Application of TiO_2 with different structures in solar cells*

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(Received 15 January 2012; revised manuscript received 11 June 2012)

The application of TiO_2-based devices is mainly dependent on their crystalline structure, morphology, size, and exposed facets. Two kinds of TiO_2 with different structures, namely TiO_2 pompons and TiO_2 nanotubes, have been prepared by the hydrothermal method. TiO_2 with different structures is characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Brunauer–Emmett–Teller (BET) surface area analysis. Solar cells based on poly(3-hexylthiophene) (P3HT) and TiO_2 with different structures are fabricated. In the device ITO/TiO_2/P3HT/Au, the P3HT is designed to act as the electron donor, and TiO_2 pompons and TiO_2 nanotubes act as the electron acceptor. The effects of the TiO_2 structure on the performance of hybrid heterojunction solar cells are investigated. The device with TiO_2 pompons has an open circuit voltage (V_{oc}) of 0.51 V, a short circuit current (J_{sc}) of 0.21 mA/cm^2, and a fill factor (FF) of 28.3%. Another device with TiO_2 nanotubes has a V_{oc} of 0.5 V, J_{sc} of 0.27 mA/cm^2, and FF of 28.4%. The results indicate that the TiO_2 nanotubes with a unidimensional structure have better carrier transport and light absorption properties than TiO_2 pompons. Consequently, the solar cell based on TiO_2 nanotubes has a better performance.

Keywords: TiO_2 pompons, TiO_2 nanotubes, heterojunction solar cell

PACS: 84.60.Jt, 88.40.−j, 88.40.jr, 81.05.Hd **DOI:** 10.1088/1674-1056/21/11/118401

1. Introduction

Polymer/organic photovoltaic cells have attracted considerable attention due to their lightness, low cost, and simple fabrication process.[1−7] In particular organic/inorganic bulk heterojunction photovoltaic cells are gaining popularity, because the active layer is constructed by organic materials as the donor and inorganic semiconductors as the acceptor. The hybrid active layer combines the advantages of high electron mobility and stability of inorganic materials with the solution-processing of organic materials. In addition, the compensated light harvest of organic materials and inorganic semiconductors enlarges the absorption range of sunlight and leads to the efficient conversion of sunlight.[4] Titanium oxide (TiO_2) nanocrystals have been considered as one of the most important inorganic semiconductors in the research of organic/inorganic bulk heterojunction photovoltaic cells due to their high photoelectrochemical activity, chemical stability, non-toxicity, easiness to preparation, and so on.[8,9] TiO_2 plays three roles in photovoltaic devices: (i) as antireflection coating or a scattering layer,[10,11] (ii) the interlayer in organic solar cells (OSC),[12] (iii) a part of the active layer of the device acting as the electron transport material in dye-sensitized solar cells (DSSC) and hybrid solar cells (HSC).[13,14] Extensive studies confirm that the crystalline structure, morphology, size and exposed facets of TiO_2 can affect the performance of a TiO_2-based dye-sensitized solar cell.[15−21] However, little attention has been paid to the influence of TiO_2 structure on the performance of heterojunction solar cells. Herein, two kinds of TiO_2 with different structure, pompon-like TiO_2 nanoparticles (TiO_2 pompons) and TiO_2 nanotubes, have been prepared and character-

*Project supported by the Ministry of Science and Technology of China (Grant No. 2011CB932802), the National Natural Science Foundation of China (Grant No. 60978060), and the Beijing Municipal Science & Technology Commission, China (Grant No. Z090803044009001).

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ized in this paper. Furthermore, they are incorporated into bilayer heterojunction devices with poly(3-hexylthiophene) (P3HT) as a donor. The influence of the TiO_2 structure on the performance of solar cells has been investigated.

