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Hydrothermal synthesis of well-aligned hierarchical TiO_2 tubular macrochannel arrays with large surface area for high performance dye-sensitized solar cells

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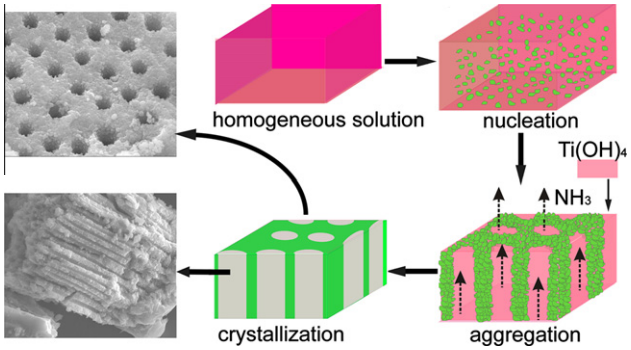
HIGHLIGHTS

- Well-aligned hierarchical TiO_2 tubular macrochannel arrays were fabricated by a hydrothermal method.
- Hierarchical TiO_2 tubular materials possess a high surface area and macro-mesoporous structure.
- Solar cells made of hierarchical TiO_2 tubular materials exhibited a high efficiency of 8.10%.

GRAPHICAL ABSTRACT



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ABSTRACT

Well-aligned hierarchical TiO_2 tubular macrochannel arrays (HTTMAs) with high surface area have been synthesized via a facile one-step ammonia hydrothermal synthesis process without using any structure-directing templates. The typical samples are made of an assembly of macrochannels with uniform openings centered at 2.2 μm and a channel density of 1.7×10^7 cm^{-2}. The interconnected macro-mesoporous samples possess a high surface area of 229.6 m^2 g^{-1} and main pore size centered at 4.1 nm. Powder X-ray diffraction and transmission electron microscopy demonstrated that the samples had a mixture of rutile and anatase phases. The light scattering properties of samples were studied by UV–Vis spectrometer in the 350–800 nm wavelength range. Dye-sensitized solar cells made of HTTMAs showed an energy conversion efficiency of 8.10% under AM1.5 illumination, which was much higher compared to that (6.24%) of cells consisting of P25 nanoparticles with the same film thickness.

1. Introduction

As an important functional semiconductor material, titania has received much attention for multiple applications such as dye-sensitized solar cells (DSSCs) [1–5], photocleavage of water [6], photocatalysis [7] and chemical sensors [8]. It is well known that the properties of TiO_2 materials are strongly related to the control of desired morphology, specific surface area, composition, size, crystallinity and porosity for various applications mentioned above [9]. TiO_2 materials with diverse morphologies, such as mesoporous films [10], spheres [11], beads [12], wires [13,14], rods [15,16], submicro-rings [17], as well as tubular structures [18–28], have been reported in recent years. Of particular interest are tubular structures which may contribute simultaneously to the extension of porosity, specific surface area, electrical transport and light absorption. Various synthetic approaches, such as the alkali

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hydrothermal method [18–20], structural-directing agent or template-assisted approaches [21–24], self-rolled strained heterofilms [25], electrochemical anodic oxidation [26,27], and multifluidic electrospinning method [28], have been developed to synthesize TiO_2 tubular structures. The alkaline hydrothermal method has been intensively investigated in an effort to produce TiO_2 nanotubes. However, it is a relatively complex procedure requiring at least three steps: (1) hydrothermal synthesis of the alkaline titanate nanotubes; (2) ion-exchange (3) dehydration reactions [18–20]. Furthermore, oriented TiO_2 tubular arrays may find more applications due to the three-dimensional orientation structure. So far, typical synthesis of oriented TiO_2 tubular arrays has to rely on AAO template or electric field assistant (anodic oxidation).

In this work, we present a facile one-step hydrothermal method for the synthesis of well-aligned hierarchical TiO_2 tubular macrochannel arrays (HTTMAs) without template or electric field assistant. Moreover, HTTMAs are also hierarchical structures consisting of a lot of macrochannel arrays with uniform openings centered at 2.2 μm and a high surface area of 229.6 $m^2 g^{-1}$. For the application in DSSC, HTTMAs, composed of two levels of structuring in nano and macro length scales, are considered to make significant contributions not only to increasing the specific surface area for dye loading but also to enhancing light absorption due to light scattering structure [11,12]. In addition, HTTMAs are expected to decrease the resistance of electrolyte diffusion via the macrochannel structure, compared to the mesoporous structure or nanotube array films. Applying HTTMAs in DSSC, an overall energy conversion efficiency up to 8.10% has been achieved.

2. Experimental

2.1. Synthesis of HTTMAs samples

In a typical synthesis, 1 ml titanium butoxide (A.R., Fluka) was added to a Teflon-lined autoclave (100 ml) containing 30 ml of 25% (w/w) $NH_3{\cdot}H_2O$ (A.R., Beijing Beihua Fine Chemicals Co., Ltd.) and 30 ml deionized water under vigorous stirring at ambient temperature. Afterward, the autoclave was sealed and then hydrothermally heated at temperature of 150 °C for 1–12 h, then cooled to room temperature. Finally, the samples were washed with deionized water and dried at 60 °C.

