Catalytic Activities of Sputtered p-type Cu₂O Electrode in Connection with TiO₂ Thin Film for Dye Degradation

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ABSTRACT

In this study, a p/n-type heterojunction was used to enhance the photocatalytic (PC) activity towards the degradation of methylene orange (MO) solution under ultraviolet (UV) irradiation. The cell consists of a p-type Cu₂O electrode and an n-type TiO₂ film of which was electrically connected together. The p-type Cu₂O electrode was prepared by radio frequency magnetron sputtering using a pure copper target under various O₂ flow rates (3-6 sccm). As expected, the Cu₂O electrode prepared at a flow of 5 sccm exhibited the highest photocatalytic activity on MO degradation among four different samples under UV irradiation. This is attributable to the electron transport favored (111) plane of the Cu₂O oxide. On the contrary, the Cu₂O electrode containing CuO phase exhibited the highest increase of MO degradation rate constant among four p/n-type heterojunctions although the band edges of the p-Cu₂O/n-TiO₂ heterojunction were properly positioned. Thus, the increase in photoactivity of the p-(Cu₂O/CuO)/n-TiO₂ heterojunction is due to the effect of the equilibration of Fermi level of which is more compatible for CuO and TiO₂ decreasing the electrochemical capacitances of the p/n heterojunction. This heterojunction offers an efficient way for photogenerated electron transport from n-type TiO₂ to holes in the p-type CuO/Cu₂O rendering enhanced PC activity.

Keywords: TiO₂; Cu₂O; heterojunction; photocatalytic degradation

1 INTRODUCTION

The photocatalytic degradation of various kinds of organic and inorganic pollutants using various semiconductor photocatalysts has been extensively studied in the past several decades. Among them, titanium dioxide (TiO₂) has been recognized as one of the most important photocatalytic materials [1]. Unlike TiO₂, cuprous oxide (Cu₂O) is a narrow band p-type oxide with a band gap of 2.0-2.2 eV and has also attracted extensive attention for its applications in solar energy conversion, as visible-light driven photocatalyst on H₂ evolution on directly splitting water [2-4] and dye degradation [5-7]. It has been reported that Cu₂O can effectively adsorb molecular oxygen, which can scavenge the photogenerated electrons to suppress the recombination of photogenerated carriers, and hence improve the photocatalytic efficiency. The merits of Cu₂O, i.e. non-toxicity and inexpensive low cost, make it a potential candidate for photocatalytic applications [8]. However, Cu₂O has been found to be photocorroded easily under photocatalytic degradation of benzamide, 4-hydroxybenzoic acid [9] or methyl orange (MO) [6], provided that the photogenerated holes could not completely induce an oxidation process in the aqueous solution. It has been found that the holes photogenerated in Cu₂O can not oxidize MO directly for whose oxidation potential is more positive (+0.94 V/SCE) than that of Cu₂O. In other words, MO can only be degraded by •OH or H₂O₂ of which has a powerful oxidation potential of +1.9 V or +2.2 V, respectively [6]. As we can see, the conduction band of Cu₂O is located at (-1.54 eV). This value is more negative than the conduction band potential of TiO₂ (-0.41 eV). In this case, thermodynamic conditions favor the photogenerated electron transfer from Cu₂O to TiO₂ and the holes are transferred from TiO₂ to Cu₂O. It has been pointed out that the oxidation potential of this semiconductor-semiconductor system can not be fully realized and a severe photocorrosion has been expected on the Cu₂O crystals [10]. Great efforts have been employed to facilitate charge transport and charge separation efficiency of p-Cu₂O coupled with a n-type semiconductor, such as WO₃ [3,4] or TiO₂ [8,11] as n-p heterojunction. In principle, the photocactivity is enhanced by the efficient transport of the majority holes from a p-type oxide (i.e. Cu₂O, CuO and Fe₂O₃) towards the external circuit to combine with the majority electrons from an n-type (i.e. WO₃ SnO₂ and TiO₂) oxide. Hence, photocorrosion of Cu₂O can be suppressed and photoactivity can be enhanced.

Several methods, such as thermal/chemical/anodic oxidations, electrodeposition and reactive magnetron sputtering, have been used to prepare Cu₂O thin films. Among them, electrodeposition method [8,12,13] and reactive magnetron sputtering technique [14] have attracted particularly attention in the past decade. Over the methods, the former is simplest method with good controllable properties [15], whereas the latter is a versatile deposition method and have been widely utilized for obtaining large-area uniform and dense TiO₂ and Cu₂O thin films with...
well-controlled stoichiometry [14]. In this study, we take the advantages of the chemical stability of TiO$_2$ which was coupled with a narrow band Cu$_2$O to form an n/p heterojunction using a reactive magnetron sputtering technique. In this p/n heterojunction, TiO$_2$ and Cu$_2$O electrodes were chosen as photoanode and photocathode, respectively, since Cu$_2$O is stable under photocathodic conditions [2].

