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Influence of carbon nanotube wall thickness on performance of dye sensitized solar cell with hierarchical porous photoanode

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ABSTRACT

The effect of carbon nanotube (CNT) diameter on the efficiency of dye sensitized solar cell (DSC) with hierarchical porous photoanode is investigated. Three different kinds of CNTs including a single-wall CNT (SWCNT) and two different multi-wall CNTs (MWCNT) with outer diameters of 10 and 60 nm are incorporated in titania sol after surface functionalization. The DSCs are fabricated based on sol–gel induced phase separation synthesized photoanodes. The most stable colloid of CNTs in ethanolic titania sol is achieved in MWCNT with higher wall thickness. The more functional carboxylic groups, which can further assist the CNT/TiO_2 attachment, could be detected in these CNTs. Impedance spectroscopy shows that the lowest series resistance is obtained in MWCNT incorporated DSC with higher diameter, which is far lower than that of SWCNT, MWCNT with low diameter, or without CNT cells. The 60 nm diameter CNT incorporated cell leads to higher efficiency compared to cells without CNT, with SWCNT, or 10 nm MWCNT due to its proper chemical stability, acceptable thermal stability, and appropriate electrical properties.

1. Introduction

Dye sensitized solar cells (DSC) have attracted much attention in recent years due to their low production cost and relatively high efficiency [1,2]. Although conversion efficiencies of more than 12% have been achieved in DSCs [3], still further improvements are needed in performance of these cells. TiO_2 mesoporous film, as a heart of this device, plays a significant role in charge separation at TiO_2/dye interface and charge transport in TiO_2 matrix [4]. Since the primary bottleneck in these cells is the charge recombination with electrolyte species during charge transport through TiO_2 matrix, many researches have focused on enhancing the charge collection efficiency in TiO_2 by applying one-dimensional routes [5–7]. Such one-dimensional nanostructures show the advantage of high charge transport due to the inexistence of grain boundaries [8].

Carbon nanotubes (CNT) with extraordinary electrical and mechanical properties are promising candidate for improving the charge transport and photogenerated current. So far, CNTs have been utilized in DSCs as a substitute of TiO_2 [9,10], in counter electrode [11–13], in photoanode with simple mixing [14,15], in solid state electrolyte [16], and in photoanode with an engineered interfacial layer [17–19]. Although major enhancement of cell performance has been reported in all cases, the incorporation of CNTs in photoanode with engineered interfacial layer seems to be the most efficient and reliable method to assist the charge injection from TiO_2 to CNT as well as reducing the deficient trap states on CNT sidewalls and increasing the ballistic charge transport.

Since the CNTs show diameter-, length-, and chirality-dependent mechanical, electrical, optical, and chemical properties [20–25], investigating the effects of CNT type and wall thickness on performance of DSC incorporated CNTs is essential. In this research, three different kinds of CNTs including single-wall CNT (SWCNT), multi-wall CNT with outer diameter of 10 nm (MWCNT-10), and MWCNT with outer diameter of 40–60 nm (MWCNT-60) were incorporated in hierarchical porous photoanodes of DSCs to investigate the effect of CNT wall thickness on performance of the device. Different acid treatment conditions of mild, medium, and severe were also applied on each CNTs to alter the dispersibility of the CNTs.

2. Experimental

2.1. Materials

Ethanol (EtOH), 1-propanol (1PrOH), tert-butanol (tBuOH), nitric acid (HNO_3), hydrochloric acid (HCl), sulfuric acid (H_2SO_4),

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titanium chloride ($TiCl_4$), tetrapropyl ortotitanate (TTiP), tetrabutyl ortotitanate (TBT), diethanol amine (DEA), acetonitrile (AN), polyethylene glycol (PEG, average molecular weight 1000), and hexa chloroplatinic acid (H_2PtCl_6) were all in reagent grade and purchased from Merck. Deionized water (DIW) was used in all experiments. SWCNT (outer diameter <2 nm, 95% purity, 350–400 $m^2 g^{-1}$), MWCNT-10 (outer diameter <10 nm, 97% purity, 250–300 $m^2 g^{-1}$), MWCNT-60 (outer diameter 40–60 nm, 97% purity, 130–160 $m^2 g^{-1}$) were provided from Shenzen Nanotech. 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), Surlyn ionomer, and 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 in AN) were all purchased from Dyesol. All chemicals were used as received.

2.2. CNT functionalization

The CNTs should be functionalized for two main reasons: debundling of the CNTs from bundles to increase their function and introducing surface carboxylic groups to improve the interfacial attachment when incorporated in TiO_2 matrix. However, high level of carboxylic functionalization reduces the dispersibility of CNTs in ethanolic base titania sol. Therefore, three different functionalization of mild, medium, and severe treatment were applied on three types of CNTs. Typically, 0.5 g of SWCNT in concentrated nitric acid : sulfuric acid in volume of 3 : 1 was sonicated for 10 min. Then, the mixture was stirred at 25 °C for 3 h for mild acid treatment. The SWCNTs were also subjected to 80 °C for 1 h for medium treatment and 140 °C for 20 min for severe treatment conditions. After dilution, the mixture was washed with DIW and centrifuged several times to ensure removal of anions. The product was dried at 60 °C and kept dried until use. The same treatment was also applied on MWCNT-10 and MWCNT-60.