2. Model and method

The synthesis of TiO_2 pompons was carried out by a hydrothermal method. 4.5-g cetyltrimethyl ammonium bromide (CTAB) and 14-ml tetrabutyl titanate (TBOT) were dissolved in 25-ml anhydrous ethanol and stirred for 1 h at room temperature. In this way, a homogeneous transparent solution was obtained. 15-ml alcohol-water (weight ratio of 1:0.5) solution was added into the above transparent solution. The resultant solution was stirred for 3 h. The pH of the solution was adjusted to 11 using NaOH solution (1 mol/l). Then the solution was transferred into a Teflon-lined autoclave and remained at 100 °C for 10 h. After that the precipitate was filtered, washed with high purity water, and dried at 100 °C for 10 h. The dried sample was calcined at 450 °C for 3 h to obtain TiO_2 pompons.

The TiO_2 nanotubes were synthesized through a hydrothermal process. We dispersed 1-g TiO_2 powder into 50-ml 10-mol/L NaOH solution, then placed the mixture in a 100-ml Teflon-lined autoclave. The autoclave was maintained at 150 °C for 24 h, and then cooled to room temperature. The precipitate was separated by centrifugation, and washed with 0.1-mol/L HCl solution, high purity water, and absolute ethanol until the pH value reached 7.0. The samples were dried at 100 °C overnight and calcined at 450 °C for 5 h in air. Finally, the TiO_2 nanotubes were obtained.

Two kinds of TiO_2 pastes were synthesized according to Ref. [22]. Then the fabrication of the photovoltaic devices was carried out in the following steps. ITO glass was used as a current collector (25-nm thickness, 60 Ω/□). It was cleaned in a detergent solution of water, ethanol, and acetone using an ultrasonic bath for 15 min, respectively. The titania pastes were deposited by spin coating at 1500 rpm on the ITO substrate, followed by calcinations at 450 °C for 1 h in air. After cooling to room temperature, a chloroform solution of P3HT was spin-coated on the TiO_2/ITO substrate. The Au electrode was then evaporated in a vacuum evaporation system (lower than 5×10^{-6} Torr) at 0.1 Å/s. The thickness of Au was about 50 nm. The active area of each device was 0.1 cm^2, which is limited by a shadow mask The structures of the devices are ITO/TiO_2 (pompons or nanotubes) /P3HT/Au.

The X-ray diffraction (XRD) patterns of the TiO_2 samples were recorded by a powder XRD instrument (Brucker D8 Advance) with Cu Ka radiation (wavelength: 1.54056 Å). Scanning electron microscopy (SEM) images were taken using a field-emission SEM (FE-SEM, Hitachi S-4800). Transmission electron microscope (TEM) images of the TiO_2 nanotubes were obtained by an FEI F-20 high-resolution TEM (HRTEM). Brunauer–Emmett–Teller (BET) specific surface area and pore size distribution profile of the TiO_2 were obtained using a Tristar II 3020 analyzer. The absorption spectra of the active layers of the devices were measured with a Shimadzu UV-3101. A 150-W Xenon lamp was used as the broadband light source and the intensity of incident light is 100 mW/cm^2. The current–voltage (I–V) characteristics of the devices were measured with a Keithley 2410 source measurement unit.

3. Results and discussion

Figure 1 shows the XRD patterns of the TiO_2 pompons and TiO_2 nanotubes. The diffraction peaks are rather sharp, which indicates that the obtained TiO_2 has a relatively high crystallinity. The observed 2θ value of the XRD patterns was 25°, 38°, 48°, and 54°, respectively. Hence, the XRD results indicate that both the TiO_2 pompons and TiO_2 nanotubes are anatase phase TiO_2 (JCPDS card No.21-1272).

