Fabrication of visible light-triggered photocatalytic materials from the coupling of \textit{n}-type zinc oxide and \textit{p}-type copper oxide

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Abstract. Coupling of copper oxide (CuO) and zinc oxide (ZnO) was done by chemical precipitation method. In this method, copper sulfate pentahydrate and zinc sulfate heptahydrate salt precursors were separately dissolved in distilled water; then were mixed together. The copper sulfate-zinc sulfate solution was then combined with a sodium hydroxide solution. The precipitates were collected and washed in distilled water and ethanol several times, then filtered and dried. The dried sample was grounded, and then undergone heat treatment. After heating, the sample was grounded again. Zinc oxide powder and copper oxide powder were also fabricated using chemical precipitation method. X-Ray Diffraction measurements of the coupled CuO/ZnO powder showed the presence of CuO and ZnO in the fabricated sample. Furthermore, other peaks shown by XRD were also identified corresponding to copper, copper (II) oxide, copper sulfate and zinc sulfate. Results of the photocatalytic activity investigation show that the sample exhibited superior photocatalytic degradation of methyl orange under visible light illumination compared to copper oxide powder and zinc oxide powder. This may be attributed to the lower energy gap at the copper oxide-zinc oxide interface, compared to zinc oxide, allowing visible light to trigger its photocatalytic activity.

1. Introduction

Photocatalysis using oxide semiconducting materials is used for environmental cleaning [1-10]. When light, with energy greater than or equal to the band gap of the semiconductor, is incident on the material, it can excite the valence electrons to the conduction band, leading to the generation of excitons (electron-hole pairs). The generated holes can react with water molecules to form highly reactive hydroxyl radicals (\textit{OH}*). The hydroxyl radical has the ability to decompose organic molecules (e.g., pollutants) since it has a high oxidation potential. Therefore, there is a need to increase the production of these hydroxyl radicals to improve the photocatalytic degradation ability of a material.

Commonly used metal oxide photocatalytic materials such as ZnO and TiO$_2$, which are \textit{n}-type semiconductors, have wide band gaps: 3.2-3.7 eV for ZnO [11], 3.2 eV for anatase TiO$_2$ and 3.0 eV for rutile TiO$_2$ [12]; thus, they are ultraviolet light-triggered. But most of the abundant light available, such as indoor light and sunlight, are primarily in the visible light region. Because of this, efforts have
been made to enhance the photocatalytic response of metal oxide materials under visible light illumination. Some of these methods include doping and coupling. On one hand, doping produces energy levels within the band gap of the material. However, the process of doping demands complicated procedures. On the other hand coupling results to a reduced energy gap at the interface leading to a lower energy is needed to generate excitons, allowing visible light to trigger its photocatalytic activity. It also increases the lifetime of charge carriers. Since coupling is merely a contact between two semiconductors, its fabrication method is relatively easy.

Copper oxide is a narrow band gapped semiconductor (1.7 eV), which corresponds to visible light. Although it is known to have low photocatalytic activities since it is intrinsically a $p$-type semiconductor, it is a good candidate for coupling with that of ZnO and TiO$_2$. The energy diagrams of coupled CuO and ZnO are shown in different literatures [13-19]. Coupling would result to the formation of an energy barrier that leads to the formation of $p-n$ heterojunction. The existence of this interface may lower the energy needed (compared to that of ZnO) to trigger the formation of excitons that is crucial in the activation of photocatalysis.

This research aims to fabricate photocatalytic material that can be triggered using visible light. This was done by coupling wide band gapped $n$-type zinc oxide and narrow band gapped $p$-type copper oxide by precipitation method. It is one of the simplest methods involving low-cost materials and equipment. In precipitation method, copper and zinc metal salts were used as precursors. These metal salts can easily be dissolved in water where it dissociates into metal ions. By using a precipitating agent, in this study NaOH, metal hydroxides are formed. These are the collected precipitates after the reaction. The hydroxides are known to be metastable and can easily oxidize into metal oxide.

2. Methodology

2.1 Fabrication of CuO/ZnO mixture via chemical precipitation
Coupled copper oxide and zinc oxide powder was prepared by precipitation method. In this method, 0.2 M CuSO$_4$·5H$_2$O metal salt and 0.2 M ZnSO$_4$·5H$_2$O metal salt were used as precursors. Both reagents were completely dissolved in distilled water separately and mixed thoroughly. Then the two solutions were combined into one solution, and poured into an aqueous solution of 0.2 M NaOH, and mixed vigorously. The formed precipitates were collected, washed with distilled water and 90% ethanol solution several times, then filtered and dried overnight. The dried samples were ground, and then heated at 500°C for 1 hr. Finally, the heat treated samples were ground again. Zinc oxide and copper oxide powders were also fabricated using precipitation method.

2.2 Characterization
X-ray diffraction (XRD) spectroscopy was used detect the different solid phases present in the sample. The XRD patterns were recorded using a Shimadzu XRD 7000, using CuKα X-rays at a scanning rate of 2°min$^{-1}$ between 3°-90°. The tube voltage and current used were 40.0 kV and 30.0 mA, respectively.

