



Original research article

Deposition of copper indium sulfide on TiO₂ nanotube arrays and its application for photocatalytic decomposition of gaseous IPAYoung Ku^{*}, Pei-Yu Lin, Yu-Cheng Liu

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ABSTRACT

TiO₂ nanotube arrays (TNTs) were modified with copper indium sulfide (Cu/In/S) by successive ionic layer adsorption and reaction (SILAR) method. The field-emission scanning electron microscopy and X-ray photoelectron spectroscopy analysis demonstrated the presence of copper indium sulfide nanoparticles on the surface of the modified TNTs. The Cu/In/S-modified TNTs exhibited higher photocurrent density and photocatalytic activity than plain TNTs. The concentration of sulfur precursor was found to be an important factor on the composition of modified Cu/In/S films by SILAR. Some composition deviations were observed on the stoichiometry of the Cu/In/S-modified TNTs, which evidently affected the electrochemical characteristics of the modified TNTs. Experiments using the modified TNTs of composition close to the stoichiometric ratio of CuInS₂ usually delivered higher photocatalytic decomposition of gaseous isopropyl alcohol in air streams and exhibited better stability during operation.

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1. Introduction

TiO₂ is known as an environmentally friendly and corrosion-resistant photosensitive material that has been employed in many fields. Compared to bulk TiO₂ powder, TiO₂ nanotube arrays (TNTs) with highly ordered one-dimensional architecture have been reported to exhibit higher photochemical reactivity than that of bulk TiO₂ particles due to their high surface-to-volume ratios and other unique properties [1–3]. However, the band gap and recombination of photo-induced charge carriers of TiO₂ limit its overall photocatalytic efficiency. Various methods have been developed to enhance the photocatalytic efficiency of TiO₂, such as doping with transition metal cations [4,5] or nonmetal anions [6] to enhance the visible light absorbance of TiO₂, and modifying with metals or semiconductors to improve the separation and transport of photo-induced carriers on TiO₂ [7].

CuInS₂ has been reported to demonstrate prominent potential for photovoltaic applications due to its relatively narrow band gap (~1.55 eV) and high absorption coefficient (> 10⁵ cm⁻¹) [8,9]. Shen et al. [10] have reported that porous TiO₂ substrate modified with

CuInS₂ exhibited higher optical absorption because of the formation of p–n junction between CuInS₂ and TNTs. Thus, the photo-induced electrons are flowing into n-type TNTs while holes are flowing into p-type CuInS₂ to achieve better separation of photo-induced carriers [10].

Various techniques for preparing CuInS₂ films on different substrates have been reported, such as elemental chemical vapor deposition [11], sulfurization of metallic precursor [12], spray pyrolysis [13], electro-deposition [14], co-evaporation [15], ion layer gas reaction [16], chemical bath deposition [17], and successive ionic layer adsorption and reaction (SILAR) [18]. Among these techniques, SILAR is supposed to be an inexpensive, simple, and eco-friendly method for depositing large area films [19]. For SILAR, thin films are obtained by immersing substrate into separately-placed cationic and anionic precursors, and then rinsing between each immersion with water. The deposition rate and the thickness of the film can be easily controlled by changing the deposition cycles of SILAR.

In order to improve the photocatalytic activity of TNTs, SILAR was used to modify TNTs with copper indium sulfide (Cu/In/S) in this study. Effects of sulfur precursor concentration used during SILAR and heat treatment of the Cu/In/S-modified TNTs on the structural characteristics and photocatalytic activity of deposited films were investigated. The photocatalytic activity of Cu/In/S-modified TNTs was examined by decomposing gaseous isopropyl

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alcohol (IPA) in a continuous, tubular photoreactor loaded with Cu/In/S-modified TNTs under controlled Xe arc lamp illumination.

2. Experimental

All chemicals used in this study were analytical grade without further purification. Titanium foils (99.53% purity) of $50 \times 39 \times 0.3$ mm were pretreated by sonicating in acetone, isopropanol, methanol, and deionized water sequentially, and then dried in N_2 environment. TNTs were prepared in an anodization reactor with pretreated Ti and Pt foils used as the working electrode and cathode, respectively, and ethylene glycol solution containing 0.7 wt% NH_4F and 7 wt% water was employed as electrolyte. The anodization reactor was operated at 40 V by a programmable DC power supply (SPS150-8, Amrel) and kept isothermal at 3 °C. The anodized Ti foil covered with TNTs was then annealed in a muffle furnace at 600 °C for 3 h in air atmosphere.

The deposition of CuInS on TNTs was carried out at room temperature. The annealed TNTs-Ti foil was immersed in the mixed cation precursor solution, containing 0.075 M cupric chloride ($CuCl_2$) and 0.05 M indium chloride ($InCl_3$), for 30 s, and was then rinsed with deionized water before it was immersed in solutions containing various amounts of sodium sulfide (Na_2S) for additional 30 s. The foil was rinsed again with deionized water to remove the unreacted ions. By repeating above SILAR steps, thin film of Cu/In/S was believed to be deposited on TNTs annealed on Ti foil.

Surface images of the Cu/In/S-modified TNTs on the foil were observed by a field-emission scanning electron microscopy (FESEM, JSM-6500F, JOLE). Modified TNTs was subsequently examined by X-ray photoelectron spectroscopy (XPS, VG ESCA Scientific Theta Probe spectrometer) and X-ray diffractometer (XRD, Rigaku RTP 300).