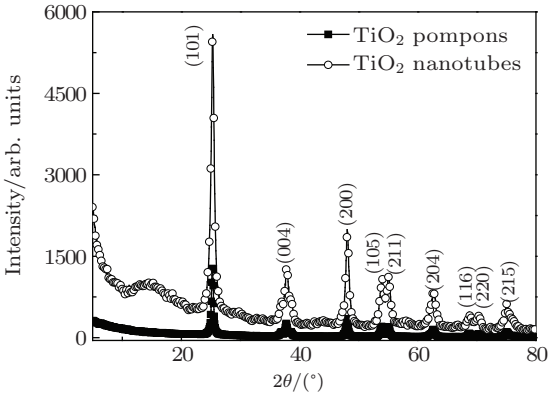


Fig. 1. XRD patterns of the TiO_2 pompons and TiO_2 nanotubes.

Figures 2(a)–2(d) show the electron microscope images of TiO_2 pompons and TiO_2 nanotubes, respectively. As shown in Figs. 2(a) and 2(b), the TiO_2 pompons contain numerous pompon-like aggregates, and

almost all of them show the same morphology. The size of the TiO_2 pompons is about 1 μm. Figures 2(c) and 2(d) show the SEM and TEM images of the TiO_2 nanotubes. A large amount of TiO_2 nanotubes have uniform inner and outer diameters along their length. The TEM images confirm that the TiO_2 nanotubes possess hollow structures. The average diameter of the TiO_2 nanotubes is about 10 nm.

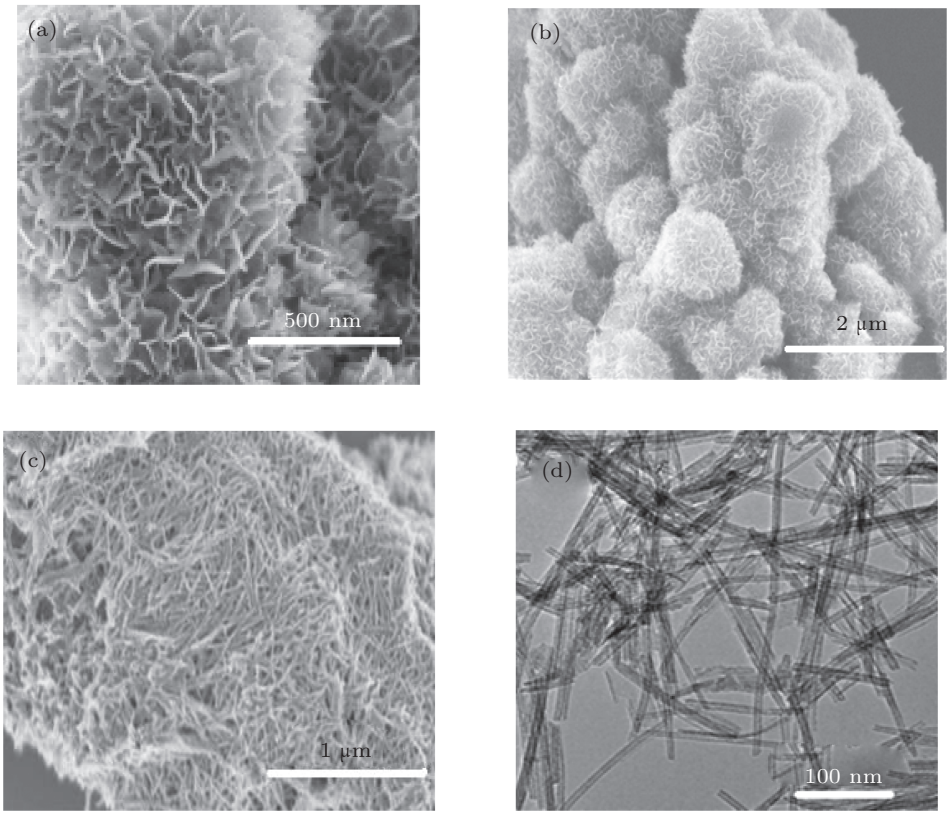


Fig. 2. SEM images of (a, b) TiO_2 pompons and (c) TiO_2 nanotubes. (d) TEM image of the TiO_2 nanotubes.

