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Fabrication of TiO_2 nanocrystals/nanorods composites thin film electrode: Enhanced performance of dye-sensitized solar cells

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ABSTRACT

The TiO_2 thin film (CTTF) composed of nanocrystals (NCs) and one-dimensional (1D) single crystalline nanorods (NRs) was prepared and then used as electrode to fabricate dye sensitized solar cells (DSCs). The kinetic parameters of electron transport in CTTF were investigated. Results indicated that due to the direct path for fast electron transport in NRs, the fabricated CTTF electrodes-based DSCs have much lower recombination rate, longer electron life time and electron diffusion length than that based on the pure TiO_2 NCs electrodes.

1. Introduction

Among various metal oxide semiconductors, TiO_2 was widely studied for its low cost, nontoxic peculiarities and chemical stability [1]. Due to its large exciton binding energy and electron mobility, TiO_2 thin films play an important role in photovoltaic devices, including dye sensitized solar cells (DSCs) [1], perovskite-sensitized solar cells [2], polymer–inorganic hybrid solar cells [3], quantum dot-sensitized solar cells [4] and inorganic solid-state solar cells [5]. In order to improve the photovoltaic properties of DSCs, the investigation on the charge transport and recombination in TiO_2 thin film becomes very important [6]. The mesoporous TiO_2 thin film prepared from TiO_2 nanocrystals (NCs) via a screen-printing method [7] can serve as both a substrate for the dye and the electron conductor in photoanode of DSCs. Generally, the electrodes of DSCs based on NCs can provide larger surface area. However, the relatively poor electron transport property of TiO_2 NCs makes it difficult for further improving the photovoltaic properties of DSCs. In recent years, one-dimensional nanomaterials, including nanotubes [8], nanorods [9] and nanofibers [10], have received great attention in fabricating DSCs due to their superior electron transport properties. In our previous work, we reported that the DSCs fabricated with seaweed-like TiO_2 nanoarrays have much lower recombination rate and longer electron life time [11]. In addition, the combination of TiO_2 NCs and TiO_2 nanorods (NRs) was reported an effective way to enhance electron transport properties [12]. However, the dynamic mechanisms of DSCs were rarely reported. In this paper, DSCs based on combined TiO_2 NRs and NCs were fabricated and the influence of NRs on the electron transport properties of DCSs was investigated.

2. Experimental

The preparation of 1D single crystalline TiO_2 nanorods (NRs) were synthesized similarly as the process in Ref. [13]. TiO_2 powder (Aldrich) was firstly added into 10 M NaOH aqueous solution. Then the mixture solution was transferred into a Teflon-lined autoclave and heated at 170 °C for 24 h. After the autoclave was cool down to room temperature naturally, the product was washed with deionized water for several times to obtain the intermediates. The intermediates were then mixed with concentrated nitric acid and maintain at $pH=2$ for 6 h. After that, they were washed with deionized water for several times until the pH value of the solution became neutral. The obtained one-dimensional micron-sized titanate materials were transferred into Teflon-lined autoclave and filled with the nitric acid liquor of $pH=2$ at 170 °C for 24 h. The cooled product was dispersed ultrasonically, centrifuged to remove nitric acid, and finally washed with de-ionized water and ethanol three times to obtained TiO_2 NRs.

The processes for preparing TiO_2 paste and fabricating solar cells were similar as Ref. [7]. Three kinds of pastes containing mixed TiO_2 NCs and NRs were prepared with NRs content of

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0, 5 and 10 wt% (labeled as pastes A–C), respectively. The CTTFs with the thickness of 7.4 μm were prepared by screen printing method with above three different pastes. Then, they were fabricated into DSCs marking with devices A–C after sensitized-treating the CTTFs with dye C106.

3. Results and discussion

The transmission electron microscopy (TEM) images showed in Fig. 1 were performed on a JEOL JEM-2100 microscopy, which indicates that the TiO_2 NRs have smooth surface and two triangular protuberances at two ends. The TiO_2 NRs show a diameter of 27–41 nm and length range from 64 to 206 nm, and the average diameter and length of TiO_2 NRs are about 32 and 137 nm, respectively. The clear and regular lattice fringes in the HRTEM image (the inset) reveal the highly crystalline nature of TiO_2 NRs. The measured distance between two adjacent fringes is 0.33 nm, being agreement with the (110) plane of rutile TiO_2 [14].

The *J–V* characteristics of device A–C in Fig. 2 reflect the performance of devices, and the detailed photovoltaic parameters are listed in the inset table. The measurements were carried out by using Keithley model 2602 A digital source meter, and A BOS-X-1000G solar simulator was used to give irradiance of 100 mW cm^{-2}. When the TiO_2 NRs content in CTTFs increased from 0 to 10 wt%, an obvious increase in the short-circuit current densities (J_{sc}) and conversion efficiency (η) were observed, and open-circuit voltage (V_{oc}) and fill factor (FF) had a slight change. The device C based on 10 wt% TiO_2 NRs CTTF electrode, whose J_{sc}, V_{oc}, *FF* and η were 17.72 mA cm^{-2}, 726 mV, 0.617 and 7.95%, respectively, exhibited the highest performance. Generally, the enhanced performance of DSCs can be mainly ascribed to two reasons, including the increasing ability of dye absorption and light harvesting of photoanode, and the improvements in electrical transport property. As shows in Fig. 3(a) the UV–vis absorption spectrums of CTTFs with different composites were monitored on a TU-1810PCS spectrophotometer to investigate (not-sensitized films as reference) the light-harvesting capacity. The peaks near 550 nm correspond to the characteristic absorption of C106 dye [15]. It can be seen that the light harvesting efficiency of CTTFs decreases slightly with the increasing of TiO_2 NRs content. Such result can be explained by the reduction of the absorbed dye molecules due to the decrease of surface area of the CTTF when the content of TiO_2 NRs increased. On the contrary, with the increasing of TiO_2 NRs content, the performance of devices enhanced. Thus, the electrical transport property enhanced by the TiO_2 NRs may play a key role in improving the performance of DSCs.

