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Facile non-hydrolytic solvothermal synthesis of one dimensional TiO_2 nanorods for efficient dye-sensitized solar cells

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ABSTRACT

One dimensional rod shaped TiO_2 nanostructures were successfully synthesized by a simple non-aqueous, alcoholysis based solvothermal process. Anatase TiO_2 nanorods (TiO_2 NRs) exhibited a surface area of 109.79 m^2/g with particle length and diameter of ~30–50 nm and ~10–15 nm (from SEM data), respectively. The photovoltaic performance of TiO_2 nanorods based electrode was investigated in the dye-sensitized solar cell (DSSC). The device based on TiO_2 NRs electrode exhibited an excellent short-circuit current density (J_{sc}) of 17.75 mA cm^{-2} and an open-circuit voltage (V_{oc}) of 0.75 V under 1 Sun AM 1.5 G solar light. Due to high dye loading, good light harvesting and fast electron transport, the optimal conversion efficiency (9.21%) of the DSSC fabricated from TiO_2 NRs was significantly higher than that of the commercial DP-25 TiO_2 nanoparticles based cell (6.43%).

1. Introduction

The development of photovoltaic devices has been considered as one of the effective ways to meet the demand of energy consumption problem. In particular, dye-sensitized solar cell (DSSC) technology is a promising candidate owing to its low cost and high energy conversion efficiency [1–3]. Conventionally, TiO_2 nanoparticles with a size of ~20 nm have been widely used as photoanode materials due to their excellent surface areas for dye loading [4,5]. High surface area, fast electron transport with reduced charge recombination and efficient light harvesting capacity are the key essentials for good photoanode materials. Alternatively, one dimensional TiO_2 nanostructures such as nanotubes, nanorods, nanowires and nanofibres have attracted much attention, which facilitate to improve the electron transport, reduce trapping of electrons and enhance light harvesting efficiency [6,7]. However, compared to direct deposition of TiO_2 nanoparticles on FTO, directly grown nanotubes, nanowires or nanorods on Ti/FTO substrates attain a lower efficiency which was attributed to decreased specific surface area [8,9]. The synthesis and application of one-dimensional TiO_2 nanocrystals as photoanodes in DSSCs have been found not only to enhance the electron transport process, but also to improve dye loading by increasing surface area. Recently, Rui et al. prepared TiO_2 nanorods with large surface area by hydrothermal treatment of water soluble peroxotitanium acid and obtained a conversion efficiency of 7.28% and enhanced electron transport properties [10]. Non-hydrolytic synthesis using an alcoholysis route led to the formation of TiO_2 nanocrystals with uniform size, well-defined morphology and good crystallinity. Hydrolysis reaction rate can be well controlled to regulate the growth of monodispersed TiO_2 nanoparticles [11,12].

In the present work, we report the synthesis of anatase TiO_2 nanorods *via* a simple one-step solvothermal method using titanium (IV) isopropoxide in the presence of isopropyl alcohol and acetic acid. The obtained TiO_2 nanorods (TiO_2 NRs) possess large surface area leading to high dye adsorption. The TiO_2 NRs photoanode based DSSC achieved an excellent conversion efficiency compared to the cell using commercial DP-25 nanoparticles.

2. Experimental

In a typical synthesis, 0.05 mol of titanium (IV) isopropoxide (TTIP) was added to 50 mL isopropyl alcohol (IPA) under mechanical stirring for 10 min. Subsequently, 6 mL acetic acid (AcOH) was added into the mixture and continued stirring for 2 h. The resulting transparent solution was transferred to a 250 mL Teflon-lined stainless steel autoclave and maintained at 150 °C for 8 h. The obtained solution containing white precipitates was washed with ethanol three times and finally dried at 110 °C to obtain TiO_2

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NRs. To prepare TiO_2 paste, 0.8 g of TiO_2 powder (TiO_2 NRs or DP-25 TiO_2) were mixed with 10 mL of ethanol, stirred and sonicated for 5 min. Terpineol (3.245 g) and ethyl cellulose (10 cP, 0.24 g) in ethanol mixture were added into the above solution and sonicated for 5 min each. Finally, the ethanol was evaporated and the paste was rolled using a three-roller miller. The preparation of TiO_2 photoanodes and the cell fabrication procedures can be found in our previous work [13]. The thickness and the active area of TiO_2 film were approximately 14 μm and 0.16 cm^2, respectively.

Structure and morphology of the samples were investigated with X-ray diffraction (XRD, Rigaku PANalytical X'Pert PRO), Raman spectroscopy (Micro-Raman, RENISHAW), field emission scanning electron microscope (FESEM, S-4800, Hitachi), transmission electron microscope (TEM, H-7100, Hitachi) and spherical-aberration corrected field-emission scanning transmission electron microscope (Cs-corrected FE-STEM, JEM-ARM200FTH, JEOL). The surface area of TiO_2 films (powder peeled off from FTO substrates) were obtained using a nitrogen adsorption surface area analyzer (Micromeritics ASAP 2020). The photovoltaic characteristic methods and dye adsorption analyzes were presented elsewhere [13]. The electrochemical impedance spectroscopy (EIS, IM6ex) was carried out using a Zahner electrochemical workstation under illumination with a frequency ranging from 100 mHz to 100 kHz at 10 mV amplitude.

