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Stacked graphene–TiO_2 photoanode via electrospray deposition for highly efficient dye-sensitized solar cells

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ABSTRACT

A series of TiO_2–graphene stacked photoanodes for dye-sensitized solar cells (DSSCs) were fabricated by electrospray (E-spray) deposition. Among devices incorporating single graphene layer with different deposition times, device with 1 min graphene deposition gave the best performance. For multi-graphene-layer involved devices, best result was obtained with 3 layers of graphene. The working principles were analyzed by scanning electron microscopy, transmittance spectra, electrochemical impedance spectroscopy and incident-photo-conversion efficiency data. We found that although graphene layers incorporated in TiO_2 photoanode slightly decreased dye adsorption, they were able to significantly improve the electron transport, and the charge recombination at the interfaces of TiO_2/dye and TiO_2/electrolyte were greatly suppressed, leading to dramatic improvement in power conversion efficiency. When inserting three layers of pure graphene into the TiO_2 photoanode, high efficiency of 8.9% was obtained, constituting an over 23.6% improvement. Further increasing graphene layers to five, although electron lifetimes is the longest, both the largest charge transfer resistance and the least amount of the dye loading lead to the lowest device efficiency. Our work demonstrated, that pure graphene layer can be successfully incorporated into TiO_2 photoanode by E-spray method with easiness of thickness control and the photoanode with graphene/TiO_2 alternatively layered structure is an excellent candidate for DSSCs.

1. Introduction

Dye-sensitized solar cells (DSSCs) have stimulated intensive interest as one of the most promising photovoltaic candidates for future clean renewable energy production due to their facile, low-cost and environmentally friendly features in both material preparation and device manufacturing [1–5]. A typical DSSC device includes four essential elements: a photoanode, dyes for solar energy sensitizing, electrolyte generally containing iodide/triiodide ions, and a counter electrode. Among the key components in DSSCs, the semiconductor photoanode is very important because it works as both the substrate for dye adsorption and the transport path for the generated electrons [6,7]. To obtain a high light harvesting efficiency, the semiconductor photoanode should provide not only a large specific surface area for dye adsorption, but also an efficient electron transport path for electron collection. Wide band gap metal oxide of TiO_2 in nanocrystalline mesoporous form is frequently used as DSSCs photoanode. The small particle size (ca. 20 nm) benefits dye adsorption and exciton generation due to the relatively large surface area of the TiO_2 nanoparticles. However, there are a lot of surface traps on the TiO_2 [8], which can slow down the electron transport toward substrate, resulting in a significant amount of charge recombination between the injected electrons and the electrolyte [9]. Great progresses have been made to overcome this drawback, such as incorporating a second semiconductor with a different band gap [10], developing novel film nanostructure [11,12] and incorporating efficient charge transport materials [13–15]. However, further improving electron transport in TiO_2 photoanode is still a major challenge in DSSC technique.

Graphene, a two-dimensional material with sp^2 hybrid carbon atoms, has attracted intensive attention because of its excellent electron mobility (250,000 $cm^2/V/s$), high transparency and theoretically high specific surface area (2630 m^2/g) [16,17]. Some researchers have studied graphene mixed TiO_2 photoanodes in DSSCs and have demonstrated that graphene could accelerate electron transfer from TiO_2 to the fluorine-doped tin oxide (FTO), which would effectively suppress unfavorable charge recombination process in TiO_2/electrolyte and TiO_2/TiO_2 interface, leading

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to an increase of DSSC power conversion efficiency [18,19]. Although considerable efforts have been made to fabricate TiO_2–graphene composite photoanode for DSSCs with improved performance [20], reports on DSSCs with pure film of graphene are rare [21], mainly due to the notorious aggregation and insolubility problems of graphene as well as the intrinsic incompatibility between graphene and inorganic materials [22]. Therefore, it is interesting to apply a simple and effective method for preparing graphene film as well as TiO_2–graphene alternatively stacked photoanodes.

For preparation of TiO_2 photoanodes, different methods such as screen printing [23], doctor-blade technique [24], spraying [25] and electrospray (E-spray) [26] have been used. Among these methods, E-spray has gained much attention considering its practical and cost-effective merits for large-scale production. Although it has been introduced for the fabrication of TiO_2-photoanode and graphene-cathode in DSSC devices [27], there has been no report on applying it to prepare TiO_2–graphene stacked-structure up to now.

In this work, we demonstrated the preparation of graphene films by E-spray deposition and proposed a novel TiO_2–graphene photoanode with stacked structure. High device efficiency of 8.9% was achieved, constituting over 23.6% improvement compared to the control device without graphene.

