodes supporting the metallic needle, and iii. a collector, also defined grounded counter electrode, which is the second electrode. The nanofibers are collected on this component or on a specific substrate, selected according to the applications. If the counter electrode is planar, the nanofibers are randomly deposited on it, with no preferred fiber direction in the plane. Consequently, with a planar counter electrode the deposition generates a no woven mat of nanofibers. Usually, the diameters distributions are not homogeneous during the process also if the values of all spinning parameters remain constant [47]. Other types of counter electrodes can be used, such as tips, rotating cylinders or discs, counter electrodes composed of two parallel bars, cross gratings composed of conductive wires and many more [47,48]. In each specific case, a particular typology of fiber deposition was achieved. It is possible theoretically to predict the correlation between the different types of counter electrodes and the voltage applied. This aspect will be discussed in the following paragraph.

The voltage is applied directly between the two electrodes. The electric field intensity can be indirectly defined as the ratio between the applied voltage and the working distance. The working distance is determined as the distance between the tip of the needle (first electrode) and the counter electrode. The spinneret is connected to a syringe in which polymer solution (or melt solutions) is loaded. With a syringe pump, the solution flows from the spinneret with a controlled and constant rate, which is known as flow rate. When a high voltage (typically from 1 to 30 kV) is applied, the drop at the tip of the needle will become highly electrified and the charges are distributed uniformly on its surface. The mutual charge repulsion causes a force directly opposite to the surface tension. As the intensity of the electric field increases, the hemispherical surface of the solution at the tip of the capillary tube elongates to form a conical shape, known as the Taylor cone. When the electric field reaches the critical value, the repulsive electric force overcomes the surface tension and a charged jet of the solution is ejected from the tip of the Taylor cone. As the jet travels in air, the solvent evaporates, leaving behind a charged polymer fiber, which deposits randomly on the counter electrode, as represented in the Fig. 2(a). Thus, it is quite important to define the correct value of working distance in order to ensure the complete evaporation of the solvent, and consequently to obtain the deposition of the dried nonwoven mat of nanofibers.

The electrified jet then undergoes a stretching and whipping process, leading to the formation of a long and thin thread. The stretching process was provided by the external electric field together with the Coulomb repulsions among all the equally charged segments of polymeric jet [50,51]. The electrified jet therefore follows a straight path directed towards the counter electrode until the formation of instabilities of the jet. The free end of the jet can be characterized by the deviation from the linear path of the jet, generated by the bending instabilities. All the interactions, not completely known, among the external electric field, the surface tension and the Columbic repulsions through the charges within the jet, induce the instabilities. The charge transport in the liquid jet is induced after the electric field application; moreover, the consequently interactions, among the charges and the external applied electric field, cause the formation of circular loops into the jet, which lead to the instauration of instabilities. One of the typical instability occurring in the process is named bending (or whipping) instability [52]: the primary jet is divided into multiple sub jets, inducing a progressive diameter (defined according to Eq. (1)) reduction of the jet from micrometer to nanometer, as sketched in the Fig. 2(b), taken from the literature [53].

$$r_0^3 = \frac{4\varepsilon \dot{m}_0}{k\pi\sigma\rho} \tag{1}$$

Where ε is the permittivity of the fluid (in C/V cm), $\dot{m}_0$ is the mass flow rate (g/s) when r0 (cm) is calculated, κ is a dimensionless parameter related with the electric currents, σ is electric conductivity (A/V cm), and ρ is the density (g/cm^3) of the electrospun material.

3. Morphology tuning by instabilities during electrospinning process

One of the previously described whipping instabilities received particular interest, being investigated in details in some works in the literature. This instability was defined as *branching effect* [53,54]. Depending on the chosen electrospinning parameters and on the charges