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High-efficiency dye-sensitized solar cells with hierarchical structures titanium dioxide to transfer photogenerated charge

Peilu Zhao [a], Shiting Yao [a], Meng Wang [a], Biao Wang [b], Peng Sun [a], Fengmin Liu [a,*], Xishuang Liang [a], Yanfeng Sun [a], Geyu Lu [a,*]

[a] College of Electronic Science and Engineering, Jilin University, PR China
[b] Changchun Institute of Optics, Fine Mechanics and Physics, PR China

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ABSTRACT

Hierarchical TiO_2 nanorod-sheet-flowers (TNRSFs) consisting of one dimensional (1D) vertically aligned rutile TiO_2 nanorods array (TNRA), 2D TiO_2 nanosheets (TNSs) and 3D TiO_2 nanoflowers (TNFs) have been synthesized via a simple NaOH-assisted hydrothermal method and employed as an photoanode for high-efficiency dye-sensitized solar cells (DSSCs). In our strategy, The TNFs layer with large thickness can potentially enable a great amount of dye adsorption and significantly strengthen the light-harvesting ability, which is beneficial for generating more charge. In addition, The TNRA and TNSs act like charge collectors, providing efficient transport pathways for electrons, which means the photogenerated charge can be collected efficiently through this conducting network. The electrochemical impedance spectroscopy (EIS) measurement shows that the TNRSF film possesses better electron transport ability and longer electron lifetime (28.4 ms) compared with the TiO_2 nanoparticals (TNPs) film. Furthermore, an overall power conversion efficiency of 8.41% (with a J_{sc} of 16.95 mA cm^{-2}, V_{oc} of 0.73 V and FF of 68%) is achieved for the DSSC based on the TNRSF photoanode, indicating a 51.8% enhancement compared with that of the TNPs photoanode (5.54%). The discoveries from this work highlight the significance of designing photoanode materials with hierarchical structures for enhanced photovoltaic performance.

1. Introduction

With the strong demand in environment-friendly and renewable energies, solar energy is now attracting global attention. Dye-sensitized solar cells (DSSCs), with advantages of simple fabrication procedures, low manufacturing cost and high theoretical efficiency, have been considered as promising candidates for next-generation solar cells [1],[2], [3] and [4]. During the last two decades, much effort has been devoted to the development of high performance of DSSCs [5], [6], [7], [8] and [9].

In a typical DSSC, light is harvested by dye molecules which are adsorbed by the photoanode materials to generate free electrons. Therefore, light-harvesting efficiency has been one of the key issues affecting the DSSC performance. Compared with designing novel dye sensitizers for absorbing a wider range of light, constructing the photoanodes to improve the amount of dye adsorption and enhance light scattering is relatively simple. Intensive researches have been proposed in order to enhance the light-harvesting efficiency of DSSCs to date [10], [11], [12], [13] and [14]. As is well known, zero dimensional (0D) TiO_2 nanoparticals (TNPs) such as P25 possesses strong dye adsorption ability because of its large specific surface area. However, The electron trap states due to impurity segregation, located at grain boundaries, are likely to be high in TNP films due to poor connectivity of the particles. 1D nanostructure with less such trap states has proven to be an effective way to facilitate electron transfer [15], [16] and [17]. However, the conversion efficiency of nanowire/nanorod-based DSSCs still stays at a relatively low level mainly due to the insufficient surface area for dye adsorption and the lack of light scattering ability. To overcome the dilemma, some strategies have been presented. For example, Joshi et al. reported that a composite made of electrospun TiO_2 nanofibers and conventional TNPs could enhance electron transport and light scattering with slight dye uptake reduction, demonstrating higher device efficiency than those made of TNPs alone [18] and [19]. Meanwhile, many researchers have worked on enhancing the surface roughness and improving the length of nanorods to increase the dye uptake. In our strategy, designing hierarchical TiO_2 photoanode nanomaterials with a light-scattering layer on the top of the electron transport layer can be widely adopted as it will

* Corresponding authors.
E-mail address: lugy@jlu.edu.cn (G. Lu).

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improve the photogenerated charge-transfer efficiency dramatically and thereby enhance the photocurrent density [20] and [21]. Although some scattering materials with high specific surface areas can provide dual-function of offering both light-scattering and large dye adsorption, they still suffer from longer electron transit time and lower effective diffusion coefficients due to the poor electrical contact between nanocrystallite domains [22] and [23].

In this work, we firstly developed a one-step hydrothermal method to directly synthesize 3D TiO_2 nanorod-flowers (TNRFs) film which was composed of 1D TiO_2 nanorods array (TNRA) and 3D TiO_2 nanoflowers (TNFs). This kind of material with unique nanostructure was applied to photoanode for DSSCs which obtained a higher photocurrent density, leading to an enhanced PCE of (6.83%) than P25 (5.54%). This is primarily attributed to the strong light-scattering ability and sufficient dye uptake of the TNFs layer. We further successfully synthesized the hierarchical TiO_2 nanorod-sheet-flowers (TNRSFs) based on the TNRF by using a NaOH-assisted hydrothermal method. The existence of 2D TiO_2 nanosheets (TNSs) can promote the electron transmit process, since TNSs establish good electrical contact between TNRA and TNFs layer, and also have tight connection with surrounding TNFs. The UV–vis reflectivity spectra indicate that the TNRSF film has higher reflectivity in the wavelength range of 400–800 nm than TNRFs film, and the UV–vis absorption spectra of the dye desorption solutions also show that the TNRSF film has excellent dye adsorption capacity. Moreover, the EIS study provides more detailed information about photoelectric properties of the cell constructed using TNRSF, demonstrating high charge-transfer efficiency and long electron lifetime. Finally, the TNRSF based cell obtains a PCE of 8.41%, exhibiting an improvement of 23.1% and 51.8% compared with cells based on TNRF and absolute TNPs film, respectively.

