



Fabrication of n-type CuInS₂ modified TiO₂ nanotube arrays heterostructure photoelectrode with enhanced photoelectrocatalytic properties

Tingting Li^{a,b}, Xinyong Li^{a,c,*}, Qidong Zhao^a, Yong Shi^a, Wei Teng^a

^a Key Laboratory of Industrial Ecology and Environmental Engineering, School of Environmental Sciences and Technology, Dalian University of Technology, Dalian 116024, China

^b College of Civil Engineering and Architecture, Liaoning Technical University, Fuxin 123000, China

^c Department of Chemical Engineering, University of Cape Town, Cape Town 7701 Rondebosch, South Africa

ARTICLE INFO

Article history:

Received 11 November 2013

Received in revised form 17 March 2014

Accepted 19 March 2014

Available online 27 March 2014

Keywords:

Photoelectrocatalytic

n-Type

CuInS₂

2-Chlorophenol

ABSTRACT

A novel n-type CuInS₂ modified TiO₂ nanotube arrays (NTs) heterostructure photoelectrode was successfully prepared via an ultrasonication-assisted cathodic electrodeposition strategy. CuInS₂ particles were uniformly decorated on the inner and external walls of the TiO₂ NTs electrode. The stoichiometry measured by XPS and ICP-OES clearly illustrated the excess indium. Mott–Schottky analysis further demonstrated CuInS₂ possessed an n-type feature. Optical characterizations indicated that the introduced CuInS₂ could extend the visible-light response range and enhance the visible light photoactivity. Moreover, the electrochemical measurements attested to a significant improvement of the interfacial electron-transfer properties. The photoelectrocatalytic (PEC) activity of CuInS₂/TiO₂ NTs electrode was evaluated by degradation of 2-chlorophenol (2-CP) under visible light irradiation ($\lambda > 420$ nm). The results indicated that the as-prepared CuInS₂/TiO₂ NTs electrode displayed much higher PEC performance than that of the pure TiO₂ NTs electrode.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Ever since Zwilling et al. synthesized TiO₂ NTs by anodization in HF containing electrolyte [1], this highly ordered one dimensional (1D) architecture has attracted tremendous scientific and technological interest in water splitting [2–4], dye-sensitized solar cell [5–8], gas sensors [9–12], degradation of hazardous wastes [13–16], owing to the outstanding properties, high physical and chemical stability, biocompatibility and efficiency of harvesting incident photons.

However, because of the wide band gap (3.0 eV for rutile phase and 3.2 eV for anatase phase), TiO₂ could only be excited by UV light, which limits the effective utilization of solar light [17]. Besides, low quantum efficiency and the recombination between the photo-generated electrons and holes are also two major factors impeding the enhancement of the photocatalytic activity [18]. In order to

overcome the above limitations, several methods could be adopted to improve the visible light utilization efficiency and the photocatalytic properties, including non-metal doping [19], metal ions doping [20,21], semiconductor modifying [22,23], and precious metal particles loading [24,25].

Modifying TiO₂ NTs with narrow band gap semiconductor is one of the effective methods facilitating the photo-induced charges separation between the foreign semiconductor and TiO₂. To date, considerable experimental efforts have been made to decorate TiO₂ NTs with narrow band gap semiconductors, such as quantum dots of CdS, CdSe and PbS, etc. [26–29]. Nevertheless, in view of the environmental harmfulness of those toxic heavy metals, the green materials are preferred. CuInS₂ has various advantages in photovoltaic applications with a narrow band gap of 1.5 eV, such as high visible-light absorption coefficient [30], good optical stability [31] and low toxicity [32]. Moreover, its conduction band edge is more negative than that of TiO₂, CuInS₂ modified TiO₂ NTs could potentially enhance the charge separation. Many literatures have reported the formation of p–n heterojunction CuInS₂/TiO₂ catalyst with excess copper [33–36]. The decoration of p-type CuInS₂ onto TiO₂ could form a heterojunction structure, which would remarkably facilitate the charge separation, interfacial transfers and visible

* Corresponding author at: Dalian University of Technology, School of Environmental Science & Technology, No. 2, Linggong Road, Dalian, Liaoning 116024, China. Tel.: +86 411 8470 7733; fax: +86 411 8470 7733.

E-mail address: xinyongli@hotmail.com (X. Li).

light utilization. On the other hand, n-type CuInS_2 also has excellent photoelectrochemical conversion efficiency and chemical stability [37,38]. By successfully combining TiO_2 NTs and n-type CuInS_2 nanoparticles to yield a novel n–n heterostructure, the more efficient utilization of the visible light and much improvement of the surface–interface charge transfer could be expected. However, to date, few literatures have reported n-type CuInS_2 due to the difficulty in the control of the excess indium. The control of the excess indium to form n-type CuInS_2 loading on TiO_2 NTs electrode still remains a challenge.

Herein, a novel n-type CuInS_2 modified TiO_2 NTs electrode with n–n heterojunction has been synthesized using a facile ultrasonication-assisted cathodic electrodeposition strategy. Based on a series of systematic characterization, $\text{CuInS}_2/\text{TiO}_2$ NTs electrode exhibited a significant visible-light activity, which could be attributed to the high visible absorption coefficient of CuInS_2 and the formed n–n heterojunction. Furthermore, the efficient PEC degradation of 2-CP under visible light irradiation with the $\text{CuInS}_2/\text{TiO}_2$ NTs electrode was carefully integrated and clarified in terms of the co-relationship between the novel structure of the composite electrode and its remarkable performance.

