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Enhancing the performance of dye-sensitized solar cells based on TiO_2 nanotube/nanoparticle composite photoanodes

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ABSTRACT

Improved efficiencies in quasi solid-state and liquid state dye-sensitized solar cells (DSSCs) are achieved by constructing TiO_2-based photoanodes with nanostructures of nanotubes (NTs) and nanoparticles (NPs). High surface area, high quality, and good crystallinity of TiO_2 NTs were synthesized through a simple reflux method by using commercial P25 NPs as a precursor. The highest conversion efficiency was investigated while the composite photoanode composed of the mixture of 10% (v/v) NTs in NPs, where assembled DSSCs exhibited the conversion efficiency of 2.4% in PEGDME-based electrolyte and 10.27% in DMPII-based liquid electrolyte, with TiO_2 composite thickness of 6 μm and 12 μm, respectively, which showed improved conversion efficiency by 20.6% and 10.5% as compared to that of pure TiO_2 NP DSSC. Electrochemical impedance spectra (EIS) demonstrate that TiO_2 NTs are beneficial to improve the electron transport property as well as possess high charge collection and light harvesting and thus lead to the enhancement of the conversion efficiency.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been the subject of extraordinary attention in energy saving for the last decade since the breakthrough work achieved by Grätzel et al. in 1991 owing to their potential for developing large-area and inexpensive photovoltaics [1]. Sandwich configuration, typically consisting of a porous TiO_2 nanoparticle (NP) photoanode sensitized by a dye for absorbing sunlight, a liquid electrolyte containing an I^-/I_3^- redox couple, and a platinized counter electrode for collecting electrons as well as catalyzing the I^-/I_3^- redox couple regeneration reaction, has been widely used to explore the performance of DSSCs. While the conversion efficiencies in DSSCs exceeding 10% have been achieved based on TiO_2 NP porous network, electron transport in such porous layers is often limited because of the lack of continuous conducting pathways, with electrons diffusing by hopping mechanism between the grain boundaries of NPs [2], causing the decrease in the transport/collection rate of electrons and the increase in interfacial charge recombination between photo-generated electrons and positive species in the electrolyte [3]. In addition, the liquid electrolyte used in DSSC is still a drawback for bringing it onto market due to the problems of the possibility of leakage, evaporation of solvent, high- temperature instability and flammability [4]. Therefore, alternative quasi solid-state DSSC device based on TiO_2nanocomposites composed of one-dimensional (1D) TiO_2 such as nanotubes (NTs) [5], nanorods [6], and nanowires [7], and TiO_2 NPs have been expected to be promising substitutes to liquid electrolyte-porous NP ones. It not only emphasize the increased stability performance by againsting solvent leakage but also the improved electron transport due to the provision of large surface area to adsorb the sensitized dye in NPs and enhanced incident light harvest and direct transport pathways in 1D architectures.

It has been demonstrated that well-defined TiO_2 NTs, with the larger enhancement of the surface area without increasing the geometric area relative to other 1D nanoarchitectures, can fundamentally benefit charge transport to the conductive substrates and prolong the electron lifetimes, and subsequently produce a remarkable improvement in photocurrent density [8]. To date, several approaches have been applied to synthesize TiO_2 NT materials including the template-assisted sol-gel method, electrochemical anodization, alkaline hydrothermal technique, and methods involving chemical/electrochemical treatment of Ti films for transformation into nanotube arrays [5,9]. These methods, however, encounter their corresponding disadvantages in practice in the fabrication of large scale and high quality TiO_2 NT/NP nanocomposites for DSSCs. For example, pre-fabrication and post-removal of the templates such as anodic aluminumoxide (AAO) nanoporous membrane in template-assisted sol-gel method is essential which usually results in impurities after synthesis and leads to an increase in the cost of materials. Specific and highly expensive fabricating apparatus is needed in electrochemical anodization that seems not economically competitive. Concerning the alkaline hydrothermal

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technique, drawbacks of structural damage and non-uniform size distribution of TiO_2 NTs always result. Chemical/electrochemical treatment of Ti-metal films is also a common way to produce NTs on Ti films, but involves complex processes in synthesis and requires back-side illumination for DSSC applications [10], leading toward expensive commercialization. Reflux treatment of commercial TiO_2 powder to form titanate species under strong alkaline conditions and followed acid and calcination post-treatment to form desired TiO_2 nanostructures provide a simple but good approach to the mass production of single-crystalline, uniform, high-quality TiO_2 NTs. So far, there are however very few reports on TiO_2 NTs fabricated from reflux treatment and the obtained NT products suffer from shortcomings of the low yield and poor quality [8b,9c]. In this work, we demonstrated the successful large-scale production of high surface area, high quality, and good crystallinity of TiO_2 NTs from P25 NPs through a simple reflux method. Further, we assembled TiO_2 NT/NP composites as electrodes for DSSCs devices with quasi solid-state and ionic liquid-state electrolytes, and then systematically investigated the effect of the NT/NP ratio as well as their corresponding optimized thickness on solar cell performances. Enhanced conversion efficiency of 1.99% for pure NP cells 2.14% for the 10% (v/v) NT/NP composite cell with thickness of 12 μm were achieved with oligo-PEGDME electrolyte under 1 Sun AM1.5 illumination (100 mW cm^{-2}); noteworthy, the conversion efficiency can achieve 10.27% as replacing the oligo-PEGDME electrolyte with ionic liquid electrolyte.

