Thin Solid Films 651 (2018) 124–130

Contents lists available at ScienceDirect

Thin Solid Films

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

Electrodeposition of Sb_2S_3 light absorbers on TiO_2 nanorod array as photocatalyst for water oxidation

Jia-Yo Hong[a,1], Lu-Yin Lin[a,*,1], Xin Li[b,1]

[a] Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, 1 Sec. 3, Zhongxiao E. Rd., Taipei 10608, Taiwan
[b] School of Chemistry and Chemical Engineering, Beijing Institute of Technology, 100081 Beijing, China

ARTICLE INFO

Keywords:
Antimony sulfide
Artificial photosynthesis
Electrodeposition
Heterojunction
Titanium dioxide

ABSTRACT

Artificial photosynthesis provides a direct approach toward addressing energy and environmental issues by producing chemical fuels such as hydrogen for fuel cells. A photoanode composed of the composite of titanium dioxide (TiO_2) nanorod and antimony sulfide (Sb_2S_3) nanoparticles was proposed in this work. The TiO_2 nanorod array is made on a fluorine-doped tin oxide glass by using the hydrothermal reaction, and the Sb_2S_3 nanoparticles were deposited on the TiO_2 nanorod array by using the electrodeposition method with different depositing currents. The electrodeposition method is more time-saving as compared with the commonly used chemical bath reaction method. The Sb_2S_3 was selected as the coating material due to its broader light absorption range and suitable band-edge positions relating to those of TiO_2 for forming a type II heterojunction, aiming to improve the poor visible light absorption and low quantum efficiency of TiO_2. A higher photocurrent density of 0.33 mA cm^{-2} (measured at 1.23 V *vs.* reversible hydrogen electrode) is obtained for the TiO_2/Sb_2S_3 photoanode in a 0.5 M Na_2SO_4 aqueous solution under the air mass 1.5 global illumination, comparing to that of 0.017 mA cm^{-2} for the TiO_2 electrode measured under the same conditions. This successful combination of two n-type semiconductors as the photocatalyst for achieving efficient water oxidation provides a conceptual blueprint for designing the composite with complementary optical and electrical properties.

1. Introduction

Artificial photosynthesis is one of the significant manners to supply clean energy *via* storing the sunlight energy into the chemical bonds of fuels like hydrogen. This concept is originated in 1972 by Honda and Fujishima who demonstrated the photoelectrochemical water splitting using n-type titanium dioxide (TiO_2) to realize a solar-to-fuel conversion process [1]. The photoanodic properties of TiO_2 have been widely studied since then. Due to the abundant and stable properties and the high photocatalytic activity in an aqueous solution under irradiation, TiO_2 is a well-known candidate for water oxidation [2]. Nevertheless, TiO_2 is merely active in the ultraviolet (UV) region which occupies less than 5% in the total energy of the solar spectrum owing to its large band gap (~3.0 eV for rutile) [3]. Also, TiO_2 has low electron mobility (1 $cm^2 V^{-1} s^{-1}$) [4] and the short minority carrier diffusion length (10–100 nm) [2,5], leading to the limitation of its quantum efficiency even in the UV region. To extend the range of light absorption in the visible light region as well as improve the charge transfer and kinetics of water oxidation, a foreign material with the higher light absorption in the visible light region and the matched band edges to those of TiO_2 or zinc oxide to develop the type-II heterojunction is required [6–10].

In recent years, attentions have been paid to construct the composite of TiO_2 and a narrow band gap semiconductor to develop highly efficient photocatalysts for achieving better charge separation and transfer as well as higher responses under visible light [11–16]. Ke et al. synthesized WO_3/TiO_2 nanocomposites to achieve high photoactivities in the Rhodamine B photodegradation under UV irradiation [17]. Smith et al. designed WO_3/TiO_2 and TiO_2/WO_3 core-shell nanorod arrays to attain better optical, chemical, and transport properties [14]. Naik et al. used a chemical co-precipitation route to fabricate $Bi_2O_3/TiO_{2-x}N_x$ nanocomposites with high visible light and photocatalytic activities [11]. Among the semiconductors with narrow band gaps, Sb_2S_3 with the band gap of 1.74 eV has attracted much attention recently [18,19]. Kim et al. designed a $Sb_2Ti_xS_y$ core-shell nanorods with the absorption band edges of above 600 nm to enhance hydrogen production [20]. Gödel et al. developed Sb_2S_3 absorbers for the sensitized solar cells using an aqueous chemical bath synthesis and achieved a power conversion efficiency of 5.1% [21]. Ito et al. synthesized Ti, Zn, and Bi-doped Sb_2S_3 absorbers for all-solid-state solar cells and attained the power conversion efficiency of 5.7% [22]. The n-type nature of Sb_2S_3

