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Titania nanofiber photoanodes for dye-sensitized solar cells

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ABSTRACT

The porous structure of electrospun TiO_2 nanofibers was characterized in-depth and the best performing nanofiber structure for application in dye sensitized solar cell was identified. Four types of TiO_2 nanofibers were investigated (electrospun from polyvinylpyrrolidone (PVP) and hydroxypropylcellulose (HPC) as templates) with diameters 100–280 nm and surface areas 9–100 m^2/g. Mesoporous TiO_2 films were prepared by supramolecular templating with a block copolymer Pluronic P123. For the preparation of composite nanofiber mesoporous films, 2% or 15% of electrospun nanofibers were added. Incorporation of nanofibers into the mesoporous film results in a decrease in dye N719 adsorption but at the same time in an increase of roughness factor. Solar efficiency of composite mesoporous films increases (unlike for pure mesoporous films) even for layer thickness higher than 2.3 μm. Thus we developed a simplified method for the preparation of thick mesoporous nanofiber electrodes with improved solar efficiency of 5.51% which outperforms that of pure mesoporous film (4.96%).

1. Introduction

The dye sensitized solar cell (DSC) is a cost effective alternative of solid-state photovoltaics [1–4]. Its key components are TiO_2 (anatase) photoanode, counter-electrode and electrolyte solution with redox mediator. Recently, the traditional I_3^-/I^- mediator was replaced by $Co^{3+/2+}$ bipyridine complexes [3,5–14], leading to the efficiency as high as 12.3% [5]. Counter electrodes are typically from Pt, but carbons [15], graphene-based materials [16–20] and electrospun carbon nanofibers [21] can be also used as cheaper electrocatalysts to replace Pt.

The optimum TiO_2 photoanode was sought among broad array of materials ranging from single crystals [22,23] to tailored nanostructures [24,25]. Titania nanowires are attractive by improved electron transport and collection, compared to that in sintered nanoparticles [26,27], but reliable and up scalable synthetic methods for their fabrication in were still lacking [27]. We have addressed this problem recently [28] through the Nanospider™ technology [29]. Its principal innovation consists in the fact that electrospinning is carried out directly from the surface of a liquid film, which allows fabrication of titania nanofibers at industrial level [29].

Electrospinning is typically used for synthesis of polymeric nanofibers [30–34], but it is extendable to synthesis of inorganic materials, too. Li and Xia [35] pioneered the preparation of electrospun titania nanofibers from solution of poly(vinyl pyrrolidone) and titanium isopropoxide. Later on, they prepared uniaxially aligned titania nanofibers [36]. Electrospun titania NF exhibit interesting chemical [37] and optical properties [38] which find various applications, such as photoelectrochemical hydrogen production [39], photocatalysis [40] and dye-sensitized solar cells [32,41–47].

Most of the cited previous works on DSCs used pure nanofiber films, which were deposited either directly on F-doped SnO_2 (FTO) [32,41,43,44] or pre-deposited TiO_2 [47] doctor bladed from a paste [46] or annealed by hot pressing [42,45]. Recently, Zukalova et al. [48] prepared hierarchical materials from a composite of titania nanofibers and organized mesoporous titania films. Here, we upgrade this initial work [28] by deeper investigation of the porous structure of nanofibers, and optimization of composite electrodes for DSC applications. We developed a simplified protocol with smaller number of deposition steps, producing photoanodes with comparable efficiency.

2. Experimental

2.1. Materials

2.1.1. Nanofibers

Nanofibers (NF) were prepared by electrospinning from appropriate polymer templates and Ti-precursors by the Nanospider™ technology [29]. Different polymer carriers were tested to control the products' properties (fiber diameter, surface area and

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Table 1
Properties of TiO$_2$ nanofibers used for incorporation into the Pluronic P123, templated electrodes; (A, anatase and R, rutile).

NF	Template	As prepared						After recalcination at 530 °C	
		Calc. temp. of NF (°C)	Fiber diameter (nm)	Crystalline structure	BET surface area (m^2/g)	Geom. surface area (m^2/g)	Crystal. size (nm)	BET surface area (m^2/g)	Crystallite size (nm)
A1	PVP	500	100 ± 30	79% A, 21% R	50 ± 0.2	∼10	7 ± 1	41 ± 0.2	10 ± 1
A2	PVP	590	280 ± 50	89% A, 11% R	9 ± 0.1	∼4	20 ± 1	9 ± 0.1	20 ± 1
A3	HPC	450	250 ± 45	100% A	63 ± 0.3	∼4	8 ± 1	32 ± 0.2	12 ± 1
A4	HPC	450	270 ± 70	100% A	105 ± 0.5	∼4	5 ± 1	85 ± 0.4	6 ± 1

crystallinity): polyvinylpyrrolidone (PVP), hydroxypropylcellulose (HPC), polyethylene oxide and polyvinyl alcohol. The prepared electrospun TiO$_2$ fibers were calcined at temperatures 450, 500 or 590 °C. The fiber diameter was determined by SEM using an internal software (as an average value of diameter of at least 30 fibers of one sample).

