Copper-Iron Oxide: A Highly Effective Photocatalyst Than TiO_2 Prepared by One-Step Sparking Process

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Abstract

Copper-iron (Cu-Fe) oxide composite films were successfully deposited on quartz substrate by a facile sparking process. The nanoparticles were deposited on the substrate after sparking off the Fe and Cu tips with different ratios and were then annealed at different temperatures. The network particles was observed after annealed the film at 700°C. Meanwhile, XRD and SAED patterns of the annealed films at 700°C consisted of a mixed phase of CuO, γ -Fe₂O₃, CuFe₂O₄ and CuFe₂O. The film with a lowest energy band gap (E_g) of 2.56 eV was observed after anneal at 700°C. Interestingly, the optimum ratio and annealing temperature show highly photocatalytic activity than annealed TiO₂ at 500 and 700°C. This is a novel photocatalyst which can be replace TiO₂ for photocatalytic applications in the future.

1. Introduction

Photocatalysis is a green technology for environmental purification, in particular the decomposition of organic pollutants [1–3]. Over the last decade, many researchers have been reported that n-type semiconductor materials successfully photodegraded organic pollutants based such as titanium dioxide (TiO₂) [4–7]. Anywise, n-type semiconductors are still limited due to their large forbidden bands, low quantum yields, and unsuitable conduction band edges [8–9]. Thus, p-type semiconductors have been developed to expand the field of photocatalysis [10]. Copper (Cu) and iron (Fe) oxide are p-type semiconductors that can exhibit much more excellent properties in many applications [10–13].

Generally, the combinations of metal oxide can produce a novel compound which might improve their physical, chemical, optical and electrical properties, such as Cu-Fe oxides [14–17]. However, the report about Cu-Fe oxides in the field of photocatalysis is infrequently found. In this work, we aim to synthesize novel Cu-Fe oxides composite films by a one-step sparking process. This process has been developed in our lab which can prepare small, uniform particles, high porous films, and determine the composite ratio [18–26]. Moreover, the sparking process requires neither complicated steps nor special equipment, cheap, fast, and non-toxic. Surface morphology, chemical and optical properties of the as-deposited composite films were improved by heat treatment. The effect of heat treatment on morphology, chemical and optical properties were reported and discussed. Furthermore, the photocatalytic activity under visible light between Cu-Fe oxides and TiO₂ films was examined and compared.

2. Experimental Details

The experiment was carried out using a high DC voltage of 2.0 kV applied to Fe tips (0.25 mm, purity 99.5%, Advent Research Material Ltd.), and Cu tips (0.25 mm, purity 99.9%, Advent Research Material Ltd, UK). Cu:Fe with the ratios of 4:0, 3:1, 2:2, 1:3, and 0:4 can be defined from the number of sparking head. The tips were placed 1.5 cm above the quartz substrate (1x1 cm²) at 1 mm spacing under atmospheric pressure. The nanoparticles were then deposited on the substrate with a deposition rate of 52.33 nm/min for 10 min after sparking off the Fe and Cu tips. The as-deposited films were then annealed at 500, 600, 700, 800, and 900°C for 60 min to improve their crystallinity.

Morphology, chemical and optical properties of the samples were characterized using scanning electron microscopy (SEM, JEOL JSM300 and SEM, JEOL JSM 6335F), transmission electron microscopy (TEM, JEOL JEM 2010), X-ray Photoelectron Spectroscopy (XPS, AXIS Ultra DLD-X-ray Photoelectron Spectrometer and a monochromatic AlK α X-ray excitation source) and UV-Vis spectroscopy (Hitachi U-4100).

Photocatalytic activity was investigated by the decomposition of methylene blue (MB) solution (Ajax Finechem). The samples were dipped into 3.0 mL of MB solution with a concentration of 10.0 μ M and then irradiated a lamp (TB814SU-Y lamp with wavelength and luminance of 340-900 nm and 6.57×10^5 Lux, respectively) for 1-5 h. Degradation of MB can be indicated by measuring the absorbance using UV-Vis spectrophotometer.

3. Results And Discussion

The effect of Cu:Fe ratio and annealing temperature on MB degradation have shown in Fig. 1a and 1b. Moreover, the annealed TiO $_2$ at 500°C and 700°C which were prepared by the sparking process were used to compare MB degradation with the Cu-Fe oxide film at 700°C against irradiation time, as shown in Fig. 1c. It is noted that the annealed Cu-Fe oxide film at 700°C with the ratio of 2:2 has the highest degradation performance than the well-known photocatalyst such as TiO $_2$. Thus, a new finding of Cu-Fe oxide which was used as photocatalyst is a strong point of this work.

