



Preparation of the Au@TiO₂ nanofibers by one-step electrospinning for the composite photoanode of dye-sensitized solar cells

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HIGHLIGHTS

- Au@TiO₂ nanofibers with various amount of Au are prepared by one-step electrospinning.
- The formation of Au@TiO₂ nanofibers is studied by structural and optical characterization.
- Photoanode of DSSC containing Au@TiO₂ nanofibers is fabricated.
- Plasmonic effect of Au@TiO₂ nanofibers on DSSC performance is presented.

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ABSTRACT

The TiO₂ nanofibers containing Au nanoparticles (NPs) were synthesized via one-step electrospinning of TiO₂ precursor, HAuCl₄·3H₂O, and polyvinylpyrrolidone (PVP) in DMF solution followed by pyrolysis. The amount of Au NPs in the Au@TiO₂ nanofibers was varied by the concentration of HAuCl₄·3H₂O in the electrospinning solution. The formation of the Au@TiO₂ nanofibers during the pyrolysis process was characterized by SEM, TEM, TGA, and UV/Vis. Dye-sensitized solar cells (DSSCs) based on composite photoanode of the Au@TiO₂ nanofibers and the TiO₂ nanoparticles were investigated. The results indicated that the efficiency of the DSSC would be enhanced by the optimal amount of Au NPs (*i.e.*, 0.5 wt.%) in the Au@TiO₂ nanofibers.

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1. Introduction

One-dimensional (1D) TiO₂ nanostructures in the shapes of tube, rod, wire, fiber, or belt have unique properties such as large surface area, wide band gap, photocatalytic activity, and chemical stability [1]. These materials have been designed and explored for photocatalytic CO₂ reduction [2], water splitting [3,4], solar cells [5–7], supercapacitors [8,9], biomedical devices [10,11], and lithium-ion batteries [12,13]. The 1D TiO₂ nanostructures can provide better pathways for charge transport than the zero-dimensional TiO₂ nanoparticles (NPs), which may reduce the recombination of electrons and holes significantly, boost the charge transfer at the interfaces, and lead to improved photovoltaic and photocatalysis performance [14,15].

Electrospinning is an innovative technique that provides a simple approach to produce polymer, ceramic, and carbon/graphite fibers with diameters typically ranging from tens to hundreds of nanometers (commonly known as electrospun nanofibers) [16,17]. For example, porous TiO₂ nanofibers with large surface area were successfully prepared by electrospinning technique [18–20]. In recent years, we have investigated the electrospun TiO₂ nanofibers for photoanodes of high-efficient dye-sensitized solar cells (DSSCs) [21–25]. Incorporation of TiO₂ nanofibers in the photoanode of DSSCs improves the efficiency of the devices because of the Mie scattering of light and superior charge transport in photoanode [21,26]. Flexible, transferable, and thermal-durable composite photoanode for DSSCs was also demonstrated by impregnating TiO₂ NPs in hybrid TiO₂ and SiO₂ nanofibrous mat prepared via dual-spinneret electrospinning [23]. Additionally, the 1D electrospun TiO₂ or SiO₂ nanofibers were useful for preparation of photoanode composed of binder-free TiO₂ NPs with good film integrity [24].

Decoration of metal oxide nanostructures with metallic

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nanoparticles provides additional venue for improved functionalities [27,28]. For DSSCs, addition of metallic nanostructures (e.g., Au and Ag NPs) in the photoanode is considered as an effective approach to enhance photon harvesting and thus improve electron-photon conversion efficiency due to enhanced light scattering, electromagnetic light focusing, and/or plasmon-resonant energy transfer by the localized surface plasmon resonance (LSPR) effect [29–31]. Similar strategies of using metal nanostructure to further improve the efficiency of solar cells have been extensively explored in the rapid developing field of inorganic-organic hybrid perovskite solar cells in recent years [32–35]. However, the effects of the metallic nanostructures on the photo-conversion efficiency have to walk a fine line between the enhanced light harvesting and the detrimental electron trapping and recombination of the metallic nanostructures [36]. To minimize the detrimental effect of the metallic NPs on the photoanode of DSSC, novel core/shell structures of metal@TiO₂ NPs were needed to avoid the direct contact between the metal NPs with the dyes and electrolytes [30].

For 1D TiO₂ nanostructures, many strategies such as UV irradiation reduction, plasma sputtering, electrodeposition, electrospinning, and hydrothermal growth have been adopted to incorporate noble metallic NPs. These metal-decorated TiO₂ nanostructures have been widely investigated for photocatalysis [27], lithium ion batteries [37], etc., but studies of these materials for DSSCs are rare. One paper reported that the electrospun TiO₂ nanofibers with the embedded Au NPs as the scattering layer improved the efficiency of DSSCs [38]. No details of Au NPs formation during pyrolysis of the nanofibers were investigated.

Herein, we report synthesis of TiO₂ nanofibers embedded with Au NPs via a one-step electrospinning route. Nanofibers of TiO₂ precursor, HAuCl₄·3H₂O, and polyvinylpyrrolidone (PVP) were prepared by electrospinning, and subsequently pyrolysis of the nanofibers formed the TiO₂ nanofibers embedded with Au NPs (Au@TiO₂ NFs). The Au@TiO₂ NFs with different amount of Au NPs were obtained by varying the concentration of HAuCl₄·3H₂O during electrospinning. The details of the Au NP formation during pyrolysis were studied. DSSCs based on the composite photoanode of TiO₂ NPs and Au@TiO₂ NF were characterized.

