Catalytic Activities of Sputtered p-type Cu_2O Electrode in Connection with TiO_2 Thin Film for Dye Degradation

Chung-Wei Yeh[*], Chung-Hsuang Hung[**], Kee-Rong Wu[***], Jui-Ching Sun[****]

[*] Kao Yuan University, Kaohsiung, Taiwan, t90026@cc.kyu.edu.tw
[**] National Kaohsiung First University of Science and Technology, jeremyh@ccms.nkfust.edu.tw
[***] National Kaohsiung Marine University, krwu@mail.nkmu.edu.tw
[****] National Kaohsiung Marine University, 981532102@mail.nkmu.edu.tw

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 Cu_2O electrode and an n-type TiO_2 film of which was electrically connected together. The p-type Cu_2O electrode was prepared by radio frequency magnetron sputtering using a pure cupper target under various O_2 flow rates (3-6 sccm). As expected, the Cu_2O 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 Cu_2O oxide. On the contrary, the Cu_2O 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-Cu_2O/n-TiO_2 heterojunction were properly positioned. Thus, the increase in photoactivity of the p-(Cu_2O/CuO)/n-TiO_2 heterojunction is due to the effect of the equilibration of Fermi level of which is more compatible for CuO and TiO_2 decreasing the electrochemical capacitances of the p/n heterojunction. This heterojunction offers an efficient way for photogenerated electron transport from n-type TiO_2 to holes in the p-type CuO/Cu_2O rendering enhanced PC activity.

Keywords: TiO_2; Cu_2O; 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 (TiO_2) has been recognized as one of the most important photocatalytic materials [1]. Unlike TiO_2, cuprous oxide (Cu_2O) 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 H_2 evolution on directly splitting water [2-4] and dye degradation [5-7]. It has been reported that Cu_2O 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 Cu_2O, i.e. non-toxicity and inexpensive low cost, make it a potential candidate for photocatalytic applications [8]. However, Cu_2O 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 Cu_2O can not oxidize MO directly for whose oxidation potential is more positive (+0.94 V/SCE) than that of Cu_2O. In other words, MO can only be degraded by •OH or H_2O_2 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 Cu_2O is located at (-1.54 eV). This value is more negative than the conduction band potential of TiO_2 (-0.41 eV). In this case, thermodynamic conditions favor the photogenerated electron transfer from Cu_2O to TiO_2 and the holes are transferred from TiO_2 to Cu_2O. 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 Cu_2O crystals [10]. Great efforts have been employed to facilitate charge transport and charge separation efficiency of p-Cu_2O coupled with a n-type semiconductor, such as WO_3 [3,4] or TiO_2 [8,11] as n-p heterojunction. In principle, the photoactivity is enhanced by the efficient transport of the majority holes from a p-type oxide (i.e. Cu_2O, CuO and Fe_2O_3) towards the external circuit to combine with the majority electrons from an n-type (i.e. WO_3 SnO_2 and TiO_2) oxide. Hence, photocorrosion of Cu_2O 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 Cu_2O 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 TiO_2 and Cu_2O 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_2O to form an n/p heterojunction using a reactive magnetron sputtering technique. In this p/n heterojunction, TiO_2 and Cu_2O electrodes were chosen as photoanode and photocathode, respectively, since Cu_2O is stable under photocathodic conditions [2].

2 EXPERIMENTAL PROCEDURE

Both Cu_2O and TiO_2 thin films were deposited on ITO (17 Ω/sq. and 100±10 nm thick, ShinAn SNP, Taiwan) substrates by radio frequency (rf) and direct current (DC) magnetron sputtering using a cupper and a titanium targets (100 mm in diameter and 99.99% purity), respectively, of a multi-target sputter (Psur-100HB, Taiwan). Some Cu_2O 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_2O 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_2O 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_2O 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_2O and TiO_2 film thicknesses were about 0.3 and 1.0 μm, 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 Kα radiation of 1.541 Å and a scan rate of 0.04°/2θ from 2θ=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_2O 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_2O 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_2O 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_2O samples.

3 RESULTS AND DISCUSSION

3.1 Microstructural and Morphological Properties

Typical surface morphologies of SEM images of some selected Cu_2O 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).

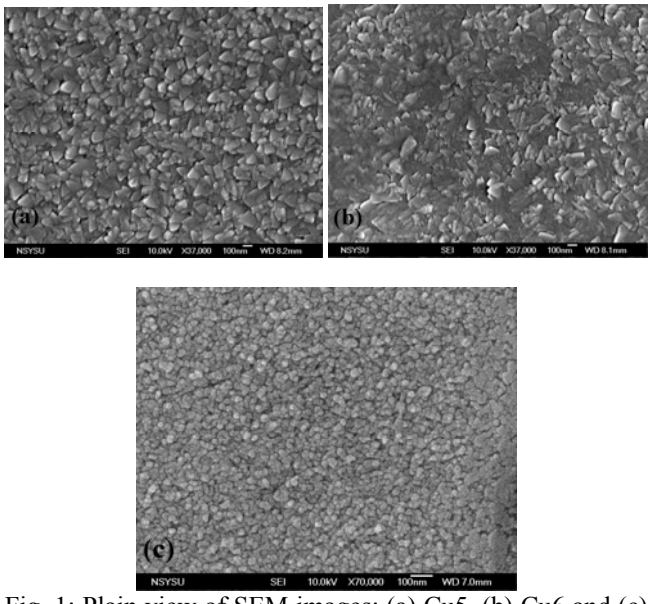

Fig. 1: Plain view of SEM images: (a) Cu5, (b) Cu6 and (c) Cu3 samples

The transmission spectra of the Cu_2O films grown on glass slide substrates at various O_2 flow rates are illustrated in Fig 2, where sample Cu5 are 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 Cu_2O 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.

