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Controlled synthesis of TiO_2-B nanowires and nanoparticles for dye-sensitized solar cells

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ABSTRACT

Controllable synthesis of the TiO_2-B nanowires (NWs) and nanoparticles (NPs) had been achieved via a facile hydrothermal route, respectively, only by tuning the solution volume. The dye-sensitized solar cells prototypes had been fabricated using TiO_2-B NW and NP electrodes, respectively. The TiO_2-B NP cells had higher photocurrent and photoelectrical conversion efficiency than the TiO_2-B NW cells though the latter exhibited larger photovoltage compared to the former. The key factors such as the photogenerated electron injection drive force, surface defects and the interfacial charge transfer, which determined the photoelectrical properties, had been systematically researched with the surface photovoltage spectra (SPS) and the electrochemical impedance spectra (EIS). The SPS proved that there was larger photoelectron injection drive force in TiO_2-B NP photoelectrode than that in NW photoelectrode. And the electrochemical impedance spectra (EIS) revealed that TiO_2-B NP cells had faster interface charge transfer compared to TiO_2-B NW cells. Both proved that NP cells had the higher photocurrents.

1. Introduction

Since the outstanding work by Grätzel et al. in 1991, dye-sensitized solar cells (DSSCs) have attracted extensive attention in recent 18 years due to their low fabrication cost and high efficiency compared to silicon solar cells [1–4]. The conventional DSSCs are composed of anatase TiO_2 photoelectrode, polypyridyl ruthenium dye, redox shuttle electrolyte and Pt counter electrode [5]. The semiconductor photoelectrode is a key component of DSSC, whose properties determine the photogenerated electron transport and dye adsorption. Anatase TiO_2 nanoparticle (NP) film is an excellent starting photoelectrode for DSSCs due to its easy fabrication, minimal cost and control over light scattering. But the primary weakness of the small electron diffusion coefficient limits the random walk of electrons through the NP film to the millisecond timescale [6,7].

Recently, one-dimensional (1-D) semiconductor photoelectrodes have been becoming research focus because they possess several attractive features including low cost, scalability, and accelerated electron transport. Several DSSCs works based on ZnO NW electrodes have been developed since 2005 [8–10]. Yang and co-workers fabricated a dense array of oriented, crystalline ZnO nanowire (NW) film in replace of nanoparticle photoelectrode. And the electron transfer through the DSSCs was faster than TiO_2 or ZnO nanoparticle films in operating cells (several hundred times). But the ZnO photoanodes show consistently lower performance than similar TiO_2 devices, primarily due to the instability of ZnO in acidic polypyridyl ruthenium solution. One-dimensional TiO_2 photoanode is still the main research aspect for its acidic-stability and rapid electron transport [11–13]. Adachi et al. used one-dimensional titania nanowire thin-film electrode to fabricate DSSCs, which had a highly full sun efficiency because of rapid electron transfer through nanowire film. But the synthesis method was so complex that it would limit its large-scale applications [11]. Synthesizing different polymorphs and dimensions of titania via simple methods and elucidating the photoelectron transfer mechanism for DSSCs were still promising works.

There are eight polymorphs of TiO_2 materials. Among these, anatase, rutile and brookite have already been employed in DSSCs, photocatalytic activity, hydrophilicity, etc [14–16]. A more exotic polymorph TiO_2-B, which is composed of edge and corner sharing TiO_6, has attracted attention as a prospective lithium electrode, humidity sensor, and supercapacitor [17–20]. It was well known that TiO_2-B NWs and nanotubes (NTs) could be obtained through the hydrothermal reaction between TiO_2 NPs and concentrated NaOH aqueous solution. Due to its tunnel structure for excellent ion intercalation and a slightly lower density than rutile, anatase and brookite, TiO_2-B material should play an important role in various application areas [21]. Gao et al. synthesized TiO_2-B nanotubes, anatase nanorods, and anatase nanoparticles, and the I–V characters of anatase DSSCs and interfacial electron transfer had been studied by the electrochemical impedance spectra (EIS) [22]. However, until now the literature lacks more reports of TiO_2-B DSSCs. Pan et al. and Asagoe et al. reported some TiO_2-B DSSCs work. But the mechanism for the enhanced η has not been clearly eluci-

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dated [23–25]. Thus, synthesizing TiO_2-B nanostructure via simple methods and clarifying the mechanism for the enhanced η are still promising works.

On the basis of the above consideration, we successfully prepared TiO_2-B NWs and NPs via a simple hydrothermal method, respectively. The morphologies of TiO_2-B could be easily controlled by tuning the solution volume. The photocurent–photovoltage properties of DSSCs based on TiO_2-B NPs and NWs had been systematically researched. And the determining factors of optoelectronic properties, such as surface states, the photogenerated electron injection drive force and interface charge transfer had been studied by the surface photovoltage spectra (SPS) and the EIS, respectively. This work will assist in understanding the photogenerated electron transport mechanism of TiO_2-B NW and NP and extend the TiO_2-B nanomaterial applications.

2. Experimental

2.1. Chemicals

The commercial TiO_2 powder (P25, Degussa), dense hydrochloric acid (37%, A. R.), sodium hydroxide (A. R.), ethanol (A. R.), Triton X-100 (A. R.) and acetylacetone (A. R.) were purchased from standard sources and used as received. The transparent conducting glass (TCO, F-doped SnO_2 layer, sheet resistance is 20 Ω/square) was used as received for film electrode substrate. The used polypyridyl ruthenium dye was cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II)bis-tetrabutylammonium (also called N719, Solaronix SA). The redox shuttle electrolyte was composed of 0.1 M LiI (anhydrous, 99%, Acros), 0.05 M I_2 ($\geq$99.8%, A. R.), 0.5 M tert-butylpyridine (99%, Aldrich) and 0.6 M N-methybenzimidazole (99%, A. R.) in 3-methoxypropionitrile (99%, A. R., Fluka).