* Corresponding author.
E-mail address: lylin@ntut.edu.tw (L.-Y. Lin).
[1] The authors contributed equally.

https://doi.org/10.1016/j.tsf.2018.02.038
Received 6 August 2017; Received in revised form 15 February 2018; Accepted 23 February 2018
Available online 25 February 2018
0040-6090/

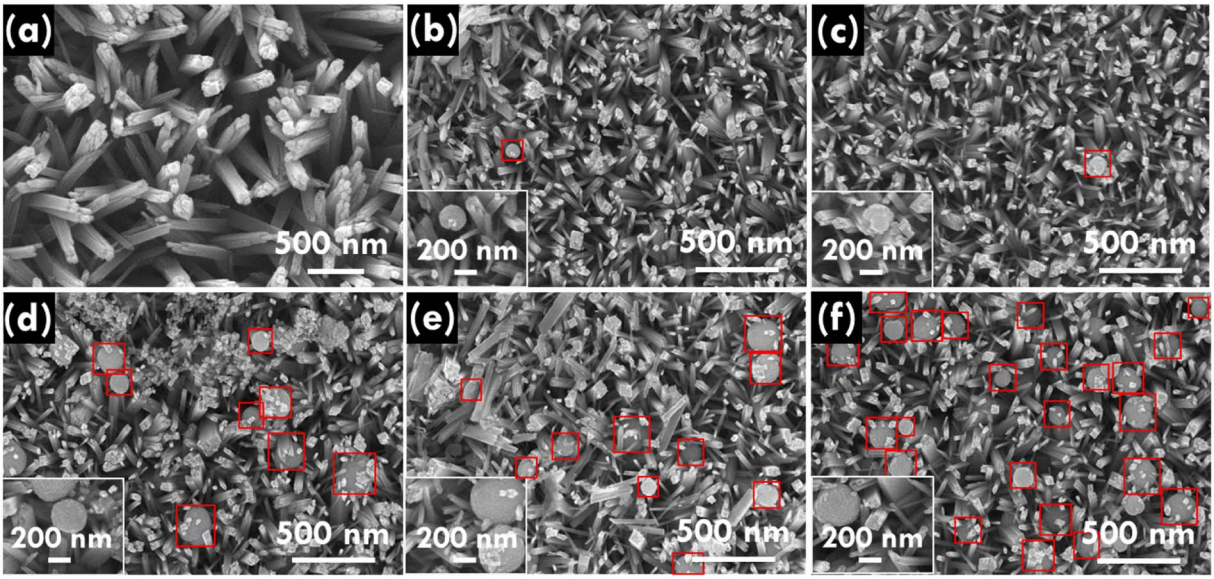

Fig. 1. The top-view SEM images for (a) TiO_2, (b) TiO_2/Sb_2S_3(1), (c) TiO_2/Sb_2S_3(2), (d) TiO_2/Sb_2S_3(3), (e) TiO_2/Sb_2S_3(4) and (f) TiO_2/Sb_2S_3(5) electrodes.

