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TiO_2 Seed Layer for Improving the Morphology and Photovoltaic Performance of Single-Crystal Rutile TiO_2 Nanorod Arrays

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Abstract: TiO_2 seed layer was introduced to improve the morphology of single-crystal rutile TiO_2 nanorod arrays (TNRs) and the cell performance of single-crystal rutile TNRs based dye-sensitized solar cells (DSCs). TiO_2 seed layer was prepared on the conductive side of fluorine doped tin oxide (FTO) glass through spin-coating of a TiO_2 colloid solution followed by annealing in a furnace. The single-crystal rutile TNRs were synthesized on bare and TiO_2 seed layer coated FTO glass, respectively, through hydrothermal synthesis. It was found that TiO_2 seed layer reduced the diameter of TiO_2 nanorod from about 100 nm to about 50 nm, and increased the density of TNRs from about 16 μm^{-2} to about 140 μm^{-2}, which resulted in about threefold increase of roughness factor of TNRs. Correspondingly, the power conversion efficiency (η) of TNRs based DSCs increased from 0.52% to 0.71%, and a η of 1.74% was obtained after $TiCl_4$ modification.
Key words: Titanium dioxide nanorod arrays; Seed layer; Morphology, Dye-sensitized solar cell; Cell performance.

1. Introduction and Experimental:

Thin films made of vertically aligned one-dimensional TiO_2 nanostructures, such as nanotube arrays[1], nanowire arrays[2], and nanorod arrays[3], could provide un-interrupted electrical pathways for photogenerated electrons in dye-sensitized solar cells (DSCs)[4]. Therefore, they are proposed to increase the electron transport rate and improve the cell performance of DSCs [5]. In recent years, single-crystal TiO_2 nanorod/nanowire arrays directly on fluorine-doped tin oxide (FTO) glass were synthesized through hydrothermal method[4,6], which could be directly used as photoanodes for DSCs after sensitization. In our investigation, TiO_2 seed layer was introduced to improve the morphology of single-crystal rutile TiO_2 nanorod arrays (TNRs) grown on FTO glass and the cell performance of single-crystal rutile TNRs based DSCs.

TiO_2 seed layer was prepared by coating a TiO_2 colloid solution onto the conductive side of FTO glass using a spin coater, followed by annealing in a furnace. The TiO_2 colloid solution was prepared as follows:

0.3500 g of titanium butoxide (99% by weight, ACROS, USA) was added dropwise into the mixture of 10 mL of absolute ethanol and 2 mL of acetic acid (99.5% by weight), subsequently the obtained solution was stirred for 2 h at room temperature in a sealed beaker. After the as-prepared solution was aged for 24 h at room temperature, a homogeneous and stable coating colloid solution was obtained. The obtained coating colloid solution was coated onto the conductive side of FTO glass using a spin coater (KW-4A, CAS, China), at the rate of 3000 rpm for 30 s. After annealing at 500 ^{0}C for 30 min in a program-controlled muffle furnace, TiO_2 seed layer were obtained. And then, single-crystal rutile TNRs were synthesized on bare and TiO_2 seed layer coated FTO glass, respectively, through a hydrothermal method, and the hydrothermal synthesis process has been reported in our previous publication[3].

After sensitization, immersion in a 0.3 mM tert-butanol/acetonitrile (1:1) solution of dye N-719 at room temperature for 36 h, they were used as photoanodes to assemble DSCs. Platinized FTO glass used as counter electrode (CE) was placed on the top of the dye-sensitized photoanode sealed with a 30-μm thick thermal adhesive film, and the electrolyte was filled into the space between the photoanode and the CE from a hole made on the CE. After sealing the hole, DSCs assembly was completed. The active area of DSCs is 0.25 cm^2.

2. Results and Discussion

2.1 Morphology and Structure

The morphology of the prepared TNRs synthesized on bare and TiO_2 seed layer coated FTO glass (named as B-TNRs and S-TNRs, respectively) were characterized by a field-emission scanning electron microscope (FE-SEM, FEI Sirion-200, USA), and their crystal structures were examined by X-ray diffraction (XRD) using a X-ray diffractometer (Philips X'pert, NLD) with Cu Kα radiation (λ=1.5418Å). Transmission electron microscopy (TEM), high-resolution TEM (HR-TEM) and selected-area electron diffraction (SAED) analyses were performed on a high-resolution transmission electron microscope (JEOL JEM-2010, Japan).