2 EXPERIMENTAL PROCEDURE

Both Cu$_2$O and TiO$_2$ thin films were deposited on ITO (17 $\Omega$/sq. and 100±10 nm thick, ShinAn SNP, Taiwan) substrates by radio frequency (rf) and direct current (DC) magnetron sputtering using a copper and a titanium targets (100 mm in diameter and 99.99% purity), respectively, of a multi-target sputter (Psur-100HB, Taiwan). Some Cu$_2$O oxides were also deposited on glass slides at the same sputtering conditions for structural and optical property comparisons. Prior to the deposition of the Cu$_2$O or TiO$_2$ thin films, the glass substrate was ultrasonically cleaned in an acetone bath and rinsed with distilled water and pre-sputtering process was applied for 10 min to clean the target surfaces for removing any possible contamination. We denoted the Cu$_2$O samples grown on ITO and glass slide substrates as Cux and Cuxg, respectively, where $x$ stands for the O$_2$ flow rates and g for glass slide substrate. The base pressure was set to 2.7x10$^{-3}$ Pa, whereas the sputtering pressure, 0.4 Pa, was maintained as the reactive argon-oxygen gas mixture was introduced. In this study, Cu$_2$O films were obtained by varying the O$_2$ flow rates of 3 to 6 sccm while keeping the total gas mixture constant at 60 sccm. During the film deposition, the substrates were fixed in a disc fixture and rotated with a speed of 4 rpm in order to ensure film uniformity. The details for TiO$_2$ thin film preparations have been described elsewhere [16]. The target to the substrate distance was fixed at 60 mm and the substrate temperature was kept at 400°C for both oxide depositions. Both Cu$_2$O and TiO$_2$ film thicknesses were about 0.3 and 1.0 $\mu$m, respectively, as determined by scanning electron microscopy (SEM).

The crystal structures of the samples were analyzed using a high resolution X-ray diffractometer (XRD, Rigaku ATX-E) operating with Cu Ka radiation of 1.541 Å and a scan rate of 0.04°/20 from 20 =20° to 60°. The microstructure of the films was investigated by a scanning electron microscope (JEOL JSM-6700F).

The PC activity of the samples was evaluated by immersing p-Cu$_2$O facing TiO$_2$ sample with a size of 25×25 vs. 65×25 mm$^2$ into 30 mL aqueous methylene orange (MO) solution with an initial concentration of 10 mg/L ($C_0$). Prior to the PC test, the samples were soaked in the aqueous MO solution in darkness for adsorption test for 1 h. All experiments without stirring were performed under UV-light irradiation (3.5 mW/cm$^2$) at about 25°C. The blank experiments were performed under the identical conditions, but a glass slide or ITO glass substrate was used instead of a Cu$_2$O or TiO$_2$ film. The reaction rate constant was determined from the linear fitting of ln($C/C_0$) as a function of reaction time ($t$), where $C$ is the residual concentration of MO in the degraded MO solution. The reaction times were set at 0.5 h intervals from 0.5 to 1.5 h. The PC activity also performed on degradation of positively charged molecules of aqueous methylene blue (MB) solution for activity comparison of the Cu$_2$O or TiO$_2$ film. After every batch of photocatalytic degradation tests, the transmittance of the degraded MO and MB solution were measured at 462 and 664 nm, respectively, by a Shimadzu UV-1601 spectrometer. Adsorption of MO or MB dye was found to be negligible on the Cu$_2$O samples.

3 RESULTS AND DISCUSSION

3.1 Microstructural and Morphological Properties

Typical surface morphologies of SEM images of some selected Cu$_2$O films are displayed in Fig. 1. Sample Cu5 clearly shows a distinct feature of the pyramidal grains lying on the surface which are corresponding to the (111) growth direction [13,15,17]. This is the key morphological feature possessing a superior photocatalytic activity [13], which will be elucidated in the following section. As the O$_2$ flow rate decreased, the above-mentioned feature of pyramidal grains gradually diminished in Fig. 1(b) of sample Cu6. On the other hand, sample Cu3 exhibits obviously different morphology showing round pebble-like grains dominant on the surface, as shown in Fig. 1(c).