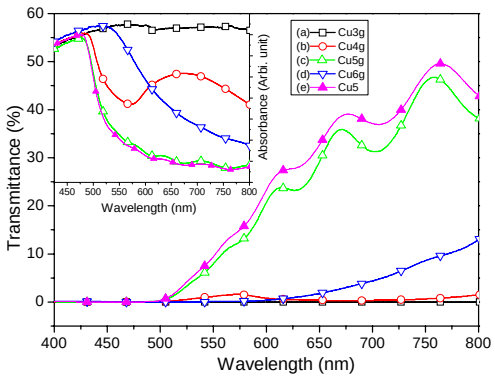

Fig. 2: Transmission spectra of the Cu_2O films grown on glass slide substrates at various O_2 flow rates; inset: absorption spectra.

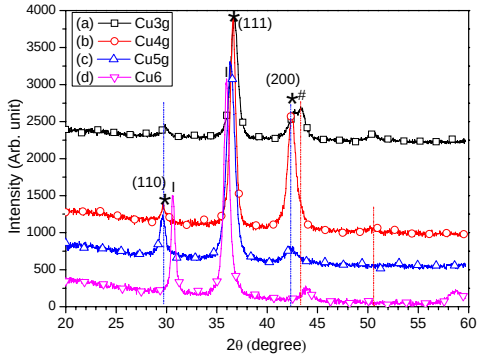

Fig. 3: XRD patterns of the Cu_2O films grown on glass slide substrates at various O_2 flow rates; ∗: Cu_2O, #: Cu, I: ITO

The XRD patterns of Cu_2O 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 O_2 flow rate of 5 sccm) are polycrystalline with preferable diffraction peaks at about 2θ=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 O_2 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 Cu_2O 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].

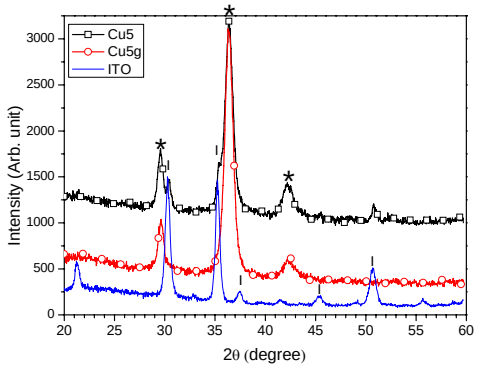

Fig. 4: XRD patterns of the Cu_2O films grown on glass slide and ITO substrates at various O_2 flow rate of 5 sccm; ∗: Cu_2O, I: ITO.

On one hand, for the Cu_2O film grown on ITO glass at an O_2 flow rate of 5 sccm, three diffraction peaks are also identified as Cu_2O (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 Cu_2O 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 Cu_2O films [15]. This may be due to the large mismatch of Cu_2O/ITO (~46%: (4.27-2.921)/2.921) system makes it difficult to grow Cu_2O epitaxially as a result of Cu_2O film with the same preferred orientation as that grown on isotropic substrate [15]. On the other hand, for Cu_2O film grown on amorphous glass slide, the lowest surface energy of the Cu_2O (111) facets prevails as the film grows [13]. This suggests that Cu_2O thin film with well-crystallized Cu_2O 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-Cu_2O/n-TiO_2 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 TiO_2, have been proposed as reactive species for the rapid decomposition of many organic compounds in liquid-phase PC reactions [1]. Alternatively, •OH and H_2O_2 produced by the photogenerated electrons on Cu_2O whose reduction potentials are +0.28 V and +0.40 V far below the