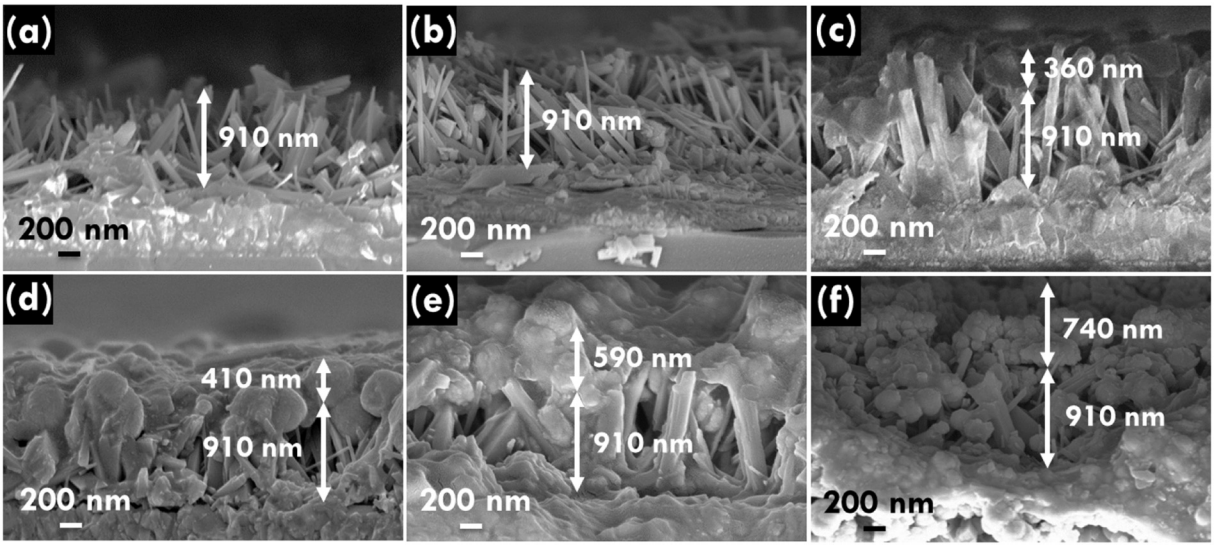

Fig. 2. The side-view SEM images for (a) TiO_2, (b) TiO_2/Sb_2S_3(1), (c) TiO_2/Sb_2S_3(2), (d) TiO_2/Sb_2S_3(3), (e) TiO_2/Sb_2S_3(4) and (f) TiO_2/Sb_2S_3(5) electrodes.

has been indicated in the previous literature [23,24], and the light absorption and the charge transfer for the pertinent system has been verified to be improved when incorporating Sb_2S_3 in the TiO_2 nanomaterial [23]. However, there are limited researches applying the composite of Sb_2S_3 and TiO_2 on water oxidation to enhance the visible light absorption and improve the charge cascade. Our group previously used the chemical bath deposition method to deposit Sb_2S_3 on TiO_2 nanorod array as the efficient photocatalyst for water oxidation [25,26]. To further apply this concept, a time-saving electrodeposition method was firstly applied in this work to construct the efficient TiO_2/Sb_2S_3 electrode for photocatalyzing the water oxidation.

Herein, a TiO_2/Sb_2S_3 composite with high visible spectral responses and type II band alignment heterojunction was developed by using the hydrothermal reaction coupled with the electrodeposition method. A photocurrent density of 0.33 mA cm^{-2} (measured at 1.23 V *vs.* reversible hydrogen electrode (RHE)) was obtained for the optimized TiO_2/Sb_2S_3 electrode, which is higher than that of the TiO_2 electrode (0.017 mA cm^{-2}). Also, a smaller onset potential was achieved for the TiO_2/Sb_2S_3 electrode comparing to that of the TiO_2 electrode. The improvement on the photocurrent density and the onset potential for the TiO_2/Sb_2S_3 electrode again indicates the feasibility of incorporating a narrow band gap material in TiO_2 as the photocatalyst for achieving the effective water splitting and also suggests the capability of the time-saving electrodeposition method for depositing the Sb_2S_3 layer on the TiO_2 electrode.

2. Experimental

2.1. Materials

Titanium tetraisopropoxide ($Ti[OCH(CH_3)_2]_4$, 97%) and dimethyl sulfoxide (DMSO) were obtained from Sigma−Aldrich. Hydrochloric acid (HCl, 35.5–36.5%) was bought Aencore. Thiourea (CH_4N_2S) and sodium sulfate (Na_2SO_4, 99%) were obtained from Showa. Antimony trichloride ($SbCl_3$, 99.5%) was bought from Acros.

2.2. Preparation of the TiO_2 and TiO_2/Sb_2S_3 photoanodes

The TiO_2 nanorod array was synthesized *via* a hydrothermal method. In a typical synthesis, 83 ml titanium tetraisopropoxidewas