2. Experimental

2.1. Preparation of TiO_2–graphene photoanode

The substrate, FTO glass, was cleaned with ethanol using an ultrasonic bath for 15 min, rinsed with DI-water and then treated with 40 s oxygen plasma. Graphene was prepared by the reduction of graphene oxide according to the modified Hummers method [28], and was then used in the photoanode fabrication. Firstly, the grinded P25 powder and the homemade graphene were dispersed in ethanol solvent with concentration of 2.5 W% and 0.123 mg/mL, respectively. Fig. 1a schematically depicts the E-spray setup, which consists of a syringe pump, a high voltage power supply, a metal nozzle and a substrate stage. The metal nozzle is a stainless steel needle with 200 μm outside diameter and 100 μm inside diameter, which is connected to the output of a high voltage of about 6 kV. The tip of the needle is placed about 2.5 cm above the substrate. Fig. 1b shows the actual photograph of the E-spray process in the cone-jet mode, which is advantageous to generate stable electrospray and lead to a smooth film on substrate [29].

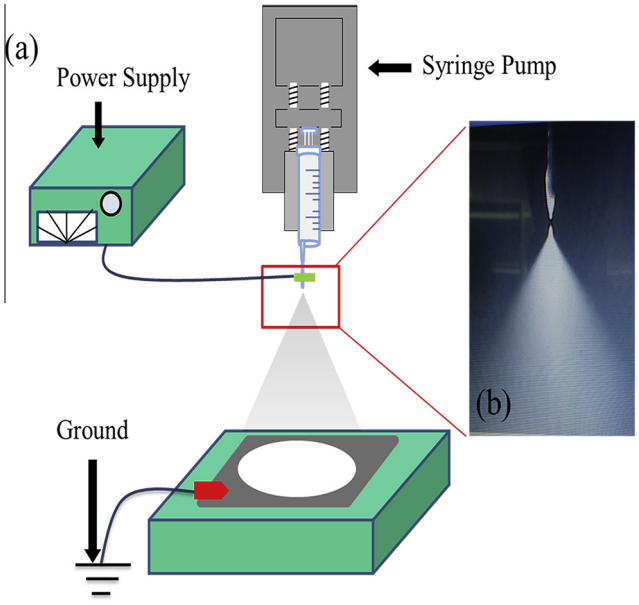

Fig. 1. (a) Schematic illustration of the technique to prepare TiO_2–graphene; (b) an actual photograph of the E-spray process.

2.2. Fabrication of DSSCs

After E-spray deposition, the TiO_2–graphene films were calcined at programmed temperature profile in a muffle furnace. The temperature profile was 150 °C for 15 min, 330 °C for 15 min and 480 °C for 30 min [30]. The thickness of calcined film was about 18 μm. When the photoanode was cooled to room temperature (RT), it was immersed into 0.3 mM ethanol solution of N719 dye at RT for 48 h. Then these sensitized photoanodes were washed with ethanol to remove unanchored dye molecules and subsequently dried in the air at RT. A counter photoanode with a hole was prepared by spin-coating 5×10^{-3} M ethanol solution of H_2PtCl_6 onto the FTO plates and sintered at 420 °C for 15 min [31]. The previously sensitized TiO_2 photoanode and the Pt counter photoanode were assembled via sealing with epoxy mixed with spacers of about 60 μm [32]. A drop of electrolyte solution was injected into the cell through the hole. Finally, the hole was sealed and the device was obtained. The active area of the assembled DSSC samples is 0.25cm^2.

2.3. Characterization

The current–voltage (J–V) data of the studied devices were measured by a computer-controlled Keithley 2400 source meter under the AM 1.5G illumination (100 mW/cm^2 of a solar simulator). The morphology observation was performed by an S-4800 scanning electron microscopy (SEM, HITACHI, Japan) at an accelerating voltage of 20 kV. The incident photon-to-current efficiencies (*IPCEs*), i.e., wavelength dependent external quantum efficiency, were obtained from an integrated system calibrated by a standard silicon photodiode. Electrochemical impedance spectroscopy (*EIS*) was recorded by Bio analytical Systems CHI660E operating in impedance A. C. mode. Dye loading amount and light transmission features were evaluated by UV–visible spectrophotometer (Shimadzu UV-3600). Thickness of photoanodes was tested by probe profilometer (Bruker Dektak XT).

3. Results and discussion

3.1. Effects of graphene thickness

First, one layer graphene was incorporated into TiO_2 photoanode to investigate the effect of graphene thickness on DSSC performance. The TiO_2 and graphene layers were prepared by E-spray method and the thickness of graphene was controlled by E-spry time. In our initial try, the graphene layer was directly deposited on FTO substrate. However, due to its poor adhesion to FTO, the graphene layer peeled off FTO substrate easily. In addition, it was found in literature that among DSSC devices with carbon/TiO_2 hybrid photoanode better performance was achieved when carbon was upon TiO_2 film [33]. Therefore, in our following experiments graphene was inserted in TiO_2, locating at 6 μm apart from top side of TiO_2 (totally 18 μm).

Fig. 2 and Table 1 depict the current density (J)–voltage (V) characteristic, and performance parameters of DSSC devices based on single graphene interlayer with different deposition times. At graphene deposition time of 1 min, the short circuit current (J_{SC})