edge level of conduction band of Cu_2O can effectively degrade organic species [6]. As expected, sample Cu5 shows the highest MO degradation rate constant among three Cu_2O samples, whereas all samples have not PC activity (0.01 h^{-1}) on MB solution but TiO_2 (0.14 h^{-1}), as listed in Table 1. In contrary to our expectation, the p-Cu5/n heterojunction showed a lower MO degradation rate constant (0.58 h^{-1}) that than two stand alone oxides (p-Cu5 || n) (0.84 h^{-1}), as displayed in Table 2. Moreover, p-Cu6/n heterojunction is conversely of a higher MO degradation rate constant (0.45 h^{-1}) than the p-Cu6 || n oxides (0.25 h^{-1}). Noted that sample Cu5 exhibits Cu_2O phase with a little or no Cu or CuO but sample Cu6 shows mostly CuO phase with certain Cu_2O phases. In principle, the photoactivity is enhanced by the efficient transport of the majority holes from a p-type oxide towards the external circuit to combine with the majority electrons from an n-type oxide. This enhancement has been reported on a Cu_2O/WO_3 heterojunction employed in splitting water. However, it runs into an opposite result in our Cu_2O/TiO_2 system. As for p-Cu_2O, its Fermi level is more positive (vs. NHE) than that of TiO_2, the energy bands of Cu_2O and TiO_2 shift upside and downside, respectively, The decrease in MO degradation rate constant of the p-Cu5/n heterojunction might be the results of a positive shift of Fermi level where a decrease in redox potentials in Cu_2O or/and TiO_2. As for dominant p-CuO phase of sample Cu6, the equilibration of Fermi level is more compatible for CuO and TiO_2 that decrease the electrochemical capacitances of the CuO/TiO_2 heterojunction [19]. This positive effect on photocatalytic activity is analogues to the results obtained by CuO/TiO_2 heterojunction employed in hydrogen production from water [20]. However, the electrochemical capacitance behavior of CuO/TiO_2 and Cu_2O/TiO_2 needs further investigation.

Table 1: MO and MB degradation rate constant (h^{-1}) of sample Cu4, Cu5, Cu6 and TiO_2

	Cu4	Cu5	Cu6	TiO_2
MO	0.28	0.30	0.24	0.31
MB	0.01	0.01	0.01	0.14

Table 2: MO and MB degradation rate constant (h^{-1}) of p/n heterojunction and two stand alone oxides (p || n)

	Cu5-TiO_2	Cu5 || TiO_2	Cu6-TiO_2	Cu6 || TiO_2
MO	0.58	0.84	0.45	0.25
MB	0.10	0.10	0.10	0.08

4 CONCLUSION

In summary, the Cu_2O electrode exhibited the highest photocatalytic activity on MO degradation among samples under UV irradiation. This is attributable to the electron transport favored (111) plane of the Cu_2O oxide. On the contrary, the Cu_2O/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 TiO_2 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-022 -004 -MY2.

REFERENCES

[1] A. Fujishima, T. N. Rao, D. A. Tryk, J. Photochem. Photobiol. C 1 (2000) 1.
[2] S. Kakuta, T. Abe, Electrochem. Solid-State Lett. 12 (2009) P1.
[3] Hu, C.C., Nian, J.N., Teng, H., Sol. Energy Mater. Sol. Cells 92 (2008) 1071.
[4] Nian, J.N., Hu, C.C., Teng, H., Intl. J. Hydrogen Energy 33 (2008) 2897.
[5] J.Y. Ho, M.H. Huang, J. Phys. Chem. C 113 (2009) 14159.
[6] L. Huang, F. Peng, H. Yu, H. Wang, Solid State Sci. 11 (2009) 129.
[7] Z. Zheng, B. Huang, Z. Wang, M. Guo, X. Qin, X. Zhang, P. Wang, Y. Dai, J. Phys. Chem. C 113 (2009) 14448.
[8] W. Siripala, A. Ivanovskaya, T.F. Jaramillo, S.H. Baeck, E.W. McFarland, Sol. Energy Mater. Sol. Cells 77 (2003) 229.
[9] Y. Bessekhouad, D. Robert, J.V. Weber, Catal. Today 101 (2005) 315.
[10] H. Chen, S. Chen, X. Quan, H. Yu, H. Zhao, Y. Zhang, J. Phys. Chem. C 112 (2008) 9285.
[11] M.K.I. Senevirathna, P.K.D.D.P. Pitigala, K. Tennakone, J. Photochem. Photobiol. A 171 (2005) 257.
[12] R. Inguanta, S. Piazza, C. Sunseri, Electrochim. Acta 53 (2008) 6504.
[13] L. Wu, L.k. Tsui, N. Swami, G. Zangari, J. Phys. Chem. C 114 (2010) 11551.
[14] K. Akimoto, S. Ishizuka, M. Yanagita, Y. Nawa, Goutam K. Paul, T. Sakurai, Sol. Energy 80 (2006) 715.
[15] Y. L. Liu, Y. C. Liu, R. Mu, H. Yang, C. L. Shao, J.Y. Zhang, Y.M. Lu, D.Z. Shen, X.W. Fan, Semicond. Sci. Technol. 20 (2005) 44.
[16] K.R. Wu, C.H. Hung, M.H. Tsai, Appl. Catal. B 92 (2009) 357.
[17] S. Ishizuka, T. Maruyama, K. Akimoto, Jpn. J. Appl. Phys. 39 (2000) L786.
[18] C. Tai, J. F. Peng, J. F. Liu, G. B. Jiang, H. Zoub, Anal. Chim. Acta 527 (2004) 73.
[19] M. Jayalakshmi, K. Balasubramanian, Int. J. Electrochem. Sci. 4 (2009) 571.
[20] J. Bandara, C.P.K. Udawatta, C.S.K. Rajapakse, Photochem. Photobiol. Sci. 4 (2005) 857.