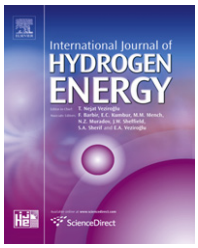
Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Highly stable CdS-modified short TiO_2 nanotube array electrode for efficient visible-light hydrogen generation

Yanbiao Liu, Haibin Zhou, Baoxue Zhou, Jinhua Li, Hongchong Chen, Jingjing Wang, Jing Bai, Wenfeng Shangguan, Weimin Cai*

School of Environmental Science and Engineering, Shanghai Jiao Tong University, No. 800 Dongchuan Rd., Shanghai, China

ARTICLE INFO

Article history:
Received 17 June 2010
Received in revised form
20 September 2010
Accepted 26 September 2010
Available online 25 October 2010

Keywords:
Short TiO_2 nanotube array
CdS
Sonoelectrochemical deposition
Hydrogen generation

ABSTRACT

A highly stable photoelectrocatalytic electrode made of CdS-modified short, robust, and highly-ordered TiO_2 nanotube array for efficient visible-light hydrogen generation was prepared via sonoelectrochemical anodization and sonoelectrochemical deposition method. The short nanotube electrode possesses excellent charge separation and transfer properties, while the sonoelectrochemical deposition method improves the combination between CdS and TiO_2 nanotubes, as well as the dispersion of CdS nanoparticles. Different characterization techniques were used to study the nanocomposite electrode. UV–vis absorption and photoelectrochemical measurements proved that the CdS coating extends the visible spectrum absorption and the solar spectrum-induced photocurrent response. Comparing the photoactivity of the CdS/TiO_2 electrode obtained using sonoelectrochemical deposition method with others that synthesized using plain electrochemical deposition, the current density of the former electrode is ~1.2 times higher that of the latter when biased at 0.5 V. A ~7-fold enhancement in photocurrent response is obtained using the sonoelectrochemically fabricated CdS/TiO_2 electrode in comparison with the pure TiO_2 nanotube electrode. Under AM1.5 illumination the composite photoelectrode generate hydrogen at a rate of 30.3 μmol h^{-1} cm^{-2}, nearly 13 times higher than that of pure titania nanotube electrode. Recycle experiments demonstrated the excellent stability and reliability of CdS/TiO_2 electrode prepared by sonoelectrochemical deposition. This composite electrode, with its strong mechanical stability and excellent combination of CdS and TiO_2 nanotubes, offers promising applications in visible-light-driven renewable energy generation.

1. Introduction

In recent years, much attention has been given to photoelectrocatalytic hydrogen generation using metal oxide semiconductors to supply clean and recyclable hydrogen energy [1,2]. Currently, TiO_2 is one of the most promising materials being developed as photocatalysts because of its special features, such as low cost, chemical inertness and photostability [3,4]. However, the high rate of photogenerated electron/hole pair recombination among TiO_2 nanoparticles and its poor activation by visible light are two major factors limiting further improvement of its photoelectrocatalytic efficiency.

In order to decrease the recombination rate within a TiO_2 electrode, researchers have fabricated nano-scaled TiO_2 of different geometric shapes and microstructures (i.e. wires, rings, belts, dots, pores and tubes) [5–7]. Among them, the TiO_2

* *Corresponding author*. Tel./fax: +86 21 5474 7351.
E-mail address: zhoubaoxue@sjtu.edu.cn (B. Zhou).

0360-3199/$ – see front matter © 2010 Professor T. Nejat Veziroglu. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijhydene.2010.09.089

nanotube array (TNA) obtained from the anodization of titanium in HF or [F^-]-based electrolyte has attracted much attention for their peculiar architecture and remarkable properties [8–15]. The nanotubular microstructures are perpendicular to the electrically conductive Ti substrate, naturally forming an Schottky-type contact and providing a unidirectional electric channel for the transport of photogenerated electrons. Moreover, the dimensions of the as-prepared nanotubes with regard to length and diameter can be precisely controlled by tuning the anodization parameters [10].

