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Comparing incorporation of carbon nanotubes in hierarchical porous photoanodes of quantum dot and dye sensitized solar cells

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Abstract

The carbon nanotubes (CNT)s are incorporated in hierarchical porous photoanodes of dye sensitized solar cell (DSSC) and quantum dot sensitized solar cell (QDSC). The short circuit current density (J_{SC}) is increased in both cases with addition of CNTs. However, the improvement in J_{SC} of QDSC is more noticeable compared to that of DSSC, which causes dramatic enhancement in efficiency (40%) of this device with incorporation of CNTs. CNTs can presumably promote the charge injection process by lowering the exciton diffusion path through quantum dots (QD) in QDSC. Moreover, CNTs entirely increase the electron lifetime in QDSC by decreasing the effect of surface trap states in the TiO_2/QD interface and encouraging the injection of electrons towards CNT channels before back recombination.

Keywords: Quantum dot sensitized solar cell; Dye sensitized solar cell; Hierarchical porous photoanode; Carbon nanotube

1. Introduction

New strategies in the photovoltaic technology based on nanostructured materials should be necessarily used to satisfy our interminable energy desire. Dye sensitized solar cells (DSSC) and quantum dot sensitized solar cells (QDSC) are two promising technologies in this area due to the simplicity of preparation method, cost effectiveness, acceptable efficiencies, tunability of light absorption, sensitivity to diffuse light, and ability to fabricate flexible solar cells [1–4].

The efficiencies of solar cells have reached to more than 12% in DSSCs [5] and 8.5% in QDSCs [6,7]. However, still further improvement in device performance is required. The major bottlenecks in these devices that should be addressed carefully are low electron lifetime and slow charge transport through polycrystalline photoanodes [8,9]. Carbon nanotubes (CNT)s with outstanding charge transport property and high surface area can be introduced as a promising candidate for incorporation in photoanodes of DSSC and QDSC to enhance charge transport [10–15]. However, truly incorporation of CNTs with engineered interface in photoanode of dye or QD sensitized solar cell can be achieved by the sol–gel method, which forms a thin amorphous titania layer on CNT sidewalls upon impregnation.

Although the DSSCs and QDSCs have apparent similarities, they have so many differences in sizes of quantum dot and dye, polysulfide and iodine/iodide electrolytes, and platinum and Cu_2S counter electrodes used in these cells, which can fundamentally affect the device function [16–18]. Therefore, the CNTs act differently in charge transport and enhancing electron lifetime in these devices and comparing the effect of CNT incorporation on device performance in both cases may be beneficial. Thus, in this article the CNTs are incorporated in hierarchical porous photoanodes of DSSC and QDSC and the results are compared in terms of cell performance and charge transport properties. The hierarchical porous photoanodes used in this study not only provide large micro channels for easy diffusion of electrolyte and QD species as well as mesoporosity for QD or dye adsorption, but also can be synthesized by the sol–gel method, which allows truly incorporation of CNTs in titania matrix. Moreover, the CdSe quantum rods with

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a higher absorption cross section and longer exciton lifetime are used in QDSC besides CdSe QDs in tandem architecture, which can potentially improve the cell performance.

2. Experimental

2.1. Material

Ethanol (EtOH), 1-propanol (1PrOH), tetrapropyl ortotitanate (TTiP), tetrabutyl ortotitanate (TBT), diethanol amine (DEA), polyethylene glycol (PEG, average molecular weight 1000), nitric acid (HNO_3), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), cadmium oxide powder (CdO), cadmium nitrate ($Cd(NO_3)_2 \cdot 4H_2O$), selenium chloride ($SeCl_4$), triethylene tetramine (TETA), sulfur powder (S), sodium sulfide (Na_2S), sodium hydroxide (NaOH), zinc acetate dehydrate (ZAD), copper chloride ($CuCl_2$), acetonitrile (AN), and hexa chloroplatinic acid (H_2PtCl_6) were all in reagent grade and purchased from Merck. Deionized water (DIW, 18.2 MΩ) was used in all experiments. The fluorine doped tin oxide conductive glass substrates (FTO, 15 Ω/sq), cis-di(thiocyanato)–N-N′-bis(2,2′-bipyridyl-4-carboxylic acid-4′-tetrabutyl ammonium carboxylate) ruthenium II (N719), iodine/iodide electrolyte (0.1 M LiI, 0.6 M 1-butyl-3-methyl imidazolium iodide, 0.03 M I_2, and 0.5 M 4-tert-butyl pyridine (TBP) in acetonitrile), and Surlyn ionomer were purchased from Dyesol. Multi-walled carbon nanotubes (MWCNT, outer diameter 40–60 nm, 97% purity, 130–160 m^2/g) were provided from Shenzen Nanotech port. All chemicals were used as received without further purification.