FE-SEM images of the samples B-TNRs and S-TNRs are shown in Fig. 1. The top views of B-TNRs (Fig. 1A) and S-TNRs (Fig. 1C) show that the FTO substrates are uniformly covered with TiO_2 nanorods. The cross-sectional views of the two samples (Fig. 1B and Fig. 1D) show that TiO_2 nanorods are nearly vertical to the FTO glass and the average nanorod lengths of B-TNRs and S-TNRs are about 3.6 and 3.0 μm, respectively. In addition, some differences of B-TNRs and S-TNRs could be observed in Fig. 1. The diameter of TiO_2 nanorods of S-TNRs is decreased obviously and the density of nanorod arrays is increased significantly, the density of TNRs is increased from 16 per square microns (B-TNRs) to 140 per square microns (S-TNRs), which means that TiO_2 seed layer could decrease the diameter of TNRs and increase the density of TNRs significantly.

On the other hand, comparing Fig. 1B and Fig. 1D, the vertical orientation of the sample S-TNRs is improved obviously by TiO_2 seed layer, and this result could be confirmed by XRD patterns of the two samples shown in Fig. 2. Firstly, the XRD patterns of the two samples agree well with the tetragonal rutile phase (JCPDS No. 89-4920), which indicates that the phases of B-TNRs and S-TNRs both are rutile. Secondly, the (002) diffraction peak of S-TNRs is sharp and its relative intensity is significantly enhanced compared to that of B-TNRs, which indicates that the TiO_2 seed layer conduces to the directional growth of the TiO_2 nanorods. This result is consistent with the FE-SEM images and it is a positive factor for electron transport in TNRs.

HRTEM and SAED patterns of the samples B-TNRs and S-TNRs are shown in Fig. 3. The sharp two-dimensional lattice images and SAED images confirmed that the TiO_2 nanorods of B-TNRs and S-TNRs are single crystalline. The nanorod diameter of B-TNRs is about 80 nm, and that of S-TNRs is about 40nm, which indicates that TiO_2 seed layer could decrease the diameter of TiO_2 nanorods significantly, and it agrees well with the results of FE-SEM images. Considering the densities of B-TNRs and S-TNRs obtained from FE-SEM images, the roughness factors (defined as the total surface area per unit substrate area) of B-TNRs and S-TNRs could be estimated to be around 19 and 68, respectively, which means that TiO_2 seed layer could increase the roughness factor and surface area of TNRs significantly. As a result, the dye adsorption of TNRs would increase obviously, which could lead to the improvement of cell performance of TNRs based DSCs.

2.2 Cell Performance

The photovoltaic performance of DSCs was derived with a Keithley 2420 digital source meter under irradiation of a solar simulator (AM 1.5, 100 mW/cm^2), and the Photocurrent–photovoltage (J–V) curves and photovoltaic parameters are shown in Fig. 4. The power conversion efficiency (η) of B-TNRs based DSC and S-TNRs based DSC are 0.52% and 0.71%, respectively, which means that TiO_2 seed layer could improve the cell performance of TNRs based DSCs obviously. In order to further improve the cell performance of TNRs based DSCs, the sample S-TNRs was post-treated through $TiCl_4$ treatment according to the previous work[4]. After $TiCl_4$ treatment, the η of DSCs based on post-treated S-TNRs (S-TNRs-M) reached 1.74%.

