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Fabrication of photoelectrode film using anodic oxidation technique for dye-sensitized solar cells

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ABSTRACT

This study uses TiO_2 nanomaterials with three different morphologies and carbon nanotubes to fabricate three layers of films for dye-sensitized solar cell (DSSC) photoelectrodes. The three layers of films with different TiO_2 morphologies include highly-ordered TiO_2 nanotubes, titania nanotubes after calcinations at 550 °C and TiO_2 nanoparticle-modified single-wall carbon nanotubes. The study compares the electron transfer performance of the prepared DSSCs are assembled by single-layer, double-layer and triple-layer films of photoanodes. After three different photoanodes are soaked in N719 dye and assembled in DSSCs, their open-loop voltage recession, electrochemical impedance, lifetime, life cycle and effective diffusion coefficient are measured. Electron transfer efficiency of photoanodes and light harvesting efficiency are further analyzed. Results show that the DSSCs prepared by three layers of photoelectrodes films have short-circuit photocurrent density 16.5 mA/cm^2, open-circuit voltage 0.835, and photoelectric conversion efficiency being as high as 8.52%. Furthermore, the electron transfer efficiency, lifetime, life cycle and effective diffusion coefficient of DSSCs assembled by triple-layer photoanodes are better than those of single-layer or double-layer photoanodes.

1. Introduction

In 1991 a Swiss scientist, Grätzel and his research team developed a new kind of solar cell, which was dye-sensitized solar cell (DSSC) [1]. This discovery was published in the journal Nature of that year. This kind of solar cell has lower photoelectric conversion efficiency than the commonly seen single-crystalline silicon or polycrystalline silicon solar cells. However, since the used working electrode of DSSC is made of titanium dioxide (TiO_2), its cost is tremendously reduced, and it has no problem of supply shortage of silicon material. Therefore, up to now, it has been extensively discussed and studied, and has entered the stage of quantitative production [2–4].

Regarding the reference about preparation of TiO_2 nanotube arrays (AOTnt), Zwilling published a paper about adoption of electrochemical anode oxidizing method to fabricate multiporous-structured TiO_2 in electrolyte with fluorine [5]. Gong published a paper about using anodizing on titanium (Ti) substrate to fabricate TiO_2 nanotube structure in HF solution, with nanotube diameter at around 100 nm and thickness at hundreds of nanometers [6]. Yang used direct-circuit (DC) magnetron sputtering to deposit pure Ti film (around 863 nm) on silicon substrate at output power 60 W and under substrate temperature 500 °C, and then employed water-based and oil-based electrolyte to carry out anodizing [7]. Their study indicated that the TiO_2 AOTnt with conversion rate greater than 100% and orderly height can be prepared. Zheng et al. attempted to reduce substrate temperature to below 300 °C under background pressure 2.0×10^{-3} Torr and output power density 1.78 W/cm^2, and carried out radio frequency (RF) sputter deposition of pure Ti thin film on tin-doped indium oxide (ITO) conductive glass [8]. Furthermore, they conducted anodizing of thin film to produce TiO_2 AOTnt. As for the references about preparation of TiO_2 Tnt by hydrothermal method, Uchida used hydrothermal method to prepare TiO Tnt with tube diameter around 8–10 nm, tube length around 100 nm, and specific surface area 270 m^2/g [9]. The Tnt was also applied to the photoanodes of DSSCs. The photoelectric conversion efficiency of the prepared cell was 2.9%. Ohsaki used hydrothermal method to prepare TiO Tnt. After further treatment, TiO_2 nanoparticles were obtained, and could be applied to photoelectrode [10]. The acquired photoelectric conversion efficiency was 7.1%.

Regarding the references about TiO_2-coated carbon nanotubes (TiO_2–CNTs), Kimi used nitric acid (HNO_3) to purify carbon

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nanotubes (CNTs) and prepare rutile TiO_2-modified carbon nanotube thin film [11]. Comparing it to the thin film with TiO_2 only, its short-circuit photocurrent density (J_{sc}) was increased by 35%, and its photoelectric conversion efficiency was enhanced by 40%. Lee used hydrogen peroxide (H_2O_2) to purify CNTs by employing sol–gel method to prepare TiO_2–CNT thin film [12]. Comparing it to the thin film with TiO_2 only, its J_{sc} was increased by 60%, and its photoelectric conversion efficiency was enhanced by 50%.