Figure 2a shows the morphology of the annealed Cu-Fe oxide film at 700°C with a ratio of 2:2. The nanoparticles were aligned to networks with the length and width of 1410 nm and 279 nm. This is because the high surface energy of nanoparticles, Cu-Fe oxide nanoclusters were agglomerated to decrease their surface energy. Meanwhile, the agglomeration of adjoining grains becomes more observable for higher kinetic energy [26–27]. According to the arrangement of the network particles, it can increase the MB decomposition which correspond to Fig. 1b.

TEM image of the annealed Cu-Fe oxide film at 700°C with a ratio of 2:2 is shown in Fig. 2b. It is clearly seen that the actual particle sizes are in the range of 4-15 nm, while its the energy dispersive x-ray shows the amount of Cu, Fe, and O are 28.26, 31.44, and 40.35 atomic %, respectively (data not shown). Moreover, the selected area electron diffraction (SAED) (inset) shows well-established diffraction rings matching most closely with CuO in the (111), (002) plane (JCPDS 48-0937), γ -Fe $_2$ O $_3$ in the (311), (220), (400) planes (JCPDS 39-1346), CuFe $_2$ O $_4$ in the (101), (211), (220), (224) planes (JCPDS 34-0425), and CuFeO $_4$ in the (006), (012), (018) plane (JCPDS 39-0246).

Comparison of the phase volumes of the annealed Cu-Fe oxide film at 600, 700, 800 and 900°C which evaluated by XPS (data not shown) are shown in Fig. 3a. It is noted that the CuFe $_2$ O $_4$ and CuFeO $_2$ were increased with increasing the annealing temperature [28]. However, an exceed CuFeO $_2$ at the annealing temperature higher than 700°C might inhibit the photocatalytic reactions. This is due to the factors causing the thin films to have an increased energy gap when the temperature is higher than 700°C

because of the effects of % rate of the crystal structure, microstructure characteristics, and the characteristics of chemical compositions [29].

Figure 3b shows the energy band gap (E_g) of the as-deposited, the annealed Cu-Fe oxide films at 500, 600, 700, 800 and 900°C which are 5.35 eV, 3.88 eV, 2.89 eV, 2.56 eV, 2.94 eV and 5.63 eV, respectively. This behavior can be described by an atom distancing increased with the increasing of annealing temperature [30]. Interestingly, the annealing at 700°C not only show lowest E_g but also show highest photocatalytic activity (see Fig. 2b). This is because the good mixing ratio between Cu and Fe oxide phase [31].

Increasing of photocatalytic activity in the annealed Cu-Fe oxide film at 700°C with a ratio of 2:2 can be described by Cu-Fe mixed phase mechanism, as shown in Fig. 4. The generation of photocatalytic mechanism is based on pairs of electrons (e^-) and holes (h^+) over the composites [32]. The E_{VB} of CuO, γ -Fe₂O₃, CuFe₂O₄, and CuFeO₂ are +2.10, +2.67, +2.06, and +2.46 eV/NHE. While, the E_{CB} of CuO, γ -Fe₂O₃, CuFe₂O₄, and CuFeO₂ are +0.52, +0.09, +0.64 and -0.14 eV/NHE, it can be theoretically calculated using the empirical formula [33]. The possible photocatalytic mechanism of the optimum condition was started by photo-generated electrons (e^-) and holes (h^+) pairs from CuFe₂O₄ and CuO. The photo-excited e^- in the γ -Fe₂O₃ and CuFeO₂ were injected into the CB of the CuFe₂O₄ and CuO. While, the photo-excited h^+ would transfer to the surface of γ -Fe₂O₃ and CuFeO₂, which can improve the charge separation and inhibit the e^-/h^+ recombination. This is a key factor for the enhancing photocatalytic activity of the annealed Cu-Fe oxide film at 700°C with a ratio of 2:2 which greater than a photocatalyst as TiO₂.

4. Conclusions

A novel photocatalyst Cu-Fe oxide films was successfully prepared by one-step sparking process. The optimum ratio of Cu:Fe and annealing temperature for MB degradation were 2:2 and 700°C. The results show the Cu:Fe ratio has direct affect to photocatalytic activity. Furthermore, the annealing temperature not only affect to the surface morphology but also affect to the E_g and photocatalytic activity. A new finding of this work is the higher performance photocatalyst than TiO₂ which can be developed and used for the phtocatalytic applications in the future.

Declarations

Acknowledgments

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Figures

Figure 1

plot of degradation versus (a) ratios of Cu:Fe, (b) annealing temperatures
(c) irradiation time of the Cu-Fe oxide films.

Figure 2

(a) SEM image, (b) TEM image and their SAED pattern (inset) of the annealed Cu-Fe oxide film at 700 °C with a ratio of 2:2.

Figure 3

(a) comparison of the Cu-Fe phases at different annealing temperatures and (b) plot of $(\alpha h\nu)^2$ versus photon energy of the films at different annealing temperatures

Figure 4

schematic diagram for photocatalytic mechanism of the optimum condition.