2.3 Test of Photocatalytic activity
The photocatalytic activities of the samples were determined through their ability to degrade methyl orange dye under visible light illumination. About 38 mM of methyl orange solution was placed in a vial. Then, 250 mg of the photocatalyst was added into the methyl orange solution and was shaken in the dark. The mixture was allowed to stand in the dark for 30 mins, and then illuminated. A light source with a UV cut-off filter was used. The degradation of methyl orange was determined by measuring the transmission of light through the sample. The intensity of the transmitted light was measured every 30 mins, for 4 hours. The photocatalytic degradation for each specific time was calculated.
3. Results and Discussion

Three powder samples were fabricated: (a) “CuO/ZnO powder”, (b) “ZnO powder” and (c) “CuO powder”. The sample labelled “CuO/ZnO powder” was fabricated using copper and zinc metal salt precursors. The second sample, labelled “ZnO powder” made use of zinc metal salt precursor, while the last sample labelled “CuO powder” made use of copper metal salt precursor. The oxidation process of the “CuO/ZnO powder” sample involved color change from blue to light brown. On the other hand, the oxidation of “ZnO powder” sample had no color change, while the “CuO powder” sample involved color change from blue to brown.

![XRD patterns](image)

**Figure 1.** XRD patterns of the prepared (a) “CuO/ZnO powder”, (b) “CuO powder”, and (c) “ZnO powder” samples. Markers correspond to: x-CuO, o-ZnO, w-Cu, +-Cu₂O, u-CuSO₄, v-ZnSO₄.

XRD shows that the three highest peaks of the CuO/ZnO powder (figure 1(a)) correspond to CuO and ZnO. The peaks corresponding to CuO occurred at 2θ~35.54° and 2θ~38.88°, while the peak corresponding to ZnO occurred at (2θ~34.76°). Other components present in the powder are Cu, Cu₂O, CuSO₄ and ZnSO₄. For the CuO powder sample (figure 1(b)), the highest peak occurring at (2θ~35.54°) correspond to CuO, however, other components were also detected including CuSO₄ and Cu. XRD also shows that all the peaks detected in the ZnO powder sample (figure 1(c)) correspond to ZnO.

The photocatalytic activities of the samples were evaluated based on their ability to photodegrade methyl orange under visible light. Figure 2 shows the graph of percent degradation as a function of illumination time for: (a) “CuO/ZnO powder”, (b) “CuO powder” and (c) “ZnO powder”. The degradation of methyl orange through time suggests the presence of photocatalytic activity of the samples. The highest percent degradation at 4 hours was found out to be 71.134% by the “CuO/ZnO powder” sample. This was followed by the “CuO powder” sample with 48.283% then the “ZnO powder” sample with 32.983%. Figure 2(a) shows that the highest photocatalytic activity was exhibited by the “CuO/ZnO powder” sample. It can be seen that the percent degradation from the initial time to 1 hour changes drastically. At 1 hour, the percent degradation reaches to 46.59%. From that point on, the percent degradation seems to saturate until it reaches the maximum at 4 hours. For the CuO powder sample, the percent degradation is very low for the first hour then increases with time at an approximately linear trend (figure 2(b)).

After 3 hours, the percent degradation reaches 30.32% and continues to increase until the fourth hour. The ZnO powder sample seems to have little to no percent degradation for the first 2 hours and 30 mins (figure 2(c)). It then increases to reach its maximum at 4 hours.
The improved photocatalytic activity of the fabricated CuO/ZnO powder compared with ZnO and CuO powder is attributed to the creation of a p-n heterojunction/interface. Figure 3 shows the energy band diagram of the coupled CuO and ZnO powder. The bending of the conduction band (E<sub>C</sub>) and valence band (E<sub>V</sub>) at the interface results to equalization of the Fermi energy level (E<sub>F</sub>) of the two materials. A positively charged depletion layer is created by the upward bending of bands in the n-type ZnO (n-ZnO) material while a negatively charged depletion layer is created by the downward bending of bands in the p-type CuO (p-CuO) material. Likewise, because of the difference of the band gaps of the two semiconductors, the difference between the valence and conduction band at the interface is lower than that of zinc oxide. Thus, the generation of excitons at the interface is triggered by visible light. It is expected that the more copper oxide-zinc oxide interfaces, the better visible light photocatalytic activity.

The visible light photocatalytic activity of CuO powder is lower compared to CuO coupled with ZnO, but higher than that of ZnO powder. It is known that CuO has low photocatalytic activity. However, this may be enhanced by coupling it with copper metal (as detected by XRD measurements) forming a Schottky-type junction/interface. Such interface/junction may work synonymously like that of the p-n heterojunction. On the other hand the low photocatalytic activity of the ZnO sample may be associated to its wide band gap, requiring high energy light source to generate excitons which will
react with water to produce OH radicals.

4. Conclusion
The researchers have successfully fabricated coupled CuO/ZnO powder samples for visible-light photocatalytic degradation of methyl orange. The CuO/ZnO powder was fabricated via chemical precipitation method which involved copper and zinc metal salts in aqueous solution as precursors and NaOH as the precipitating agent. The precipitates were grounded and heated to form the final powder samples, then were dispersed in methyl orange solution. Its photocatalytic activity was evaluated by its ability to degrade methyl orange under visible light illumination. The fabricated CuO/ZnO powder sample exhibited superior percent degradation compared to the CuO and ZnO powder samples. This is attributed to the formation of a p-n heterojunction.

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