2. Experiments

2.1. Synthesis of the materials

All starting chemicals were analytical grade and used without further purification. The synthetic process of the 3D TNRF and hierarchical TNRSF is shown in Fig. 1, which consists of two steps,

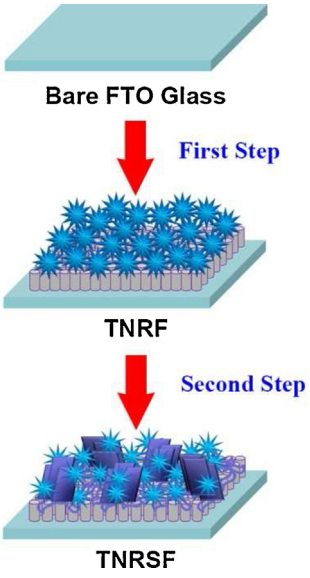

Fig. 1. Schematic illustration of the fabrication process of the hierarchical 3D TNRSF via two steps of hydrothermal reaction.

and the second step applies a NaOH-assisted route to synthesize the TNRSF. In brief, 4 mL HCl (36 wt.%) was added to 6 mL deionized water with vigorous stirring, then X mL Tetrabutyl titanate (TBT) was added into the mixed solution and stirred until form a transparent solution. The mixture was transferred into a 45 mL Teflon-lined autoclave. A piece of F-doped SnO_2 (FTO) glass (resistivity 14 Ω /square, Nippon Sheet Glass, Japan) ultrasonically cleaned in acetone and deionized water for 30 min, respectively, was placed in the autoclave which was then sealed and heated at 180 °C for 3 h. After the autoclave cooled to room temperature, the TiO_2 film grown on the FTO was washed several times with distilled water and dried in an oven at 80 °C for 6 h. To investigate the dosage of precursor TBT on the morphology and property of the product, the X value was set to 0.2, 0.3 and 0.4, while the corresponding products were denoted as TNRF-2, TNRF-3 and TNRF-4, respectively. Finally, the TNRF-X samples were calcined at 500 °C for 1 h with a heating rate of 2 °C min^{-1} in air. The TNRF-3 was selected for the next step due to its great photoelectric properties based on our previous test. The second step: generating of the nanosheets, according to our previous experience [24], we applied a simple strategy to directly convert the 3D TNRF into a novel hierarchical structure to further improve the light-harvesting efficiency and electron transport property of the film. The TNRF-3 film was placed at the bottom of the Teflon-lined which contained 30 mL of 10 M NaOH solution with the nanorods side facing up, and maintained at 180 °C for 4 h, then allowed to cool to room temperature naturally. The as-prepared sample was washed with distilled water thoroughly, and the TNRSF film was obtained by exchanging alkaline ions in sodium titanate with protons from a dilute HNO_3 aqueous solution, following a heat treatment in a muffle furnace at 500 °C for 1 h.

2.2. Fabrication of the DSSCs

To prepare a screen-printable P25 paste, 0.6 g of P25 powder was dispersed in the mixture of 10 mL of ethyl alcohol and 2 g of α- terpineol and treated with an ultrasonic bath for 60 min to form a slurry, then 1 g of ethyl cellulose and 6 g of ethyl alcohol were added to the slurry with continuous stirring for 24 h to obtain viscous white paste. The P25 paste was coated on the clean FTO glass using the doctor blade technique. After drying at 120 °C for 15 min, the P25 film was subsequently annealed at 450 °C for 30 min in air. Then the five films were immersed in a 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min before being sintered at 500 °C for 30 min. After cooling down to 80 °C, the films were loaded with dye by immersing it in a 0.4 mM dye solution (dye: N-719, solvent: t-butanol and acet-onitrile mixture with volume ratio of 1:1) for 24 h at room temperature. Finally, the dye-sensitized films were sandwiched together with the Pt-coated FTO counter electrode. The acetonitrile/valeronitrile (v/v, 85/15) electrolyte containing 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.03 M I_2, 0.1 M guanidinium thiocyanate and 0.5 M 4-tertbut-ylpyridine (Aldrich) was injected into the space between the anode and the cathode by using a vacuum back-filled method.

2.3. Measurements of DSSCs' performance

The crystal structure of the as-synthesised sample was investigated by X-ray diff ; ;raction (XRD; Rigaku TTRIII, with Cu Kα1 radiation). A filed-emission scanning electron microscopy (FESEM, JEOL JSM-7500F, operated at an acceleration voltage of 15 kV) and a transmission electron microscopy (TEM, JEOL EM-2100, using an acceleration voltage of 200 V) were employed to characterize the morphological and structural properties of all the samples.