3. Results and discussion

X-ray diffraction patterns of the TiO_2 NRs powder and its corresponding film are shown in Fig. 1a. All diffraction peaks are assigned to tetragonal crystal structure of anatase phase TiO_2 [JCPDS 021-1272]. The diffraction peaks marked with "♦" symbol on TiO_2 film sample are ascribed to SnO_2 from FTO glass. The crystallite size calculated based on (101) diffraction peak is ~10 nm. The lattice constants of TiO_2 crystallites are $a=3.786$ Å; $c=9.469$ Å. The (004) diffraction peaks both in TiO_2 powder and TiO_2 film samples appear sharp, indicating the anisotropic crystal growth of anatase TiO_2 lattice along the c-axis [10]. Fig. 1b illustrates the Raman spectra for TiO_2 NRs powder and film. The characteristic Raman modes at 148.3 (E_g), 198.6 (E_g), 400.0 (B_{1g}), 517.9 (A_{1g}) and 641.8 (E_g) cm^{-1} are well matched with the active modes ($A_{1g}+B_{1g}+3\,E_g$) of anatase TiO_2. These results are in good agreement with the XRD data.

The morphology of TiO_2 powder obtained after autoclave reaction was analyzed by electron microscopy. The FESEM image (Fig. 1c) resembles the morphology of rod-shaped TiO_2 nanostructures, closely packed with randomly oriented arrangement of nanorods of about 40–50 nm in length and 5–10 nm in width. Fig. 1d displays the FESEM image of TiO_2 film coated on FTO glass after annealing. It reveals the compactly arranged uniform rod shaped nanostructures. TiO_2 film remains the same structure, with a slightly altered size of about 35–40 nm in length and 10–15 nm in width. The precise morphological and internal crystalline structure analyzes were further investigated by TEM/HRTEM and SAED. Nearly well dispersed rod shaped or spindle like TiO_2 nanostructures were observed from TEM image (Fig. 2a). The average length and width of nanorods are ~30–50 nm and ~10–15 nm, respectively, which are consistent with the SEM images. Lattice fringes of individual nanorod are clearly viewed from HRTEM image (Fig. 2b). The lattice spacing of 0.35 nm can be indexed to (101) plane of anatase phase TiO_2, resulting a crystal growth along [001] direction [14]. The rings observed in SAED pattern (Fig. 2c) are well matched with the anatase phase. The esterification reaction between isopropyl alcohol and acetic acid leads to the release of hydroxyl groups, which favoring the homogeneous hydrolysis reaction of metal oxide precursor. The anisotropic rod like crystal growth of TiO_2 can be attributed to the chelating effect of AcOH on the TiO_2 surface [15].

The Brunauer–Emmett–Teller (BET) surface area of rod shaped nanocrystals obtained from TiO_2 film is 109.79 m^2/g, which is

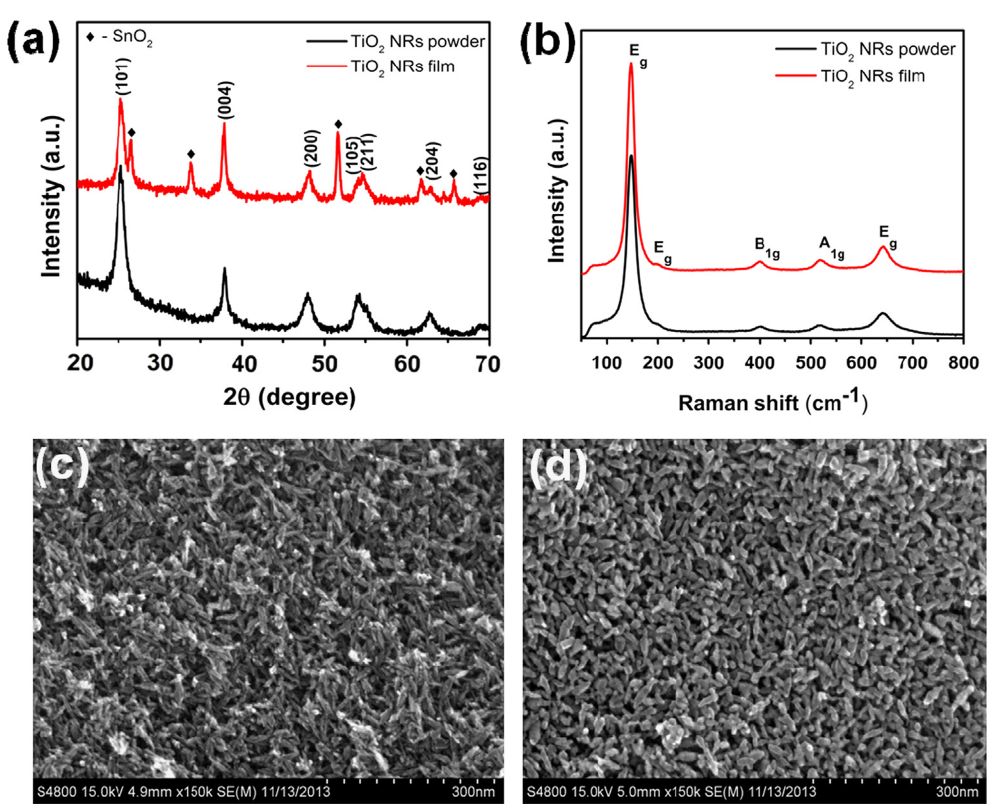

Fig. 1. (a) XRD pattern, (b) Raman spectra, and (c and d) SEM images of TiO_2 NRs powder and film.