2.2. Synthesis of TiO_2-B NWs and NPs

TiO_2-B NWs were prepared by adding 3 g of P25 powder to 16 ml of 15 M NaOH aqueous solution. After the solution was stirred for 1 h, the resulting suspension was transferred into a Teflon stainless steel autoclave of volume 20 ml. After heating at 170 °C for 72 h and cooling down to room temperature, the product of hydrothermal reaction was recovered by centrifugation and washed with 0.05 M HCl and ethanol several times until pH 7. Finally, this product was annealed to 450 °C for 5 h. The synthesis conditions for the NPs were similar to those used for the NWs, the only difference was the used solution volume of 13 ml. More solution volume contributed to NWs formation. Acid washing produced layered hydrogen titanates which were known to transform into TiO_2-B after heating. The synthesis conditions were similar to the report of Armstrong et al. with only a slight change of NaOH content [14].

2.3. Fabrication of dye-sensitized TiO_2-B NW and NP electrodes and the assembly of DSSCs

TiO_2-B paste for the fabrication of photoelectrodes was obtained by homogeneously mixing 2 ml distilled water, 5 drops of Triton X-100, 2 drops of acetylacetone and 1 g of TiO_2-B NWs or NPs, respectively. A doctor-blade technique was used to fabricate the electrodes on a TCO substrate. A thin film was obtained using a glass rod to scrape off the excessive paste. After air-dried for 30 min, they were sintered at 450 °C (ramping rate 2 °C) for 30 min. TiO_2 electrodes had been obtained after 3 times repetitive coating on the cooled down sintered film electrodes. The thickness of TiO_2 film was estimated to be 5 μm by scanning electron microscope (SEM) image. The TiO_2-B NW and NP electrodes were sensitized by immersing in 0.5 mM N719 dye solution for 12 h, respectively.

The counterelectrode was prepared following previous publications [26]. The dye-sensitized TiO_2-B NW or NP electrodes with Pt counter electrode were adhered together using epoxy resin, respectively. The space between the electrodes was filled with the electrolyte by capillary action.

2.4. Characterization

The transmission electron microscopy (TEM) images of TiO_2-B NWs and NPs were recording using JEM-3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. Carbon-coated copper grids were used as the sample holders. Raman spectra were recorded with a HR 800 micro-Raman spectrometer (Jobin Yvon, France) excited by an argon ion laser with a wavelength of 457.9 nm. The X-ray diffraction (XRD) patterns were recorded on a D/Max-2550 γA X-ray diffractometer (Rigaku, Japan) using Cu Kα radiation with wavelength of $\lambda = 0.15406$ nm. The SPS were carried out on a laboratory-built surface photovoltage spectroscopy (by Jilin University Photochemisity Lab). A 400-W Xenon lamp with a monochromator was used as light source. The setup scheme and the principle of SPS were also shown in literature [23].

The EIS were performed with a computer-controlled IM6e impedance measurement unit (Zahner Elektrik, Germany). EIS were obtained by applying sinusoidal perturbations of 10 mV over the V_{oc} at the frequency range from 0.05 to 100 kHz. All EIS measurements were carried out under illumination of 10 mW cm^{-2}. The obtained spectra were fitted with ZsimpWin software in terms of appropriate equivalent circuits. Photocurrent–photovoltage curves were recorded by a BAS100B electrochemical analyzer (Bioanalytical Systems Inc., USA). A 400-W Xenon lamp with a UV filter was used as light source. Its illumination intensity was about 40 mW cm^{-2}. The irradiation area of DSSCs was about 0.12 cm^2.

3. Results and discussion

3.1. Structure characterization of TiO_2-B NWs and NPs

TiO_2-B NWs/NPs were synthesized via a simple hydrothermal method as described in Section 2. Carrying out this reaction at 170 °C with 16 ml of 15 M NaOH solution yielded NWs, whereas less NaOH aqueous solution yielded NPs. This is maybe because the autoclave filling fraction had a strong influence on the nanomaterial morphology. One possible explanation for this result was that the pressure inside the autoclave is strongly dependent on the filling fraction because of the different volumes of water expansion. When the filling fraction is big (80%), the big pressure inside the vessel contributed the formation of NWs. When the filling fraction is small (65%), the small pressure contributed the formation of NPs, which is similar to the observations of Poudel et al. [27]. After being washed with diluted hydrochloric acid, the product completed exchange of Na^+ by H^+ to form hydrogen titanates. They converted to TiO_2-B cylindrical morphology after heating at 450 °C for 5 h. Fig. 1 shows the XRD patterns of the P25 NPs and TiO_2-B NWs, respectively. As well known, the diffraction peaks of P25 were consistent with that of anatase and rutile, and anatase was the main phase [18]. Although the diffraction peaks of TiO_2-B NWs were broadened due to dimension confinement effect, they well matched the pattern of TiO_2-B (JCPDS 46-1238). The XRD pattern of TiO_2-B NPs was same with that of TiO_2-B NWs. Further confirmation that the NWs/NPs are composed of TiO_2-B is obtained from laser Raman spectroscopy. Fig. 2 shows a Raman spectrum of the NWs and NPs, which was an excellent match with that of bulk TiO_2-B [14]. Thus, through a facile hydrothermal route, the materials with the polymorph of TiO_2-B had indeed been obtained. Evidence that the TiO_2-B NWs/NPs possessed their morphologies is shown in Fig. 3. The low-resolution