2.2. CNT functionalization

For CNT functionalization, MWCNTs were subjected to ultrasonication in concentrated HNO_3:H_2SO_4 (3:1 vol%) for 10 min. Then, the mixture was refluxed at 80 °C for 1 h. After dilution, the mixtures were washed with DIW and centrifuged several times to ensure removal of anions. The product was dried at 60 °C and kept dried until use.

2.3. CdSe quantum dots (QD)s synthesis

CdSe QDs were synthesized by a modified homemade solvothermal reactor based on a previous report [19]. CdO powder and $SeCl_4$ were dissolved in TETA in the solvothermal reactor heated to 220 °C for 24 h under continuous stirring and external pressure. Then, the precipitates were separated, centrifuged, and redispersed in ethanol. Finally, stepwise size selective centrifugation was applied to obtain CdSe QDs.

2.4. Photoanode preparation

Sol preparation method for depositing blocking layer was reported elsewhere [20]. For preparation of blocking layer, TTiP was dissolved in 1PrOH. The solution of 1PrOH, DIW, and HCl was prepared and added drop-wise to the former solution under vigorous stirring and stirred for 1 h. The sol composition was TTiP:DIW:HCl = 1:4:0.5 with 0.17 M concentration. The blocking layer was deposited by spin coating of the prepared sol on pre-cleaned FTO substrates and dried at 100 °C for 10 min. The thickness of blocking layer was about 100 nm. Then, the film was calcined at 450 °C for 1 h.

The preparation of hierarchical porous photoanode was also previously reported [21]. For preparing the hierarchical porous photoanode, TBT was dissolved in EtOH. Then, DEA was added to the solution. The solution of DIW and EtOH was prepared and added drop-wise to the former solution. The stable dispersion of MWCNTs colloid and solution of PEG in EtOH were added to the prepared sol. The final composition of the sol was TBT:DEA:DIW = 1:1:1 with 0.75 M concentration and 0.32 wt% CNT. The dip coating method was used to deposit the sols on FTO substrates at a speed of 60 mm/s and the films were dried at 300 °C for 10 min. The processes of dip coating and drying were repeated 50 times in order to reach the desired thickness. Finally, the photoanodes were calcined at 550 °C for 1 h.

2.5. DSSC fabrication

The DSSC fabrication was according to the previous report [22]. The $TiCl_4$ treatment was performed by placing the photoanodes in 40 mM solution of $TiCl_4$ in DIW at 70 °C for 30 min, followed by washing with DIW and EtOH, and then heat treating at 450 °C for 30 min. Next, the photoanodes were sensitized by 0.3 mM N719 dye solution in AN:tBuOH for 24 h. A drop of H_2PtCl_6 solution in EtOH was placed on FTO glass and the substrate was heated at 400 °C for 15 min to prepare the platinum decorated counter electrode. The sensitized photoanode and counter electrode were assembled into a sandwich type cell and sealed with Surlyn ionomer. The active area of TiO_2 photoanode was 0.16 cm^2. A drop of iodine/iodide electrolyte was injected into the cell by evacuation through a predrilled hole. Finally, the hole was sealed.

2.6. QDSC fabrication

QDSC fabrication method was discussed elsewhere [19]. Briefly, SILAR method was used to deposit a very thin CdS layer on porous photoanode. The $Cd(NO_3)_2$ in EtOH and Na_2S in DIW and MeOH were used as the cationic and anionic solutions, respectively. Each SILAR cycle contains dipping the photoanode in cationic and anionic solutions for 1 min and then rinsing with corresponding solvent followed by air drying. Four SILAR cycles were deposited on photoanodes. Then, stable dispersion of CdSe QDs in EtOH was used for deposition on FTO/TiO_2/CdS photoanode by electrophoretic deposition applying 150 V/cm for 1 h. Finally, a very thin ZnS barrier layer was deposited on photoanodes by SILAR. The ZAD in DIW and Na_2S in DIW were used as cationic and anionic solutions, respectively. Two SILAR cycles were applied on the photoanodes.

The polysulfide solution containing 1 M Na_2S, 1 M S, and 0.1 M NaOH in DIW was used as the electrolyte in QDSCs. The counter electrode was also prepared by SILAR deposition