The photocurrent response measurements were carried out in 0.1 M KCl electrolyte with a 30 W of 365 nm UV light irradiation to examine the separation of photo-induced carriers for plain and various Cu/In/S-modified TNTs. The applied bias potential was 0 V versus Ag/AgCl (3 M KCl) for 350 s. In the beginning applied bias potential without UV illumination to stable until 60 s and then turned on the light until 300 s; the results are shown in Table 1. UV light intensity was measured by a photometer (IL1400A, International Light) equipped with a UV detector (SEL005/WBS320/TD, International Light). The bias potential and electrical current density of photoanode were provided and measured by the potentiostat (PGSTAT30, Autolab).

The photocatalytic system used for decomposition of IPA in this study is composed of gaseous source unit, a continuous flow planar photoreactor, Xe arc lamp humidity control unit and measurement unit, as shown in Fig. 1. The Ti foil covered with Cu/In/S modified TNTs was assembled at the bottom of the reactor. Air flow containing 200 ppmv IPA was prepared and flowed through the photoreactor for 30 min without lamp irradiation so as to saturate IPA adsorption on the Cu/In/S modified TNTs. Photocatalytic decomposition of IPA was then initiated with light emitted from a pre-warmed 500 W Xe arc lamp (Newport, 66142) fixed on the top

of the planar reactor. The temperature of the photoreactor was maintained at 25 °C for all experiments. Light intensity on the surface of Cu/In/S-modified TNTs was measured by a radiometer (International Light Technologies, ILT 1400). The air stream flown out of the photoreactor was periodically sampled during the experiment by a Valco E2C6UWT autosampler, and IPA concentration of the air stream was determined by a gas chromatography (China Chromatography, GC 2000) equipped with a flame ionization detector.

3. Results and discussion

The top-view images of the plain (without Cu/In/S modification) and Cu/In/S-modified TNTs by FE-SEM are present in Fig. 2. For the plain TNTs, only an uniform vertical alignment was noticed, while Cu/In/S nanoparticles with average diameters of about 10 nm were clearly observed on the surface of modified TNTs. The XPS spectra of the TNTs modified with Cu/In/S and annealed at 150, 300, and 450 °C are shown in Fig. 3. The core level spectrum of Cu $3p_{3/2}$ is located at 932.5 eV, indicating that only Cu^+ species was found for the modified TNTs without annealing. The In $3d_{5/2}$ core level spectrum exhibits a strong peak at 445.5 eV for the modified TNTs without annealing, which is related to the In $3d_{5/2}$ binding energy [20]. However, the In $3d_{5/2}$ peak is shifted slightly higher by around 0.5 eV for the modified TNTs annealed at higher temperatures, indicating the presence of In^{3+} species. The S 2p core level spectrum exhibits two peaks at 161.8 eV for $CuInS_2$ and at 169 eV for the presence of SO_4^{2-} [21]. Sulfate content was found to be decreased while the presence of S^0 (164.2 eV) was observed for Cu/In/S-modified TNTs annealed at higher temperatures. The XRD spectra of modified TNTs annealed at temperatures were also studied; however, the signals of $CuInS_2$ were unnoticeable for XRD analysis possibly because the amount of $CuInS_2$ on modified TNTs was too small to be detected.

Table 1 displays the Cu/In/S-modified TNTs without annealing exhibiting higher photocurrent density (0.019 mA cm^{-2}) than that of the plain TNTs without annealing (0.012 mA cm^{-2}), indicating that more photo-induced electrons could be transferred. Similar to the observations reported by Wang et al. [22], elucidating that the presence of sulfate species on the Cu/In/S-modified TNTs without annealing might enhance the capture of photo-induced electrons by oxygen, thus in hindering the recombination of electron–hole pairs [22]. Nevertheless, the annealed Cu/In/S-modified TNTs constantly demonstrated lower photocurrent densities, which may be ascribed to the deactivation of TNTs by elemental sulfur coverage and structure damage of $CuInS_2$ as detected by XPS as shown in Fig. 3.

The XPS spectra of TNTs modified with Cu/In/S by repeating 3 SILAR cycles in 0.025, 0.05, 0.1, 0.2, and 0.4 M Na_2S solution without annealing are shown in Fig. 4. The binding energy value of Cu $2p_{3/2}$ was determined to be 932.5 eV, higher than those of Cu_2S (931.8 eV) and CuS (931.6 eV), indicating almost no Cu_xS ($0.5 < x < 2$) was present in the modified TNTs. Moreover, the binding energy values of In $3d_{5/2}$ and S 2p were 445.2 and 161.8 eV, respectively, in good agreement with the binding energies for $CuInS_2$. SO_4^{2-} was found on the surface of Cu/In/S modified TNTs fabricated in sulfur precursor solution of various concentrations during SILAR process.

Table 2 illustrates the elemental percentages of Cu/In/S films formed on the modified TNTs determined based on XPS results. It is noticed that the existence of both Cu and In in the films is enhanced, but the molar ratio of Cu/In is increased with increasing sulfur precursor concentration, possibly due to the difference of physical adsorption speed and rate of Cu^+ and In^{3+} species on the surface of TNTs during the Cu/In/S modified preparation [23]. Previous studies have reported that the $CuInS_2$ formation is highly

Table 1
Photocurrent density of the un-annealed and annealed Cu/In/S modified TNTs.

Sample	Annealing temperature (°C)	Photocurrent density (mA cm^{-2})
TNTs	—	0.012
Cu/In/S modified TNTs	—	0.019
Cu/In/S modified TNTs	150	0.011
Cu/In/S modified TNTs	300	0.007
Cu/In/S modified TNTs	450	0.006

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