2. Experimental

2.1. Materials

Fluorine-doped tin oxide glass (FTO, TEC-7, 7 Ω/sq., 2.2 mm thick) was used as the substrate for DSSC device. All chemicals were used without further purification. Acetic acid (99%), sodium hydroxide (NaOH, 99+%), tert-butanol (99%), HNO_3 (65%), polyethylene glycol (PEG, M.W. = 20,000), oligo-polyethylene glycol dimethylether (oligo-PEGDME, M.W. = 250 g mol^{-1}) and hydrochloric acid (HCl, 65%) were purchased from Merck. Lithium iodide (LiI, 99.9%), potassium iodide (KI, 99.9%), Iodine (I_2, 99%), tert-butyl pyridine (TBP, 97%), were obtained from Aldrich. $(Bu_4N)_2[Ru(4,4'\text{-}(COOH)\text{-}2,2'\text{-bipyridine})_2(NCS)_2]$ (N719) dye and1,2-dimethyl-3-propylimidazolium iodide (DMPII) were from Solaronix. Commercial TiO_2 P25 NPs (P25), titanium tetraisopropoxide (TTIP, 97%), and acetonitrile (99.99%, HPLC grade) were purchased from, Degussa, Acros, and ECHO, respectively. Surlyn 1702 Hot-melt sealant was from DuPont.

2.2. Preparation of TiO_2 NTs and NPs

TiO_2 NPs with average size of 16 nm and pure anatase structure were prepared according to the reported procedure (Fig. S1) [11]. TiO_2 NTs were prepared from a chemical reflux process. 2 g of P25 TiO_2 NPs mixed with 200 mL of 10 M NaOH solution was stirred at 110 °C for three days. The resultant precipitate was collected by centrifugation and then washed with 0.1 M HCl aqueous solution and deionized water several times until its pH value reaching 1–2. Finally, the washed precipitates were calcined at 500 °C for 30 min.

2.3. Preparation of TiO_2nanocomposite paste

The NT/NP paste was prepared by mixing the certain volume ratio of stable NP suspension with NT suspension, which can prevent from massive aggregation. TiO_2 NT suspension was prepared by thoroughly mixing 30 wt% PEG 20000 with TiO_2 NT aqueous solution which was pre-concentrated to 10 wt%. The process to fabricate NP suspension was similar to that of NT suspension. Five pastes were prepared by adding 0, 0.1, 1.0, 3.0, and 10 mL of NT suspension into 1.0 mL NP suspension, and labeled as T0P1, T0.1P1, T1P1, T3P1, and T10P1, respectively; their corresponding DSSC devices are denoted as ***Cell 1***, ***Cell 2***, ***Cell 3***, ***Cell 4***, and ***Cell 5***, respectively.

2.4. Fabrication of TiO_2 NT/NP based quasi solid-state DSSCs

The TiO_2 NT/NP nanocomposite films with the thickness of 4∼20 μm were prepared by spreading the paste onto FTO conducting glass by using the doctor blade technique and calcined at 500 °C for 30 min. The active area of the electrode was controlled at 0.283 cm^2. The TiO_2 NT/NP nanocomposite electrodes were soaked in 1:1 acetonitrile/tert-butanol solution containing N719 dye (0.3 mM) for 24 h and then rinsed with acetonitrile solution several times. The dye-adsorbed TiO_2 electrode and Pt-sputtered counter electrode were attached with hot-melt sealant of 25-μm thick. A few drops of the oligo-PEGDME electrolyte containing 1.2 M KI, 0.12 M I_2 and 0.3 M TBP were introduced into the space between these two electrodes via a pre-drilled hole on the counter electrode by using vacuum filling process. Finally, the hole was sealed by a glass slide with a sealant through the hot pressing process.

2.5. Characterizations and measurements

The morphology of as-prepared TiO_2 products was examined by JEOL 2010 high-resolution transmission electron microscope (HR-TEM) operated at 220 kV. Samples for TEM were prepared by placing a drop of products pre-dispersed into Milli-Q water by sonicating onto a copper grid with aultrathin-carbon film and subsequently evaporating the drop in oven. The surface morphologies of the as-prepared TiO_2 samples were recorded by using a Zeiss Ultraplus field-emission scanning electron microscope (FE-SEM). The crystal structure was characterized by Raman spectroscopy and X-ray powder diffraction. Raman spectra were obtained using a JOBIN-YVON T64000 Raman/PL spectrometer with a semiconductor laser of $\lambda = 532$ nm as a light source. X-ray powder diffraction patterns were recorded by a MAC M18XHF X-ray diffract meter equipped with Cu kα radiation ($\lambda = 1.5407$ Å). Specific surface areas of the TiO_2 NTs with acid and calcination post-treatment were measured by Brunauer–Emmett–Teller (BET) method through Micromeritics ASAP 2020, using nitrogen as an absorber. Solar cell conversion efficiency measurements were performed using an AM 1.5 solar simulator (91160A, Newport) as a light source and PARSTAT 2263 Advanced Electrochemical System. The light intensity was calibrated to 100 mW cm^{-2} using a reference mono-Si solar cell under 1 sun illumination. The electrochemical impedance spectra (EIS) was measured by applying the open-circuit voltage under 1 sun illumination and recorded over the frequency range of 100 kHz–100 mHz with ac amplitude of 10 mV by using a PARSTAT 2263 Advanced Electrochemical System. The total ion conductivity of electrolyte is defined and calculated as follows [12]:

$$\sigma = \frac{l}{\left|Z\right| \cdot A}$$

where σ is the total conductivity; $|Z|$ is the impedance which were measured using a symmetric FTO/Pt/electrolyte/Pt/FTO electrochemical cell under dark; l and A are the cell dimensions (length and area, respectively).

Linear sweep voltammetry was employed for measuring the diffusion-limited current. The diffusion-limited current density (J_{lim})of the electrolytes was measured using a symmetric