2.3. Preparation of titania blocking layer

Sol preparation and deposition of blocking layer methods were discussed elsewhere [26]. Briefly, TTiP was dissolved in 1PrOH for 10 min. In another beaker, solution of 1PrOH, DIW, and HCl was added drop-wisely 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. FTO substrates were cleaned ultrasonically with detergent solution, EtOH, acetone, and DIW. The prepared sol was deposited on FTO substrates with spin coating method (3000 rpm, 30 s) and dried at 100 °C for 10 min. The coated substrates were calcined at 450 °C for 1 h.

2.4. Preparation of porous composite photoanode

The hierarchical interconnected porous photoanodes were utilized for DSC fabrication due to the advantages of existence of macro-channels which provides the high diffusion of sensitizers and redox species (especially in solid state electrolyte), besides mesoporosity which offers the high surface area necessary for sensitizer adsorption. Also, it provides a very high quality engineered interface in case of CNT incorporation thanks to direct incorporation of CNTs in initial titania sol.

The synthesis of hierarchical porous photoanodes was also previously reported [27]. The TBT was dissolved in EtOH. Then, DEA was added to the solution and stirred for 2 h. The solution of DIW and EtOH was prepared and added drop-wisely to the former solution and stirred for another 1 h. The stable colloid of each CNT samples and PEG in EtOH were added to the prepared sol and stirred for 1 h. The obtained sol was maintained for 2 h to complete the reactions. The final composition of the sol was TBT:DEA:DIW = 1:1:1 with 0.75 M concentration and 0.32 wt% CNT. The sols were deposited on FTO coated substrates with dip coating method at speed of 60 mm/min and dried at 300 °C for 10 min. The process of dip coating and drying was repeated 50 times in order to reach the desired thickness. Finally, the photoanodes were calcined at 550 °C for 1 h. It should be noted that calcination in lower temperatures led to high amount of organic residues. Furthermore, calcination in vacuum or inert gas environment should be avoided due to their negative role on titania band gap narrowing, which decreases the transparency of titania layer in visible range.

2.5. DSC fabrication

The photoanodes were placed in 40 mM $TiCl_4$ solution at 70 °C for 30 min, washed with DIW and EtOH, and then heat treated at 450 °C for 30 min. The sensitization of the photoanodes was performed by their impregnation in 0.3 mM N719 dye solution in AN:tBuOH for 24 h. Platinum decorated counter electrode was fabricated using washed FTO glass substrate. A drop of H_2PtCl_6 solution in EtOH was put on FTO glass and the substrate was heated at 400 °C for 15 min. The sensitized photoanode and counter electrode were assembled into a sandwich type cell and sealed with 25 μm thickness 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 predrilled hole. Then, the hole was sealed by Surlyn and microscope glass slide.

2.6. Characterization of the device

The infrared spectra were recorded using Fourier-transformed infrared (FTIR) spectrophotometer, Bruker TENSOR27, in transmittance mode at 400–4000 cm^{-1} with KBr as blank. Raman spectra were performed using BRUKER (SETERRA, spectral resolution <3 cm^{-1}) micro Raman spectrometer equipped with the confocal microscope. The excitation wavelength was 785 nm line of argon laser operating at the power of 25 mW. High resolution transmission electron microscope (HRTEM), Philips CM30, was applied to study the CNT sidewalls. Field emission scanning electron microscopy (FESEM), Hitachi S4160, was utilized to investigate the morphology of porous films. Atomic force microscopy (AFM), Dual Scope DS 95-200/50, was performed to investigate surface roughness of the films. X-ray diffraction (XRD), Philips X-pert pro PW1730, Cu-k_α, was conducted to study the phase structure of the photoanodes. The transmittance spectra of porous photoanodes were recorded with UV–Vis spectroscopy, PG instrument T80+, spectrophotometer. Photovoltaic measurements were performed using an AM1.5 solar simulator. The power of simulated light was calibrated to 1000 W/m^2 with Si photodiode. *J–V* curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Potentiostat Palmsense digital source meter. All the tests were conducted in room temperature. For repeatability test, two cells with the same conditions for each parameter were fabricated. Electrochemical impedance spectra of DSCs were recorded using a Potentiostat EG&G 273A analyzer. The obtained impedance spectra were fitted with Z-view software. The spectra were measured under AM1.5 illumination condition and in the frequency range of 0.1–1 MHz with oscillation potential amplitudes of 10 mV at room temperature.

3. Results and discussion

3.1. Characterization of CNTs

The suspensions of medium acid treated functionalized SWCNT, MWCNT-10, and MWCNT-60 in ethanol remained for 7 days are