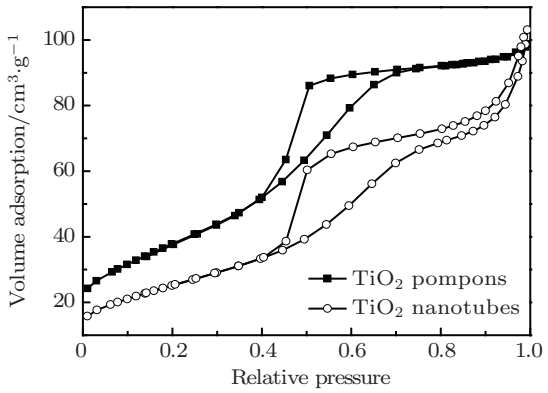


Fig. 3. Nitrogen adsorption isotherms of the TiO_2 pompons and TiO_2 nanotubes.

Figure 3 shows the nitrogen adsorption isotherms of the TiO_2 pompons and TiO_2 nanotubes The isotherms are actually typical IV-type adsorption isotherms (type H_2 hysteresis loop), indicating the existence of mesopores. In addition, the BET specific surface areas of powder samples were analyzed. Pore-size distribution was calculated from the isotherms obtained by using the Barret–Joyner–Halenda (BJH) method[23] The BET surface areas and the pore information of TiO_2 pompons and TiO_2 nanotubes are listed in Table 1.

Table 1. Pore size (D), pore volume (V), and BET surface area (S_{BET}) of the TiO_2 pompons and TiO_2 nanotubes.

Sample	D/nm	V/cm^3·g^{-1}	S/m^2·g^{-1}
TiO_2 pompon	6.2	0.165	137.5
TiO_2 nanotube	3.9	0.162	91.3

UV–visible absorption spectra of active dual layers (TiO_2/P3HT) containing TiO2 with different structures were also observed (see Fig. 4). The absorbed wavelength of active layers containing the TiO_2 nanotubes was dramatically improved compared with that based on the TiO_2 pompons from 200 to 800 nm.

This arises mainly from two intrinsic optical properties of dense unidimensional nanostructure arrays. The light scattering is enhanced by the antireflective effect and increased light absorption path length between nanotubes.[24,25] Moreover, P3HT can link with TiO_2 though the S-end atom.[18] TiO_2 nanotubes have a special structure with both interior and exterior walls, which is favorable for the link between P3HT and TiO_2 nanotubes. The absorption of the active layer containing TiO_2 pompons shows the overlapping absorption bands of P3HT and TiO_2. The TiO_2 pompons have bigger surface areas than the TiO_2 nanotubes, and theoretically they can absorb more dye molecules. However, the TiO_2 pompons are easy to conglomerate during the process of fabrication into film. Thus, the absorption of the active layer with the TiO_2 pompons is not improved. This enhanced absorption spectrum is expected to lead to a larger number of photogenerated excitons, and thus a larger photocurrent.

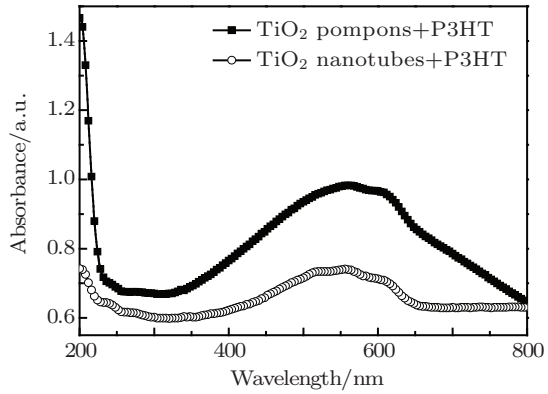


Fig. 4. UV–visible absorption spectra of the active layers.

