

Photo-catalytic Properties of TiO₂ Nanotube Arrays Sensitized with In₂S₃ under Visible-light Irradiation

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ABSTRACT

In this work, we report on the preparation of the anodically-grown TiO₂ nanotube arrays sensitized with In₂S₃ nanoparticles by using the SILAR (successive ionic layer adsorption and reaction) process. We evaluate the photo-catalytic properties of the prepared hetero-structures under visible-light illumination. The results reveal that the TiO₂/In₂S₃ system has enhanced photo-catalytic characteristics including higher chopping height. Improved performance of the heterojunction is attributed to the narrower band gap of In₂S₃ and its favorable position within the conduction band relative to that of TiO₂.

Key words : Titanium dioxide (TiO₂) nanotube, Indium sulfide (In₂S₃), Visible light, Photo-catalyst

1. Introduction

The global energy demand has been ever increasing owing to intensified industrialization and population growth. Meeting the demand mostly by fossil fuels has given rise to serious problems worldwide such as depletion of energy resources and spreading of environmental pollution. There have been various efforts to settle the matter, among which include decomposition of pollutants by photo-catalytic reaction, high-tech water purification, photo-catalytic fuel generations, and environmentally-benign production of energy.¹⁾

Titanium dioxide (TiO₂) has excellent chemical stability under highly-corrosive environment and high photo-catalytic activity under UV irradiation. It is, furthermore, harmless to human. TiO₂ occurs in nature in four different polymorphs; orthorhombic brookite, tetragonal anatase and rutile, and monoclinic TiO₂(B). The polymorphism depends on how much distortion the TiO₆ octahedron has. Consequently, the distortion leads to changes in electronic band structure as well as in density of TiO₂. Thermodynamically, the structures can be classified into the semi-stable phases (TiO₂(B), brookite, and anatase) and the stable phase (rutile). It is well-known that the stable rutile can be easily obtained from the semi-stable phases by thermal treatment.²⁾

TiO₂ exhibits a peculiar photo-catalytic ability via excitation of electrons by sunlight. This ability, however, is limited only to the UV range of sunlight (about 4% of the whole spectrum) owing to the relatively wider optical band gap of

TiO₂ (3.0 ~ 3.2 eV) and rather rapid recombination of photo-generated electrons with holes. To extend the absorption range of TiO₂ to the visible light (corresponds about 48% of the sunlight spectrum), various hetero-structured nano systems have been studied by incorporating with semiconductors with the narrower band gaps such as CdS (2.42 eV), PbS (0.37 eV), CdSe (1.74 eV), and CdTe (1.45 eV). In these hetero-junction systems, excited electrons and holes can be properly separated and their recombination rates, thus, can be reduced.³⁾

This study involves in In₂S₃ with the band gap of 2.0~2.3 eV as an effective sensitizer that is capable of functioning in the visible-light range. Note that In₂S₃ also can replace other toxic sensitizers such as CdS or PbS. We prepared the catalytic systems by depositing In₂S₃ nanoparticles on the TiO₂ nanotube electrode (oxidized anode). We analyzed their microstructural features by FE-SEM (field emission scanning electron microscope) and TEM-EDS (transmission electron microscope-energy dispersive spectroscopy), and measured their photocurrent densities under visible-light irradiation. Based on the results, we suggested the photo-catalytic mechanism of the TiO₂/In₂S₃ system.

2. Experimental Procedure

2.1. Preparation of In₂S₃/TiO₂/Ti electrode

Titanium foils (0.127 mm thick, 99%, Alfa aesar) of 3x1 cm were sonicated in the prepared solution of trichloroethylene (DC Chemical, 99.5%), acetone (OCI Company Ltd, 99.5%), and methanol (OCI Company Ltd, 99.6%) for 5 min. They were then dried on a hot plate at 80°C for 10 min. The solution for anode oxidation was prepared by mixing 50 ml of DI water, 950 ml of formamide (99%, Alfa aesar), and 0.15 M ammonium fluoride (Duksan pure chemical) for 15 min. The Ti foils (+) were immersed in the oxidation solution at a con-

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tinuous stirring and anodized for 3 h at 35 V using a Pt-mesh as the counter electrode (-). The anodized electrode was cleaned with DI water, dried for 15 min at RT, and annealed for 4 h at 550°C in air.

We followed the successive ionic layer adsorption and reaction (SILAR) process for the deposition of In_2S_3 nanoparticles: Aqueous solution of 0.1 M indium chloride (Sigma aldrich) was prepared, and the samples were immersed in the solution for 1 min at RT. The samples were then treated in the same way in a aqueous solution of 0.03 M sodium sulfide (Sigma aldrich), where its pH was adjusted at 7~8 using HCl. The process was repeated for 10 and 20 cycles.