2. Experimental

2.1. Materials

Ti sheets (0.5 mm thick, 99.7% purity, Beijing Academy of Steel Service, China) were cut into samples of size 20 mm \times 40 mm. All the chemicals were of analytical grade and used as received without further purification. Doubly distilled deionized water was used for the preparation of all solutions and the rinse of Ti sheets.

2.2. Preparation of TiO_2 nanotube arrays on Ti substrate

The highly ordered TiO_2 nanotube arrays were prepared by anodization in a two-electrode electrochemical cell. Before anodization, the Ti foils were first polished with different abrasive papers, and chemically etched in a mixture acid for 40 s, which was prepared by mixing hydrofluoric acid, nitric acid and deionized water (1:4:5 in volume). These foils were rinsed in an ultrasonic bath of ethanol and deionized water for 15 min, respectively, and then dried in nitrogen stream. Anodization was conducted in 0.2 wt% HF aqueous electrolyte with a platinum electrode served as the cathode. A potential of 20 V was kept for 30 min at room temperature. TiO_2 nanotube arrays were subsequently annealed at 500 °C for 1 h with heating and cooling rate of 2 °C min^{-1} .

2.3. Preparation of CuInS_2 -loaded TiO_2 nanotube arrays

CuInS_2 nanoparticles were deposited onto the TiO_2 NTs by using an ultrasonication-assisted electrodeposition method. A typical three-electrochemical cell was equipped with a platinum electrode as a counter electrode, saturated calomel electrode (SCE) as a reference, and the TiO_2 NTs as the working electrode. Prior to electrodeposition, the TiO_2 NTs was first immersed in a solution containing 0.02 M indium chloride tetrahydrate ($\text{InCl}_3 \cdot 4\text{H}_2\text{O}$), and then immersed in a 0.01 M copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) solution. Both of the impregnations were under ultrasonication for 5 min with 100 watt power and 80 kHz frequency in a digitally-controlled ultrasonic cleaner (Shumei KQ3200DB). In this process, the ultrasonication plays a role like a capillary action to help the metal ions to diffuse through the nanochannels of TiO_2 [45]. Then, the TiO_2 NTs was put in the typical three-electrochemical cell containing 0.1 M sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)

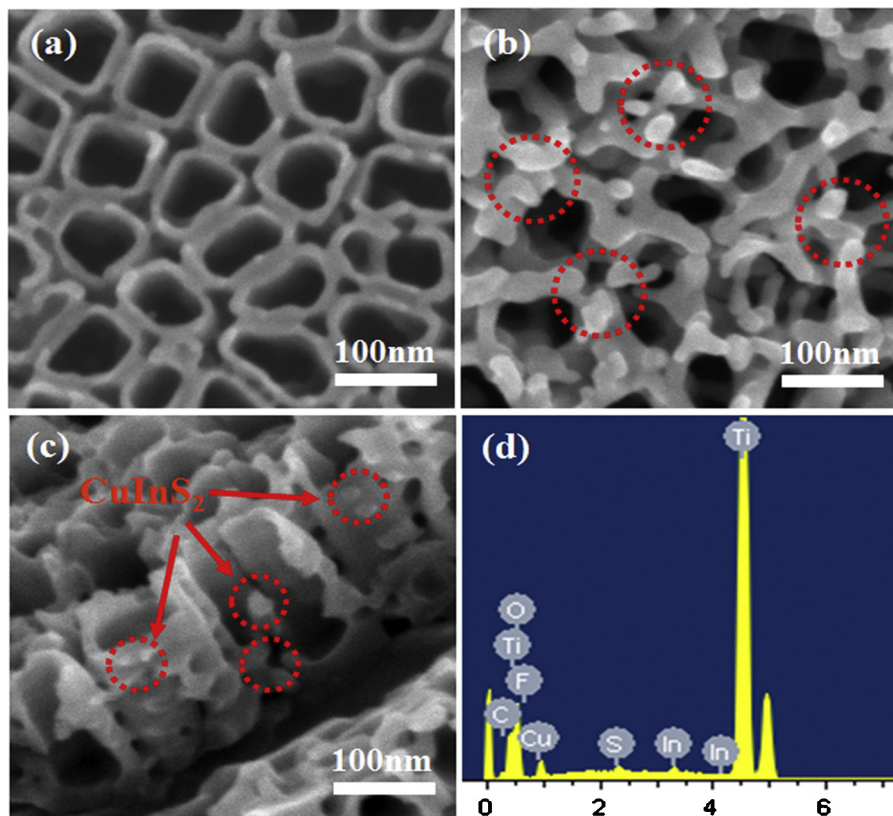


Fig. 1. FESEM image: (a) top-view of TiO_2 NTs, (b) top-view image of $\text{CuInS}_2/\text{TiO}_2$ NTs, (c) cross section of $\text{CuInS}_2/\text{TiO}_2$ NTs and (d) EDX of the as-prepared $\text{CuInS}_2/\text{TiO}_2$ NTs with the experimental parameters as follows: deposition time = 5 min, deposition voltage = -0.9 V, deposition cycles = 10 repetitions, concentration = 0.02 M In and 0.01 M Cu, 0.1 M S, dose of LiCl = 5 mL.

Download English Version:

<https://daneshyari.com/en/article/6501370>

Download Persian Version:

<https://daneshyari.com/article/6501370>

[Daneshyari.com](https://daneshyari.com)