Figure 5 shows the I–V characteristics of the devices with different structures of TiO_2 and the intensity of illumination is 100 mW/cm^2. The inset figure shows the structure of the device. From the I–V curve, the properties of the devices are obtained that the device with the TiO_2 pompons gave a performance with an open circuit voltage (V_{oc}) of 0.51 V, a short circuit current (J_{sc}) of 0.21 mA/cm^2, and fill factor (FF) of 28.3%. Another device with the TiO_2 nanotubes exhibited a performance with V_{oc} of 0.5 V, J_{sc} of 0.27 mA/cm^2, and FF of 28.4%. The photovoltaic properties of the two devices are summarized in Table 2. The TiO_2 structure can exert an influence on the J_{sc} of TiO_2 based devices and affect V_{oc} and FF slightly. The higher J_{sc} of the TiO_2 nanotubes based device can be attributed to the effective light scattering effects and the dual-channel for effective electron transport. The study shows that the hollow structured waveguided materials can stop or slow the light and trap the rainbow [26]. Hence the special hollow structure of the TiO_2 nanotube has a stronger light scattering effect and it increases the light absorbance of the nanotube film to 400–800 nm (Fig. 4). The dual-channel of the TiO_2 nanotubes can effectively transport electrons and hold back the photogenerated carrier recombination, thus it increases the short circuit currents. From this work, the effect of the TiO_2 structure on the performance was approved.

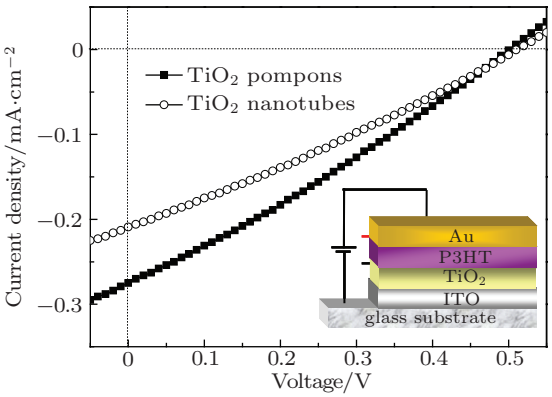


Fig. 5. (colour online) Current–voltage characteristic curves of the cells using TiO_2 pompons and TiO_2 nanotubes. Inset: schematic diagram of the heterojunction solar cell.

Table 2. Photovoltaic properties of the two devices based on TiO_2 pompons and TiO_2 nanotubes.

Device	V_{oc}/V	J_{sc}/mA·cm^{-2}	FF
ITO/TiO_2 pompons/P3HT/Au	0.51	0.21	28.3
ITO/TiO_2 nanotubes/P3HT/Au	0.50	0.27	28.4

4. Conclusion

In summary, we have synthesized two different kinds of anatase TiO_2 powder, TiO_2 nanotubes and TiO_2 pompons. Both the TiO_2 nanotubes and TiO_2 pompons have been employed for heterojunction solar cell fabrication and their device performance has been compared. The structures of the devices are ITO/TiO_2 (pompons or nanotubes) /P3HT/Au. It was found that the J_{sc}, V_{oc}, and FF of TiO_2 nanotubes cell were 0.27 mA/cm^2, 0.50 V, and 28.4% under a xenon lamp intensity of 100 mW/cm^2, respectively. However, the TiO_2 pompons cell has J_{sc} of 0.21 mA/cm^2, V_{oc} of 0.51 V, and FF of 28.3% under the same light intensity. From the above inves-

tigations, it is concluded that the J_{sc} of the heterojunction solar cell depends remarkably on the TiO_2 structure, and the V_{oc} and FF are correlated with the structure of TiO_2. The TiO_2 nanotubes-based device has a higher J_{sc}, which can be attributed to the effective light scattering effects and the dual-channel for effective electron transport. The special hollow structure of the TiO_2 nanotubes has stronger light scattering effects. Moreover, it can increase the light absorbance of the nanotubes film. The dual-channel of TiO_2 nanotubes can effectively transport electrons and hold back the photogenerated carrier recombination, and thus increase the short circuit currents.

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