2.2. Characterization

We analyzed microstructures of the hetero-junctions made of In_2S_3 nanoparticles, TiO_2 nanotubes, and Ti foil by field emission scanning electron microscope (JSM-6500F, JEOL) and transmission electron microscope (JEM2100, JEOL). We measured their photocurrent with Potentiostat (AT Frontier/VERSASTAT3) in a aqueous solution (pH = 12.4) of 0.1 M $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (Sigma Aldrich, $\geq 99.99\%$). We used Nafion membrane (Dufont/NR211) to transfer H^+ ions selectively. Here, electrolyte Na_2S acted as a hole scavenger by suppressing the photo-corrosion ($\text{In}_2\text{S}_3 + 2\text{h}^+ \rightarrow \text{In}^{3+} + \text{S}$) which is common for chalcogenide compounds with S, Se, and Te. The adopted three-electrode setup consisted of $\text{TiO}_2/\text{In}_2\text{S}_3$ photo-anode, Pt-mesh (AT Frontier) counter electrode, and Ag/AgCl reference electrode (AT Frontier).

During the photocurrent measurement, we irradiated the samples with white light of 100 mW/cm^2 provided from 1 kW xenon lamp (Newport) using UV and IR filters. We adopted cyclic voltammetry (single) mode with silicon detector (Newport). The true photocurrent was calculated by chopping height ($j_{\text{on}} - j_{\text{off}}$) obtained from on-off irradiation to eliminate any dark current.

3. Results and Discussion

Figure 1 illustrates the schematic of charge transfer and the photo-catalytic oxidation in relation to the band structure of the TiO_2 nanotube sensitized with In_2S_3 nanoparticles. Note that the band structure of the prepared heterojunction has a unique feature that the electrons generated on In_2S_3 by photo-absorption transfer to TiO_2 and the holes generated on TiO_2 transfer to In_2S_3 . Thus, the separation between electrons and holes is easily achieved. The holes accumulated in the valence band of In_2S_3 will participate in the four chemical reactions in Fig. 1. It implies that oxygen is generated from water by going through in various chemical reactions in stepwise fashion instead of one-step direct generation.

Figure 2 shows the representative electron microscopes of TiO_2 nanotube sensitized with In_2S_3 : (a) FE-SEM and (b) TEM bright field images before sensitization, and (c) FE-SEM and (d) TEM images after sensitization of 20 cycles.

Note that the nanotubes are in groups of 20 ~ 30 individual nanotubes. The grown nanotubes are about 34 nm thick, and they partly reveal the formation of lattice fringe. The images show that the diameters of In_2S_3 nanoparticles are about 20 nm and they cover the entire surface of TiO_2 nanotube. Fig. 3 is TEM-EDS result of the $\text{TiO}_2/\text{In}_2\text{S}_3$ system showing 57.85 wt% of Ti, 34.31 wt% of O, 6.12 wt% of In, and 1.72 wt% of S. It clearly indicates that the grown nano-

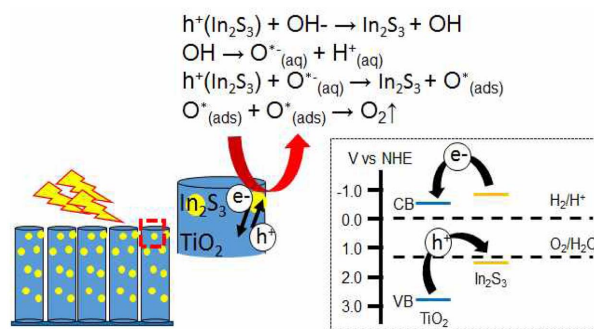


Fig. 1. Schemes of charge transfer and photo-catalytic oxidation by TiO_2 nanotube photo-anode sensitized with In_2S_3 nanoparticles.

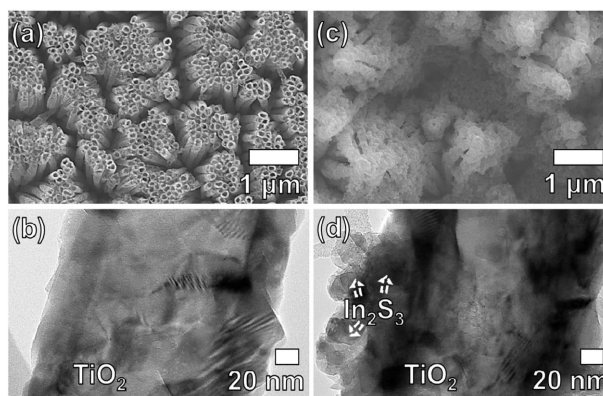


Fig. 2. Representative electron microscopes of TiO_2 nanotubes sensitized with In_2S_3 by successive ionic layer adsorption and reaction: (a) FE-SEM and (b) TEM images before sensitization (c) FE-SEM and (d) TEM images after sensitization, respectively.

