Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Electrochemistry Communications 9 (2007) 354–360
electrochemistry communications
www.elsevier.com/locate/elecom

TiO_2@CdS core–shell nanorods films: Fabrication and dramatically enhanced photoelectrochemical properties

Huimin Jia [a], Hua Xu [a], Yan Hu [a], Yiwen Tang [b], Lizhi Zhang [a,*]

[a] *Key Laboratory of Pesticide and Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, PR China*
[b] *Institute of Nano-Science and Technology, Central China Normal University, Wuhan 430079, PR China*

Received 9 September 2006; received in revised form 1 October 2006; accepted 2 October 2006
Available online 1 November 2006

Abstract

In this paper, we prepared TiO_2@CdS core–shell nanorods films electrodes using a simple and low-cost chemical bath deposition method. The core–shell nanorods films electrodes were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and UV–vis spectrometry techniques. After applying these TiO_2@CdS core–shell nanorods electrodes in photovoltaic cells, we found that the photocurrent was dramatically enhanced, comparing with those of bare TiO_2 nanorods and CdS films electrodes. Moreover, TiO_2@CdS core–shell nanorods film electrode showed better cell performance than CdS nanoparticles deposited TiO_2 nanoparticles (P25) film electrode. A photocurrent of 1.31 mA/cm^2, a fill factor of 0.43, an open circuit photovoltage of 0.44 V, and a conversion efficiency of 0.8% were obtained under an illumination of 32 mW/cm^2, when the CdS nanoparticles deposited on TiO_2 nanorods film for about 20 min. The maximum quantum efficiency of 5.0% was obtained at an incident wavelength of 500 nm. We believe that TiO_2@CdS core–shell heterostructured nanorods are excellent candidates for studying some fundamental aspects on charge separation and transfer in the fields of photovoltaic cells and photocatalysis.

Keywords: Core–shell; CdS; TiO_2; Nanorods; Photoelectrochemical property

1. Introduction

Since Fujishima and Honda found a TiO_2 anode could split water into H_2 and O_2 under UV irradiation [1], titanium dioxide has received considerable attention over the past three decades in photovoltaic and photocatalysis applications [2–8]. However, it is well known that the band gap of TiO_2 (3.2 eV) limits its absorption to the ultraviolet region of the solar spectrum. It has been reported earlier that many investigators could improve the visible light absorption of TiO_2 nanocrystals by incorporation of substitutional atoms into the lattice, including both non-metal and metal atoms [9,10]. Although this incorporation of substitutional atoms improves the visible light absorption in TiO_2 electrodes, they have not yet proven suitable for efficient photoelectrochemical cell application in some cases. Besides the numerous studies on dye-sensitized TiO_2 solar cells, some efforts have been made on the sensitization of TiO_2 photoelectrodes with narrow band gap semiconductors [11]. Semiconductors such as CdS, CdSe, CdTe, PbS, Bi_2S_3, $CuInS_2$, and so on, which absorb light in the visible, can serve as sensitizers because they are able to transfer electrons to large band gap semiconductors such as TiO_2 or ZnO.

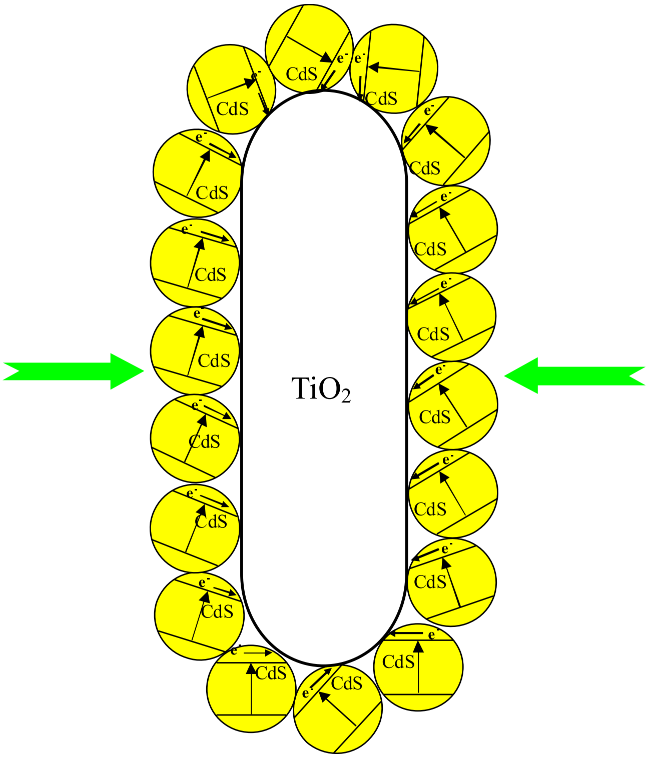
Recently, we prepared the nanocrystalline CdS films electrodes using a doctor-blade technique combined with hydrothermal method and studied their photoelectrochemical property [12]. CdS is found to be one of the promising materials for solar cells because of suitable band gap, optical absorption, long lifetimes and easy fabrication for photoelectrochemical cell applications [13–15]. Meanwhile, TiO_2/CdS composites have been extensively investigated for their applications in solar energy cells, catalysis, water

---

[*] Corresponding author. Tel./fax: +86 27 67867535.
E-mail address: zhanglz@mail.ccnu.edu.cn (L. Zhang).