As for the references about electrochemical impedance spectroscopic (EIS) analysis of DSSC, Lin analyzed TiO_2 nanotube photoanodes by electrochemical impedance [13]. The effective electron diffusion coefficient of DSSC with N719 dyes was 9.93×10^{-5} cm^2/s, and the photoelectric conversion efficiency was 9.01%. Wu analyzed ZnO-nanowire photoanodes by electrochemical impedance. The effective electron diffusion coefficient of DSSC with N3 dye was 9.0×10^{-4} cm^2/s, and the photoelectric conversion efficiency was 0.73% [14]. Lin et al. took TiO_2-NP/Ti and TiNT/Ti as the DSSCs of photoanodes in EIS analysis [15]. The research results show that the effective electron diffusion coefficients are 5.0×10^{-5} cm^2/s and 6.3×10^{-5} cm^2/s, and the photoelectric conversion efficiencies are 4.3% and 3.3% respectively. Lin employed anodizing method to prepare TiO_2 height AOTnt on Ti plate, and transferred TiO_2 Tnt onto FTO conductive glass, intending to explore the electron transport properties of this kind of photoanode. The photoelectric conversion efficiency of the prepared DSSCs was 9.1% [16]. Since electrochemical impedance spectroscopy (EIS) can analyze the electron transport properties of different components inside DSSCs, the experiment of the study focuses on the DSSCs prepared by single-layer, double-layer and triple-layer photoanodes to carry out EIS analysis, so as to analyze the electron transport properties among different layers, including the electron transport properties of photoanodes, such as reaction rate constant for recombination, electron lifetime, charge transfer resistance relating to recombination of electron, effective electron diffusion coefficient, electron transport resistance in TiO_2, electron diffusion length, and probability of the collection of electrons by counter-electrode Pt. The study also compares the photoelectric conversion efficiency and electron transport properties of the three prepared DSSCs.

2. Experimental procedures

In the fabrication process of TiO_2 AOTnt, arc ion sputter equipment is used to coat Ti film on FTO conductive glass. After that, anodizing method is employed to produce TiO_2 AOTnt. For the coating of Ti film by arc ion sputter equipment, argon (Ar) is supplied in the process of FTO so as for shooting arc current of maximum Ti ion flux to deposit Ti metal coating. The conditions of coating process are target material Ti at purity 99.7%, work pressure 0.5 Pa, arc current 90A, supply of Ar, and deposition time 30 min. Then, anodizing is used to produce TiO_2 AOTnt. The anodized electrolyte is composed of ammonium fluoride (NH_4F), ethylene glycol (EG) and deionized water, and takes Ti plate (99.5% Ti, 0.25 cm^2) as the cathode, and FTO conductive glass of Ti-coated metal film (99.5% Ti, 0.25 cm^2) as the anode. Under the conditions of voltage 60 V and 25 °C, the electrolyte consisting of NH_4F at 0.75 wt%, EG at 99 wt% and DI at 1 wt% carries out anodizing. After reaction ends, the sample is soaked in ethanol for vibration by supersonic vibrator for 10 min to remove the electrolyte residue on the surface. After that, it is placed in high-temperature treatment furnace to carry out calcinations under 450 °C, and TiO_2 AOTnt can be acquired.

To prepare Tnt, 20 g of sodium hydroxide was placed in perfluoroalkoxy (PFA) and 50 ml of deionized water was added to prepare a 10 M NaOH solution. Then, 1.5 g of Degussa P25 powder was added to the 10 M sodium hydroxide solution. The solution was stirred at room temperature for 30 min, and then placed in an autoclave for hydrothermal treatment. Finally, the sediment was dried in an oven at 80 °C, thus yielding Tnt. Furthermore, Tnt was then calcinated by heating at 5 °C/min from room temperature to 550 °C, at which it was held for 3 h to complete the phase transformation. The calcinated sample fabricated from Tnt is referred to as Tnt-C550.