2. Experimental

2.1. Materials

Titanium (IV) n-butoxide (TNBT), N,N-dimethylformamide (DMF), isopropanol (IPA), ethanol, acetic acid (HAc), chloroauric acid trihydrate (HAuCl₄·3H₂O), Titanium(IV) oxide (P25 TiO₂) nanoparticles, polyvinylpyrrolidone (PVP, M_w = 1,300,000), and poly(ethylene oxide) (M_w = 30,000) were purchased from Sigma-Aldrich Chemical Co (St. Louis, MO) and used without further purification. The F-doped SnO₂ glass (FTO, 8 Ω/□) was provided by Hartford Glass Co.. Parafilm spacer was purchased from Fisher Scientific; the platinum precursor (Platisol T), N719 dye, and the electrolyte (Iodolyte AN-50 electrolyte) were purchased from Solaronix (Switzerland).

2.2. Preparation of electrospun Au@TiO₂ NFs

The nanofibers of TiO₂ and Au@TiO₂ were prepared by electrospinning followed by pyrolysis. The solution for electrospinning was prepared by two steps. The solution of TNBT was prepared by adding 1.5 g HAc aqueous solution (1.0 M) to 3g TNBT; the solution of HAuCl₄·3H₂O and PVP was prepared by dissolving HAuCl₄·3H₂O and 1.1 g PVP in the mixed solvent of 4.9 g IPA and 8.2 g DMF. The mass of HAuCl₄·3H₂O added was calculated so that the nominal weight percent of Au NPs in the Au@TiO₂ NFs after pyrolysis was set

at 0.5 wt.%, 1.0 wt.%, and 5.0 wt.%, respectively. The two solutions were mixed and stirred for 24 h prior to electrospinning.

During electrospinning, a positive DC voltage of 10 kV from a high voltage power supply (ES30P, Gamma High Voltage Research, Inc.) was applied to the prepared solution through a stainless steel needle. The feed rate was set at 1.5 mL h⁻¹ by using a syringe pump (KDS 200, KD Scientific, Inc.). The electrospun precursor nanofibrous mat was collected on a laboratory-produced rotating drum (with diameter of ~25 cm) covered with aluminum foil. The as-spun nanofibrous mat was kept in ambient condition for 48 h to allow for complete hydrolysis/condensation of the TiO₂ precursor; thereafter, the mat was heated to 500 °C at the ramp rate of 1 °C/min and held at 500 °C for 5 h with constant airflow (Lindberg 54453, Heavy Duty Tube Furnace) to obtain the Au@TiO₂ NFs. Electrospun TiO₂ NFs without Au NPs were prepared following the same procedure.

A Zeiss Supra 40 variable-pressure field-emission scanning electron microscope (SEM), a JEOL JEM-2100 transmission electron microscope (TEM), and a Rigaku Ultima Plus XRD were employed to characterize the morphological and structural properties of the electrospun nanofibers. The average nanofiber diameter for each sample was obtained through measuring 50 randomly selected fibers from SEM image using the software of Image J. Thermal decomposition property of HAuCl₄·3H₂O was characterized by thermos gravimetric analysis (TGA/SDT Q600 V20.9 Build 20); the heating rate was set at 10 °C/min, and the TGA curve was recorded from 25 to 400 °C under 50 ml/min flow of Argon. The amount of sample for TGA analysis was ~10 mg. Shimadzu UV-2450 spectrophotometers was employed to characterize the formation of Au NPs in the Au@TiO₂ NFs at various temperatures.

2.3. Assembly and evaluation of DSSCs

The Au@TiO₂ NFs were first shortened by sonication of the aqueous dispersion of the nanofibrous mat for 1 h; the shortened nanofibers were mixed with P25 TiO₂ NPs, ethanol, DI water, poly(ethylene oxide) (M_w = 30,000), and acetic acid to form paste for doctor-blading. The weight ratio of the Au@TiO₂ NFs to P25 TiO₂ NPs was set at 1 to 3 based on our previous publications [21,26].

For preparation of photoanode, a clean FTO/glass substrate was first coated with a compact layer of TiO₂, then the mesoporous film composed of TiO₂ NPs and Au@TiO₂ NFs was formed via doctor-blading of the TiO₂ paste followed by sintering at 450 °C for 45 min. After sensitized by the N719 dye for 24 h, the photoanode and the counter electrode (FTO/glass with Pt catalyst) were sealed with Parafilm; finally, the Iodolyte AN-50 electrolyte was injected into the cell. The cell performance was evaluated with a Keithley 2400 SourceMeter. A 150 W Solar Simulator (Newport Co.) was used to simulate 100 mW cm⁻² sunlight. The light intensity was adjusted using a Hamamatsu S1133 reference cell calibrated by the National Renewable Energy Laboratory (Golden, Colorado).

3. Results and discussion

Representative SEM images and the corresponding fiber diameter distributions of the TiO₂ NFs and the Au@TiO₂ NFs are shown in Fig. 1. Randomly overlaid nanofibers without microscopically identifiable beads were observed for both TiO₂ and Au@TiO₂ NFs. The average diameter of the TiO₂ nanofibers was ~100 nm with a relatively wide size distribution. The Au@TiO₂ nanofibers had similar average diameter and diameter size distribution. The result suggested that adding of chloroauric acid in the precursor solution had little effect on the electrospinning process and the dimensions of the resultant nanofibers.

The morphologies of the neat TiO₂ NFs and the Au@TiO₂ NFs were further characterized by TEM (Fig. 2). The neat TiO₂ NFs were

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