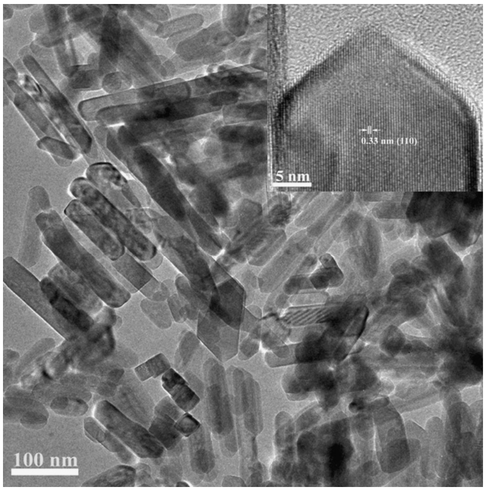
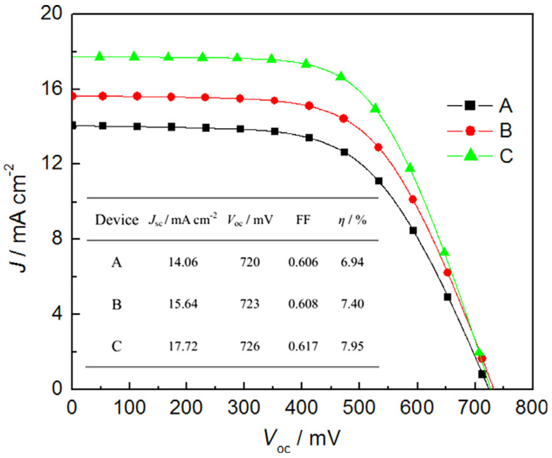


Fig. 1. TEM and HRTEM (inset) images of the TiO_2 nanorods.



Device	J_{sc} / mA cm^{-2}	V_{oc} / mV	FF	η / %
A	14.06	720	0.606	6.94
B	15.64	723	0.608	7.40
C	17.72	726	0.617	7.95

Fig. 2. *J–V* characteristics of devices measured under AM1.5G sunlight (inset Table: Detailed photovoltaic parameters).

The charge recombination rate constant (K_r), density of states (*DOS*) and chemical capacitance (C_μ) of devices A–C were studied by transient photoelectrical decay measurement [15]. As shown in Fig. 3(b), the K_r values for all the three devices increase exponentially with the increasing of V_{oc}. Moreover, device A shows the highest K_r value followed by device B and C. For example, at $V_{oc}=616$ mV, the K_r values of devices A–C are 59.3, 47.2 and 31.9 s^{-1}, respectively. The higher K_r value indicates quicker charge recombination at TiO_2/electrolyte interfaces and more wastage of photogenerated electrons, which finally leads to the poor photovoltaic performance of device A. The TiO_2 NRs can provide direct electron transport path for photoelectron and then promote the electron transport. As a result, the K_r in TiO_2/electrolyte interface for device C was reduced, and the photoelectron can be transported more quickly to external circuit. The curves of *DOS* and C_μ vs V_{oc} for the DSCs with different electrodes are showed in Fig. 3(c). The *DOS* and C_μ increase exponentially with the increasing of V_{oc}, and the *DOS* and C_μ values of device C is maximum and that of device A is minimum under the same V_{oc} condition. The higher *DOS* value of device C probably due to more electrons gather in the TiO_2/electrolyte interface ascribing its lower K_r value than other devices. Under the certain light, the TiO_2 surface states and trap states are increased with the increasing of *DOS*. It may be noted that the higher *DOS* of device C should give a lower V_{oc}. However, this does not occur because the TiO_2 NRs also act to strongly reduce the K_r.

In order to further confirm the TiO_2 NRs content-dependent enhancement of the electron transport ability of the TiO_2 NCs/NRs - based thin film electrode, the electrochemical impedance measurement was performed on the electrochemical workstation (IM6ex, Germany, Zahner) in the frequency range of 1 mHz–00 kHz. A Z-view data processing software was applied to calculate the kinetic parameters of electronic transport [16]. Fig. 4 shows the relations between electron lifetime (τ_n), electron diffusion coefficient (D_n) and electron diffusion length (L_n) vs applied bias voltage (V_b). It can be seen that under the same V_b, the values of τ_n and L_n increase and D_n slightly decrease with the increasing of TiO_2 NRs content. When the V_b is 500 mV, the τ_n of device C based on 10 wt% TiO_2 NRs CTTF electrode was 12.50 ms, which is about 8 times to pure TiO_2 NCs electrode (1.45 ms). High τ_n value means an effective inhibition for the charge recombination reaction, which is consistent with the variation of K_r. The L_n in device has been estimated by measuring D_n and τ_n: $L_n=(D_n\tau_n)^{1/2}$ [16]. The L_n of device C is larger than that of device A and B. The electron