Single-walled CNT (SWCNT), with diameter of 20–30 nm and consisting of amorphous carbon and carbon-encapsulated metal nanoparticles was purified by a concentrated acid mixture, with 100 ml HNO_3 refluxing for 5 h in a silicone oil bath maintained at 150 °C. The filtrate was washed by a dilute NaOH solution and distilled water, followed by drying it in an oven at 100 °C. The sol–gel solution (SGS) was prepared by using titanium tetra-isopropoxide [$Ti(OC_3H_7)_4$], isopropanol (IPA), nitric acid (HNO_3) and distilled water (H_2O). The weight ratio for SGS preparation was kept at 1:10:1:0.2 for $Ti(OC_3H_7)_4$:IPA:H_2O:HNO_3. The solution was under reflux at the temperature of 80 °C for 1 h using a magnetic stirrer. For each sample, 0.5 g of SWCNT was mixed with 50 ml of SGS, and stirred in closed vials for 3 h. The impregnated SWCNT were separated from the solution by filtration process. The blended solution was placed in an oven for baking at 80 °C for 1 h. After that, it was sinterthermally treated in a furnace at 450 °C for 2 h, and the composite powder of TiO_2/SWCNT was acquired.

The paper takes single-layer photoanode (AOTnt film), double-layer photoanode (AOTnt–Tnt550 film) and triple-layer photoanode (AOTnt–Tnt550–TiO_2/SWCNT film) as the photoanode films for us to explore the electron transport properties. The single-layer photoanode (AOTnt film) is the TiO_2 AOTnt; the double-layer photoanode (AOTnt–Tnt550 film) is the TiO_2 AOTnt with Tnt550 coating; and the triple-layer photoanode (AOTnt–Tnt550–TiO_2/SWCNT film) is the double-layer photoanode of AOTnt–Tnt550 film coated with a layer of TiO_2/SWCNT composite powder.

Photoelectrodes were soaked in N719 dye for 24 h. After soaking for 24 h, acetonitrile was used to cleanse the surface of photoelectrodes to remove N719 dye, letting it not be absorbed on the surface of photoelectrodes, but be dried to obtain photoelectrodes of DSSCs. In addition, redox electrolyte $I^-/I3^-$ was poured into the gap of counter electrodes coated with platinum (Pt). Photoelectrodes and counter electrodes were integrated compactly, and a fish tail clip was used to fix them well in order to prevent formation of bubbles, which may form sandwich structure in DSSCs. The test of DSSCs adopted 150-W Xe light, and combined with simulated sunlight (AM 1.5) and Keithley 2400 to form I–V curve analyzer. Before test, the distance between light and specimen was adjusted, and the density of light was set at 100 mW/cm^2. Results showed the I–V curve and the data of V_{oc} (V), J_{sc} (mA/cm^2), FF and η%. The electrolyte used in the study was an acetonitrile (ACN) solution containing 0.1 M LiI, 0.05 M I_2, and 0.5 M TBP (tert-butylpyridine). A Pt counter electrode was coated on the FTO conductive glass by sputtering. The TiO_2 electrode and counter electrode were tightly bonded and fixed by a binder clip to prevent production of air bubbles, which may form a sandwich-structured DSSC. A 150 W xenon (Xe) lamp was used to simulate sunlight (AM 1.5), and an I–V curve analyzer (Keithley 2400) was used to measure the performance of the prepared DSSC. The open-circuit voltage V_{oc} (V), short-circuit photocurrent density J_{sc} (mA/cm^2), fill factor (FF), and photoelectric conversion efficiency (%) of each DSSC were also measured.

The packaged DSSCs were applied with AC voltage (mostly being sine wave signal) in a small magnitude. Electrode potential was made to cause perturbation around the balanced electrode potential. After a steady situation was achieved, the magnitude and phase of the responded current signal were measured, and impedance was further obtained. After that, according to the assumed