Considerable attempts aimed at improving the visible light absorption of TiO_2 by depositing a noble metal (e.g., Ag, Pt, Au, etc.) on its surface or doping it with transition metals (e.g., Fe, Zn, etc.) or non-metal elements (e.g., N, C, S, etc.) have been met with certain success [16–20]. Although incorporation of alternative atoms improves the visible light absorption of TiO_2 electrodes, they have not yet been proven suitable for highly-efficient photoelectrocatalytic applications [21]. Other efforts concerned with band-gap shifting of TiO_2 have focused on the sensitization of TiO_2 electrodes by combining them with narrow band-gap semiconductors. In particular, the band-gap of CdS ($E_g = 2.4$ eV) and its relatively high absorption coefficient in the visible region make it highly desirable for use in photovoltaics and photoelectrochemistry in comparison with other semiconductors [22–28]. A coupled CdS/TNA photoanode may be suitable for efficient solar energy conversion (Fig. 1). Upon illumination, the excited electrons from CdS can be rapidly transferred to the TiO_2 nanotubes, arriving at the electron collectors through the nanotubular microstructure [23]. However, the excellent mechanical stability of TNA, as well as the excellent electron transport properties between evenly distributed CdS nanoparticles with TiO_2 nanotubes, is crucial for the desirable visible-light-driven photoelectrocatalytic reactivity and for the engineering applications of a CdS/TNA electrode.

Several factors affect the successful fabrication of efficient CdS/TNA electrodes. Firstly, the morphological structure of TNA film directly influences the stability and the photoelectrocatalytic reactivity of CdS/TNA electrode. Long nanotubes usually tend to tilt, rupture or even peel off the substrate when an external mechanical force is applied to the surface of the film or when there is a change in environmental temperature [7]. As demonstrated in other literatures [29,30], the increase in nanotube length may not contribute positively to the photoelectrocatalytic performance of the electrode materials. Recently, a short, robust and highly-ordered TiO_2 nanotube array (short TNA or STNA) electrode was successfully prepared by our group via sonoelectrochemical anodization (i.e. anodization under ultrasonic wave irradiation) [31]. This electrode material exhibits excellent charge separation and transfer properties in comparison with long TNA electrode synthesized by conventional magnetic agitation technique, as confirmed by the obviously enhanced photocurrent response of STNA electrode.

Secondly, the combination between CdS nanoparticles and the TNA film is significantly affected by the CdS deposition pathways. To date, CdS nanoparticles can be fixed onto the TNA surface by various methods, including layer-by-layer deposition [32], sequential chemical bath deposition [33,34], self-assembly techniques [35], etc. Of these different synthesis techniques, the electrochemical deposition technique offers the simplest and most controllable way of synthesizing CdS/TNA electrodes [36]. However, obtaining a composite electrode with better quality, evenly distributed CdS nanoparticles, and a strong combination of CdS and TiO_2 nanotubes may be more useful if ultrasonic waves can be integrated into the electrochemical process. The sonochemical process can help increase mass transfer throughout the reaction system and accelerate the diffusion of Cd^{2+} ions onto the nanotubes [13,31].

Based on the above design ideas and our previous work [7,14,30,31,34,37], a highly stable photoelectrocatalytic electrode made of CdS-modified STNA for efficient visible-light hydrogen generation is prepared via sonoelectrochemical anodization and sonoelectrochemical deposition (SED, electrochemical deposition under ultrasonic wave irradiation) method in this work. The detailed synthesis process, characterization, and photoelectrochemical property testing for this composite catalyst are also discussed.

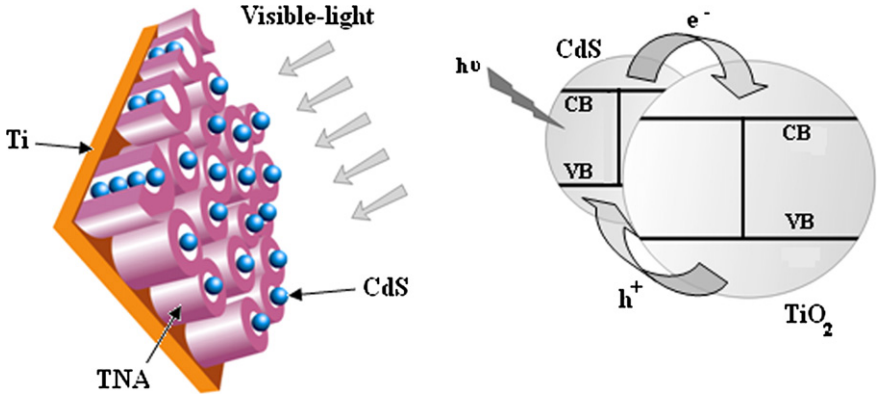


Fig. 1 – Schematic diagram illustrating the microstructure of CdS-modified TNA (left) and the charge transfer from excited CdS to TNA (right). CB and VB refer to the energy levels of the conduction and valence bands, respectively, of CdS nanoparticles and TiO_2 nanotubes.