2.1.2. Nanoparticle/nanofiber mesoporous films

Mesoporous TiO$_2$ films were prepared by supramolecular templating with a block copolymer Pluronic P-123. The TiO$_2$ thin films were grown using titanium ethoxide as the Ti-precursor in a sol–gel method [49]. For preparation of films with nanofibers 2% or 15% of nanofibers were added into the stock solution. Before use the annealed nanofibers were milled under liquid nitrogen. Thin mesoporous films were prepared at room temperature by dip coating onto slides of FTO glass (TEC from Libbey-Owens-Ford, 8 Ω/sq). The deposited layer was calcined in air at 350 °C. Thicker films consisting of more layers were prepared by repeating of the deposition procedure. To form well developed anatase crystals in the framework, the films were finally thermally post-treated at 530 °C.

2.2. Characterization methods

SEM images of nanofibers and films were obtained by Hitachi S-4800 microscope and Nova NanoSEM 230, FEI. XRD spectra of the samples were measured by XRD-6000, Shimadzu and crystal size was calculated using Scherer formula. The BET surface areas of powder nanofiber samples were determined from nitrogen adsorption isotherms at −196 °C using the Micromeritics ASAP 2020 Instrument and Nova4000, Quantachrome. Adsorption isotherms of krypton at −196 °C were measured for the TiO$_2$ films with a Micromeritics ASAP 2020 instrument using our previously developed method [50,51]. The film thickness was measured by DEKTAK profilometer. TGA analysis was performed by Netzsch STA449F1 thermogravimeter.

The Ru-bipyridine dye coded N719; chemical name: di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′ dicarboxylato) ruthenium(II) was used as a model molecule to investigate adsorption properties of TiO$_2$ films. Adsorbed amount of dye was analyzed by UV–vis spectrophotometry (UV/VIS/NIR spectrophotometer Lambda19 (Perkin-Elmer)). Electrochemical lithium insertion was studied by cyclic voltammetry using the Autolab PGSTAT30 (Ecochemie) potentiostat under argon atmosphere in a glove box. For photoelectrochemical tests, Solar Cell I-V Curve Testing System, Model IV5 (PV Measurements, Inc.) was used.

2.3. Assembling of solar cells

Electrode was dipped into a solution of C106 dye; chemical name: NaRu(4,4-bis(5-(hexylthio)thiophen-2-yl)-2,2-bipyridine) (4-carboxylic acid-4-carboxylate-2,2-bipyridine) (NCS)$_2$. The reason for choosing C106 dye for DSC tests consists in larger extinction coefficient and red-shifted spectral maximum compared to those of N719 [52].

The DSC was assembled with a counter electrode from platinized FTO, which was prepared by deposition of 5 μL/cm^2 of 10 mM H$_2$PtCl$_6$ in 2-propanol and calcination at 400 °C. The cell was filled with EL-PHE (Dyesol) electrolyte solution. The cell active area for illumination (0.159 cm^2) was defined by a mask.

3. Results and discussion

3.1. Nanofibers

In our initial attempts towards nanofibers synthesis, we adopted the protocol of Li and Xia [35] using polyvinylpyrrolidone as a polymeric template. Solutions for fabrication of nanofibers were selected based on their viscosity, conductivity and ability to be electrospun. Thermogravimetric analysis of PVP showed its incomplete calcination at temperatures used for fabrication of nanofiber/nanoparticle composite electrodes [28], thus hydroxypropylcellulose was also chosen as the other polymer carrier for preparation of TiO$_2$ nanofibers for DSC application. The electrospun nanofibers were calcined at temperatures from 450 to 590 °C and characterized by SEM (fiber diameter), adsorption isotherms (BET surface area) and XRD. The properties of used TiO$_2$ nanofibers are summarized in Table 1.

The diameter of A1 nanofibers was almost three times smaller than diameter of nanofibers A2, A3 and A4. Nanofibers A4 have the highest BET surface area (105 m^2/g) and nanofibers A2 the lowest (9 m^2/g). Based on the fiber diameter geometrical surface area on nanofibers can be estimated. Big difference between geometric surface area and BET surface means that the nanofibers are highly porous. Nanofibers A2, A3 and A4 have similar diameter but rather different BET surface area which suggest the different porosity. Comparing BET surface areas and the geometric area of the fiber provides the contribution of inner surface of pores to the surface area. Geometric surface area of A1 nanofibers is 10 m^2/g whilst the BET surface area is 50 m^2/g, it means that approximately 80% of the surface area is inner surface of pores. In the case of A2 nanofibers the BET surface area is only 9 m^2/g, and contribution of inner surface of pores is about 56%. In the case of nanofibers A3 and A4 the contribution of inner surface of pores is even higher, 94 and 96%, respectively. The morphology of nanofibers A2 and A4 is shown in Fig. 1. Porous structure of A2 nanofibers is visible in Fig. 1B and C, the nanofibers look highly porous but surprisingly they have a small surface area. A4 nanofibers in Fig. 1(E) and (F) give an impression of being nonporous, but their inner pores are much smaller and their inner pore surface contributes much more to the total surface area of the nanofibers. Only 4% of real surface area of A4 nanofibers is the contribution of outer geometrical surface area, while for A2 the contribution of outer geometrical surface area is about 44%.

Fig. 2A shows X-ray diffraction pattern of nanofibers. Crystalline structure and crystal size of nanofibers is shown in Table 1. Nanofibers prepared from HPC as a template (A3 and A4) were calcined during their fabrication at 450 °C and have the anatase structure. Nanofibers prepared from PVP as a template (A1 and A2) were calcined during the fabrication at 500 or 590 °C and the structure is a mixture of anatase and rutile (Fig. 2A and Table 1). The