The transmission spectra of the Cu$_2$O films grown on glass slide substrates at various O$_2$ flow rates are illustrated in Fig 2, where sample Cu5 is presented for comparison.
The inset shows the corresponding absorption spectra of the samples. The absorption edge of Cu5g and Cu5 are estimated to be the same at 2.25 eV, which is in good agreement with characteristic of bulk Cu2O and the value reported by Liu et al. [15]. As CuO becomes a dominant phase in sample Cu6, the absorption edge red-shifts to longer wavelengths at 750 nm (1.7 eV). Alternatively, once Cu appears in sample Cu4, the transmittance drastically reduces as shown in Fig. 2(a) and (b). This finding is supported by the XRD patterns presented in Fig. 3. Hence, Cu6 is dark brown and Cu5 appears reddish brown in color.

Fig. 2: Transmission spectra of the Cu2O films grown on glass slide substrates at various O2 flow rates; inset: absorption spectra.

Fig. 3: XRD patterns of the Cu2O films grown on glass slide substrates at various O2 flow rates; *: Cu2O, #: Cu, I: ITO

The XRD patterns of Cu2O films deposited on glass slide substrates at different oxygen flow rates are shown in Fig. 3. It was observed that the XRD patterns of sample Cu5g (grown at an O2 flow rate of 5 sccm) are polycrystalline with preferable diffraction peaks at about θ=29.7°, 36.6° and 42.4° corresponding to the (110), (111) and (200) planes, respectively, as shown in Fig. 3(c). Other phases, such as CuO and Cu, are hardly traced in sample Cu5g. However, as shown in Fig. 3(d), CuO is the dominant phase in sample Cu6, whereas Cu is noticeable in sample Cu4g and significantly increases with a decrease in O2 flow rate. Some diffraction peaks of CuO and Cu phase were observed in sample Cu6 and Cu3, respectively, which

has detrimental effect on photocatalytic property of the samples [6]. Noted also that the (111) diffraction peak of sample Cu5g is much stronger than that of other planes, which is similar to the characteristic patterns reported by Liu et al. [15]. The grain size of the Cu2O is estimated to be 34 nm from the dominant diffraction (111) peak according to the Scherrer formula. The preferred diffraction of (111) plane is beneficial to both photochemical stability and PC activity [7,13].

On one hand, for the Cu2O film grown on ITO glass at an O2 flow rate of 5 sccm, three diffraction peaks are also identified as Cu2O (110), (111) and (200) planes, as shown in Fig. 4 where bare ITO glass substrate was presented for comparison. There is no noticeable difference in the XRD patterns of Cu2O films grown on glass slide and ITO substrates although the choice of substrate materials has been revealed a crucial role in the formation of crystalline Cu2O films [15]. This may be due to the large mismatch of Cu2O/ITO (~46%: (4.27-2.921)/2.921) system makes it difficult to grow Cu2O epitaxially as a result of Cu2O film with the same preferred orientation as that grown on isotropic substrate [15]. On the other hand, for Cu2O film grown on amorphous glass slide, the lowest surface energy of the Cu2O (111) facets prevails as the film grows [13]. This suggests that Cu2O thin film with well-crystallized Cu2O microstructure can successfully deposit on any commercial glass or ITO glass with good photocatalytic activity by using this technique.

3.2 Photocatalytic Properties

To investigate the PC capabilities of the p-Cu2O/n-TiO2 heterojunction, the PC degradation of both MO and MB were performed. MB can be oxidized by an attack by •OH, and DMSO is an efficient radical scavenger of •OH [18]. Hydroxyl radicals, produced by the photogenerated holes on TiO2, have been proposed as reactive species for the rapid decomposition of many organic compounds in liquid-phase PC reactions [1]. Alternatively, •OH and H2O2 produced by the photogenerated electrons on Cu2O whose reduction potentials are +0.28 V and +0.40 V far below the
Cu2O/WO3 heterojunction employed in splitting water. This enhancement has been reported on a circuit to combine with the majority electrons from an n-type oxide. The enhancement of the majority holes from a p-type oxide towards the external circuit is enhanced by the efficient transport of the photoactivity in MO degradation among samples under UV irradiation. This is attributable to the electron transport favored (111) plane of the Cu2O oxide. On the contrary, the Cu2O/CuO film exhibited the highest increase of MO degradation rate constant among p/n heterojunctions.

This may be due to the effect of the equilibration of Fermi level of CuO and TiO2 resulting in a decrease in the electrochemical capacitances of the p/n heterojunction.

Acknowledgements

The authors would like to thank the National Science Council of Taiwan, ROC, for financial support this research under Contract No. NSC 98-2221-E-004-MY2.

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