2.2. Preparation of TiO_2 films and DSSCs

To prepare the screen-printable TiO_2 paste, 12 g of HTTMAs powder was mixed with 2 ml of acetic acid, 50 g of terpinol (anhydrous, #86480, Fluka), 6 g of ethyl cellulose powder (30–50 mPas, #46080, Fluka) and 100 ml of ethanol. Then, this mixture of raw materials was ground mechanically in a planetary ball mill using zirconia grinding media at 600 rpm for 12 h. Finally, the obtained slurry was concentrated by rotary-evaporator to remove ethanol and water. As a comparison, the screen-printable paste made from commercially available TiO_2 nanoparticles (P25, Degussa AG) was also prepared by the same procedure.

A layer of TiO_2 paste was coated on fluorine-doped tin oxide (FTO) conductive glass (14 Ω/square, Nippon Sheet Glass Co., Ltd.) by screen-printing procedure, and then dried at 125 °C for 6 min. This coating and drying procedure was repeated until a desired thickness of TiO_2 film was obtained.

The electrodes coated with TiO_2 films were annealed at 500 °C for 30 min in air. After that, the electrodes were immersed in a 0.05 M $TiCl_4$ aqueous solution at 70 °C for 30 min, then rinsed with deionized water and annealed at 500 °C for 30 min. After cooling to 80 °C, the TiO_2 electrodes were immersed in 5×10^{-4} M ruthenium bipyridyl dye (N719, Solaronix) in 1:1 volume ratio of ethanol and acetonitrile. The counter electrodes were produced by thermal decomposition of 5 mM H_2PtCl_6 from isopropanol on FTO glass and calcined at 380 °C for 20 min. The photoanode and counter electrode were assembled and sealed as a sandwiched cell by using a surlyn spacer (25 μm thick, DuPont). The electrolyte, consisting of 0.5 M LiI, 0.05 M I_2, 0.6 M N-methylbenzimidazole, 0.1 M guanidinium thiocyanate, and 0.5 M tert-butylpyridine in acetonitrile, was also introduced into the DSSC by a vacuum filling method.

2.3. Characterization

The crystal structure of the as-synthesized HTTMAs materials was analyzed using X-ray diffraction (XRD, Bruker) with CuKα radiation. The morphology of HTTMAs samples was observed by a thermal field emission environment scanning electron microscope (FESEM, Quanta 400). Transmission electron microscopy (TEM) observations were carried out with a high-resolution transmission electron microscope (JEOL, JEM-2010). The absorption and diffuse reflection spectra were obtained using an UV–Vis–NIR spectrometer (Hitachi U-4100) equipped with an integrating sphere. The pore characteristics were analyzed by a nitrogen adsorption–desorption apparatus (Belsorp mini II, Bel Japan, Inc, Japan). The film thickness was characterized by the 3D optical profiling system (Wyko NT1100). Current–voltage (*I–V*) characteristics of the solar cells were recorded by using a digital sourcemeter (Keithley, 2400) under simulated AM 1.5 sunlight with an output power of 100 mW cm^{-2} produced by a solar simulator (Oriel-Newport, 91192). A 0.188 cm^2 active area was defined by a hole punched through the surlyn frame and was additionally masked from illumination by black shadow mask to the same size.

3. Results and discussion

3.1. HTTMAs characteristics

Fig. 1 shows the XRD patterns of as-synthesized HTTMAs samples obtained at 150 °C for 12 h. The samples exhibit the crystal structure of mixtures of rutile and anatase phase according to two sets of measured diffraction lines. One set of diffraction peaks can be indexed to the (112), (204), and (224) planes of anatase phase (JCPDS 83-2243). The other set of diffraction lines are attributed to the (110), (200) and (301) planes of rutile structure (JCPDS 76-0318). Furthermore, trace amounts of brookite phase ((020) reflection at $2\theta = 32.85°$) is also observed.

Fig. 2 shows the FESEM image of the as-prepared HTTMAs samples. It could be seen that the typical samples are made of an assembly of macrochannels with uniform openings centered at 2.2 μm, a thickness up to 96 μm, and a channel density of

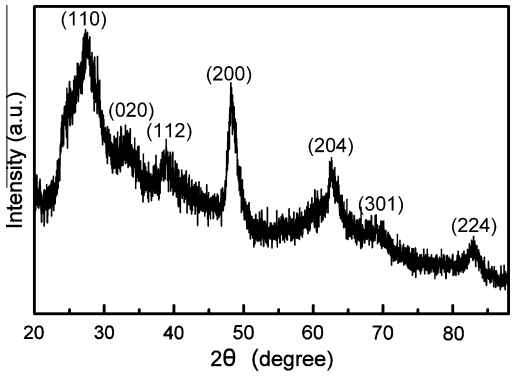

Fig. 1. XRD pattern of as-synthesized HTTMAs films after 12 h of hydrothermal reaction at 150 °C.