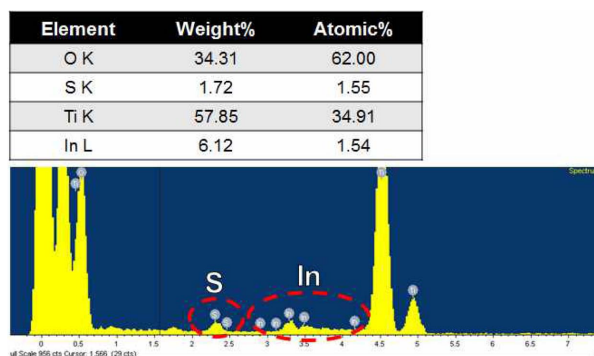


Fig. 3. TEM-EDS results of TiO_2 nanotube sensitized with In_2S_3 by successive ionic layer adsorption and reaction.

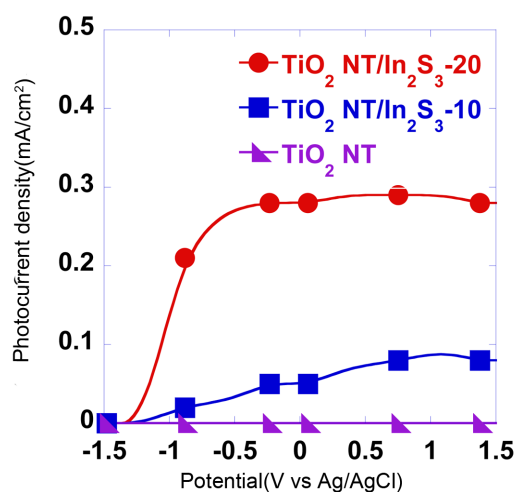


Fig. 4. Photocurrent density ($j_{on}-j_{off}$) of TiO₂ nanotubes sensitized In₂S₃ under visible light irradiation.

tubes by anodic oxidation are TiO₂, and the deposited nanoparticles by SILAR process are In₂S₃.

The photo-catalytic current density of the In₂S₃/TiO₂ system in the visible-light spectrum was evaluated by Potentiostat. An aqueous solution of 0.1 M Na₂S 9H₂O (pH = 12.4) was prepared as electrolyte and the three-electrode setup was adopted in the measurement. Fig. 4 is the chopping height ($j_{on}-j_{off}$) diagram of TiO₂ nanotubes sensitized In₂S₃ under visible-light irradiation in the on-off mode, which corresponds to the true photocurrent density. The measured chopping heights were 0.052 and 0.2800 mA/cm² for 10 and 20 cycles of the SILAR process, respectively. By doubling the cycle, the photo-current density increased more than 5 times. Considering 0 mA/cm² for TiO₂ nanotube with no sensitizer, the increase in photo-current density with increasing cycles of the sensitizing process is evident.

The results indicate that, by incorporating with In₂S₃, TiO₂ becomes a desirable heterojunction and displays high photo-activity in the visible-light spectrum. We believe that the newly-formed band structure enables the photo-excited electrons to transport easily to the conduction band of TiO₂

away from holes. This will lead to a reduced recombination rate of photo-generated electrons and holes.

4. Conclusions

In this study, we prepare a hetero-junction photo-catalyst made of TiO₂ nanotubes grown by anodic oxidation and In₂S₃ nanoparticles deposited by SILAR process. The prepared TiO₂ nanotubes are about 34 nm thick and the deposited In₂S₃ nanoparticles after 20 cycles of SILAR process are about 20 nm in diameter. The coupled semiconductor system demonstrated an enhanced photo-catalytic characteristics via visible-light absorption.

The increased visible-light absorbance is attributed to the narrower band gap of In₂S₃ nanoparticles and its favorable position of the conduction band relative to that of TiO₂, that promotes separation of the photo-generated electron-hole pair, reducing recombination. We also emphasize the fact that In₂S₃ is harmless to human and can replace other toxic sensitizers such as CdS or PbS. Further study is under way to resolve the photo-corrosion phenomenon which occurs after a long-term photocatalytic reaction of In₂S₃.

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