1388-2481/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2006.10.010

purification and electrochromic devices [16–18]. For instance, Gerischer and co-workers demonstrated that semiconductors such as CdS, which absorb in the visible, were capable of injecting electrons into TiO_2 films [11]. Vogel and co-workers reported excellent visible-spectrum properties of a photocell made by the combination of in situ prepared CdS particles (4–20 nm) with a highly porous nanocrystalline TiO_2 electrode [19]. After depositing CdS microcrystals onto a TiO_2 semiconductor, Kohtani and co-workers found that the resulting photoelectrochemical properties were strongly influenced by the CdS sensitizer [20]. Recently, we developed a general water/chloroform interface based method to prepare rutile TiO_2 nanorods with high photocatalytic activity [21]. In order to combine the unique property of these rutile TiO_2 nanorods with the excellent visible absorption ability of CdS nanoparticles, we seek to fabricate TiO_2@CdS core–shell photoelectrodes effectively working under visible light. It is known that the coupling of CdS and TiO_2 has a beneficial role in improving charge separation. Excited electrons from CdS nanoparticles can quickly transfer to TiO_2 nanorods as shown in Scheme 1. Owing to high contact area and excellent capacity of charge transport in one-dimensional nanostructure, the resulting TiO_2@CdS core–shell heterostructure nanorods films are promising for both fundamental study and application in photovoltaic cells. To the best of our knowledge, this is the first report on photoelectrochemical properties of TiO_2@CdS core–shell nanorods films. In this paper, we studied the photoelectrochemical properties of TiO_2@CdS core–shell nanorods films and investigated the influence of the different deposition time on the cell performance, and compared the properties with those of pure TiO_2 nanorods and CdS nanoparticles film as well as CdS nanoparticles deposited TiO_2 nanoparticles (P25) film photoelectrodes.



Scheme 1. Schematic diagram illustrating charge injection from excited CdS nanoparticles into TiO_2 nanorods.

2. Experimental

The rutile TiO_2 nanorods powder was synthesized by a hydrothermal method [21]. Typically, 5 mL of $TiCl_4$ was slowly dissolved in 25 mL of deionized water at 4 °C. The resulting solution was added to 50 mL of chloroform in 100 mL Teflon-line stainless autoclave. The autoclave was stored at 150 °C for 12 h, and then air-cooled to room temperature. The product formed between the layers of water and chloroform was collected by centrifugation and washed with deionized water and ethanol, finally dried at 50 °C in air.

For the preparation of films, 0.2 g of TiO_2 nanorods powder was added into a mortar, then 0.02 g of ethyl cellulose and 2.0 mL of terpineol were mixed with TiO_2 by grinding until a meringue-like gel was formed. The indium-doped tin oxide (ITO) substrates were cleaned with distilled water and ethanol by sonication. Both edges of the conducting glass substrates were covered with adhesive tape. A drop of the paste was added to one of the bare edges of the ITO substrates, and flattened with a glass rod by sliding over the tape-covered edges [22], followed by drying at 60 °C for about 6 h. Finally, TiO_2 nanorods films were annealed at 450 °C for 30 min in air atmosphere.

TiO_2@CdS core–shell nanorods films were prepared by chemical bath deposition techniques. The chemical bath deposition process involved immersing the substrate into an aqueous bath containing cadmium chloride, thiourea, ammonium nitrate, potassium hydroxide [23]. First, 10 mL of 0.02 M $CdCl_2 \cdot 2.5H_2O$ and 10 mL of 0.5 M KOH were mixed at room temperature under continuous magnetic stirring. Then 10 mL of 1.5 M NH_4NO_3 and 10 mL of 0.2 M CH_4N_2S were added to form a colorless solution. The substrates were immersed vertically into the resulting solution for deposition of CdS at 85 °C. The solution was continuously stirred for a homogenously distribution of the chemical components during the deposition. The resulting films were washed with distilled water and absolute ethanol. The reaction process can be described as follows:

$$Cd^{2+} + 2OH^- \rightarrow Cd(OH)_2\downarrow$$

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

$$Cd^{2+} + 4NH_3 \rightarrow [Cd(NH_3)_4]^{2+}$$

$$(NH_2)_2CS + OH^- \rightarrow CH_2N_2 + H_2O + HS^-$$

$$HS^- + OH^- \rightarrow S^{2-} + H_2O$$

$$Cd(NH_3)_4^{2+} + S^{2-} \rightarrow CdS\downarrow + 4NH_3\uparrow$$