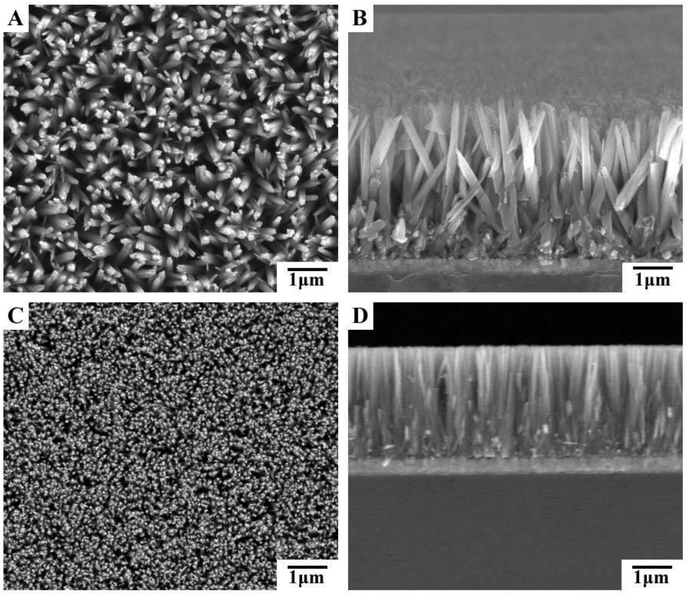

Fig. 1. FE-SEM images of B-TNRs, (A) Top-view and (B) cross-sectional view; FE-SEM images of S-TNRs, (A) Top-view and (B) cross-sectional view.

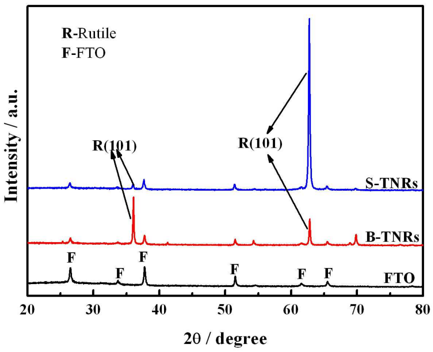

Fig. 2. XRD patterns of FTO glass (FTO), B-TNRs, and S-TNRs.

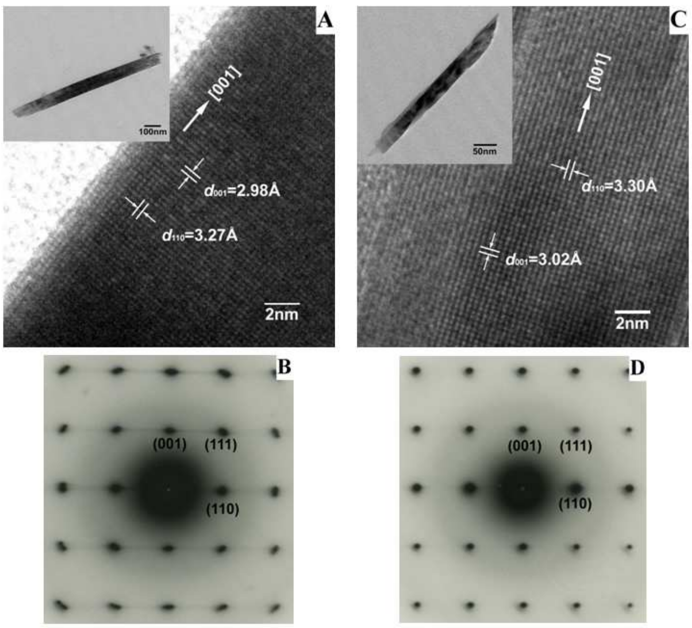

Fig. 3. HRTEM images of an individual nanorod of the sample (A) B-TNRs and (C) S-TNRs SAED images of an individual nanorod of the sample (B) B-TNRs and (D) S-TNRs.

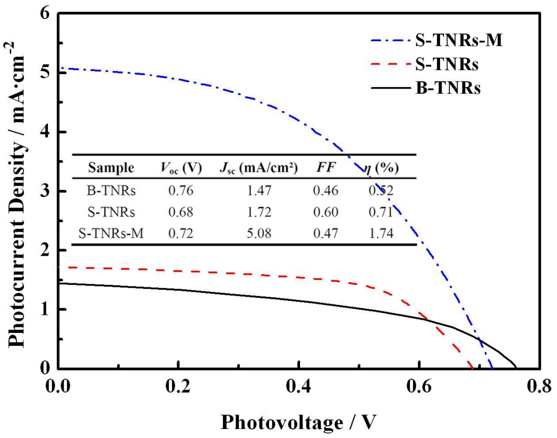

Fig. 4. *J–V* curves and photovoltaic parameters of the DSCs based on B-TNRs, S-TNRs, and S-TNRs-M.

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