Photo-catalytic Properties of TiO\(_2\) Nanotube Arrays Sensitized with In\(_2\)S\(_3\) under Visible-light Irradiation

Hyun Kim and Bee Lyong Yang†

School of Advanced Materials and System Engineering, Kumoh National Institute of Technology, Gumi 730-701, Korea

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ABSTRACT

In this work, we report on the preparation of the anodically-grown TiO\(_2\) nanotube arrays sensitized with In\(_2\)S\(_3\) 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 TiO\(_2\)/In\(_2\)S\(_3\) system has enhanced photo-catalytic characteristics including higher chopping height. Improved performance of the heterojunction is attributed to the narrower band gap of In\(_2\)S\(_3\) and its favorable position within the conduction band relative to that of TiO\(_2\).

Key words : Titanium dioxide (TiO\(_2\)) nanotube, Indium sulfide (In\(_2\)S\(_3\)), 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 photocatalytic reaction, high-tech water purification, photo-catalytic fuel generations, and environmentally-benign production of energy.\(^1\)

Titanium dioxide (TiO\(_2\)) has excellent chemical stability under highly-corrosive environment and high photo-catalytic activity under UV irradiation. It is, furthermore, harmless to human. TiO\(_2\) occurs in nature in four different polymorphs; orthorhombic brookite, tetragonal anatase and rutile, and monoclinic TiO\(_2\)(B). The polymorphism depends on how much distortion the TiO\(_6\) octahedron has. Consequently, the distortion leads to changes in electronic band structure as well as in density of TiO\(_{2}\). Thermodynamically, the structures can be classified into the semi-stable phases (TiO\(_2\)(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.\(^2\)

TiO\(_2\) 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 TiO\(_2\) (3.0 ~ 3.2 eV) and rather rapid recombination of photogenerated electrons with holes. To extend the absorption range of TiO\(_2\) 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, exited electrons and holes can be properly separated and their recombination rates, thus, can be reduced.\(^3\)

This study involves in In\(_2\)S\(_3\) 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 In\(_2\)S\(_3\) also can replace other toxic sensitizers such as CdS or PbS. We prepared the catalytic systems by depositing In\(_2\)S\(_3\) nanoparticles on the TiO\(_2\) 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 photocatalytic mechanism of the TiO\(_2\)/In\(_2\)S\(_3\) system.

2. Experimental Procedure

2.1. Preparation of In\(_2\)S\(_3\)/TiO\(_2\)/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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continuous 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$_2$S$_3$ 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$_2$S$_3$ 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 Na$_2$S·9H$_2$O (Sigma Aldrich, ≥ 99.99%). We used Nafion membrane (Dufont/NR211) to transfer H$^+$ ions selectively. Here, electrolyte Na$_2$S acted as a hole scavenger by suppressing the photo-corrosion (In$_2$S$_3$ $+$ 2h$^+$ $\rightarrow$ In$^{3+}$ $+$ S) which is common for chalcogenide compounds with S, Se, and Te. The adopted three-electrode setup consisted of TiO$_2$/In$_2$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 ($j_{on}$ $-$ $j_{off}$) 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$_2$S$_3$ nanoparticles. Note that the band structure of the prepared heterojunction has a unique feature that the electrons generated on In$_2$S$_3$ by photo-absorption transfer to TiO$_2$ and the holes generated on TiO$_2$ transfer to In$_2$S$_3$. Thus, the separation between electrons and holes is easily achieved. The holes accumulated in the valence band of In$_2$S$_3$ 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$_2$S$_3$: (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$_2$S$_3$ nanoparticles are about 20 nm and they cover the entire surface of TiO$_2$ nanotube. Fig. 3 is TEM-EDS result of the TiO$_2$/In$_2$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$_2$S$_3$ nanoparticles.

Fig. 2. Representative electron microscopes of TiO$_2$ nanotubes sensitized with In$_2$S$_3$ 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$_2$S$_3$ by successive ionic layer adsorption and reaction.
The photo-catalytic current density of the In\textsubscript{2}S\textsubscript{3}/TiO\textsubscript{2} system in the visible-light spectrum was evaluated by Potentiostat. An aqueous solution of 0.1 M Na\textsubscript{2}S·9H\textsubscript{2}O (pH = 12.4) was prepared as electrolyte and the three-electrode setup was adopted in the measurement. Fig. 4 is the chopping height ($j_{\text{on}}-j_{\text{off}}$) diagram of TiO\textsubscript{2} nanotubes sensitized In\textsubscript{2}S\textsubscript{3} 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/cm\textsuperscript{2} 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/cm\textsuperscript{2} for TiO\textsubscript{2} 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 In\textsubscript{2}S\textsubscript{3}, TiO\textsubscript{2} 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 TiO\textsubscript{2} 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 photocatalyst made of TiO\textsubscript{2} nanotubes grown by anodic oxidation and In\textsubscript{2}S\textsubscript{3} nanoparticles deposited by SILAR process. The prepared TiO\textsubscript{2} nanotubes are about 34 nm thick and the deposited In\textsubscript{2}S\textsubscript{3} 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 In\textsubscript{2}S\textsubscript{3} nanoparticles and its favorable position of the conduction band relative to that of TiO\textsubscript{2}, that promotes separation of the photo-generated electron-hole pair, reducing recombination. We also emphasize the fact that In\textsubscript{2}S\textsubscript{3} 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 In\textsubscript{2}S\textsubscript{3}.

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REFERENCES