Photocatalytic activity of BiVO₄ and ZnO-CuO nanoparticles under solar irradiation

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Abstract. A ZnO-CuO heterojunction was synthesized by a coprecipitation method using a mixture of different volumes of equimolar (0.5 M) aqueous solutions of zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and copper sulfate pentahydrate (CuSO₄·5H₂O) heated to 100 °C. Bismuth vanadate (BiVO₄) was synthesized by mixing stoichiometric amounts of partially dissolved solutions of Bi(NO₃)₃·5H₂O and NH₄VO₃. The resulting solution was then sonicated in an ultrasonic bath for 2 h at 45 °C. The synthesized photocatalysts have degraded methyl orange or methylene blue under solar irradiation.

1. Introduction
Visible light-driven photocatalysts have attracted extensive attention because they utilize solar energy effectively to solve urgent energy and environmental issues [1]. We have used two methods to enhance the photocatalytic properties in the visible region: surface modification of known metal oxides (ZnO, TiO₂) and new materials with a small band gap [2, 3]. Heterojunction construction using a p-n junction is a surface modification for known photocatalysts [2, 4], so we synthesized a ZnO-CuO heterojunction. Monoclinic scheelite bismuth vanadate (m-BiVO₄) has become one of the most promising photocatalysts because of its narrow bandgap (2.4 eV), high stability, nontoxicity and effective visible light photocatalytic response [5]. The synthesis of the photocatalysts was performed by either coprecipitation or assisted with ultrasonication routes because they are powerful and inexpensive routes for the synthesis of nanostructured materials [6].

2. Experimental
ZnO-CuO heterojunctions were synthesized by a coprecipitation method using a mixture of different volumes of a 0.5 M aqueous solution of zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and a 0.5 M aqueous solution of copper sulfate pentahydrate (CuSO₄·5H₂O) under stirring and heating to 100 °C; afterward, approximately 30 ml of a 1.0 M sodium hydroxide solution was added and stirred for 1 h. At that point, a brown precipitate was formed. Table 1 shows the different volumes used to synthesize different ZnO-CuO heterojunctions.

Bismuth vanadate (BiVO₄) was synthesized mixing stoichiometric amounts of a partially aqueous solutions of 0.5 M Bi(NO₃)₃·5H₂O and 0.5 M NH₄VO₃. The solutions were mixed under vigorous magnetic stirring for 1.5 h at room temperature. The resulting solution was then sonicated in an ultrasonic bath (Branson Model MT 1510) at 42 kHz and 75 W for 2 h at 45 °C. A yellow solid was formed, which was separated from the supernatant by centrifugation (Eppendorf Centrifuge 5810R). The precipitate was then washed using distilled water and centrifugation. Finally, the resultant yellow solid was dried at 80 °C for 12 h.
Table 1. Volume quantities of the precursor salts used to synthesize the ZnO-CuO heterojunctions.

| Sample (%) | CuSO$_2$·5H$_2$O (mL) | Zn(NO$_3$)$_2$·6H$_2$O (mL) |
|------------|------------------------|-----------------------------|
| ZnO-CuO    |                        |                             |
| 50-50      | 50.00                  | 41.98                       |
| 95-5       | 5.01                   | 80.00                       |
| 99-1       | 1.80                   | 80.00                       |

The structures of the synthesized samples were determined by X-ray diffraction using a Bruker D8 Advance diffractometer with CuK$_\alpha$ radiation (0.15045 nm wavelength) operated at 40 kV and 40 mA. The morphology of the nanoparticles was investigated by a field emission scanning electron microscope (FESEM) using a Hitachi SU8230.

An aqueous solution of methyl orange (MO) or methylene blue (MB) was used as a model contaminant for studying the photocatalytic performance of the prepared materials under solar irradiation. A solution with either 0.1 g of BiVO$_4$ or 0.5 g ZnO-CuO powder in 100 mL of a 10 ppm MO or MB aqueous solution was made and irradiated with sunlight for 3 h around midday on a sunny day. Samples of 30 mL were collected before and after 3 h of solar irradiation and filtered before analysis. The absorbance of the solution was measured with a Lambda 25 Perkin Elmer spectrophotometer.

3. Results and Discussion
Zinc oxide has a hexagonal structure, and copper oxide has a cubic structure. Figure 1 shows the pure phases of ZnO and CuO and the ZnO-CuO heterojunction. All diffraction peaks can be indexed as belonging to the ZnO and CuO phases.

Figure 1. XRD patterns of ZnO (asterisk), CuO (circle), and ZnO-CuO heterostructures.

Figure 2 shows an FESEM image of ZnO 95%-CuO 5% heterojunctions, which are agglomerated and clearly show small and large particles. The small particles could correspond to the CuO and the large ones to the ZnO of the nanocomposite, which agrees with the XRD measurements.
Figure 2. FESEM image of a ZnO 95%-CuO 5% heterojunction nanocomposite. Scale bar indicates the magnification.

Figure 3 shows the XRD pattern of the obtained BiVO₄ powder. All diffraction peaks can be indexed as belonging to the monoclinic scheelite BiVO₄.

Figure 3. XRD pattern of the BiVO₄ powder.

The morphology of the BiVO₄ powders was studied by FESEM, and Figure 4 shows a typical micrograph for the obtained sample of BiVO₄, which looks similar to small crystals with a smooth surface.

Figure 4. FESEM images of BiVO₄ powder.
ZnO-CuO and BiVO₄ solutions with either MO or MB were irradiated under sunlight for 3 h, during which evidence of photocatalytic degradation was observed. Figure 5a shows a typical experiment of the photocatalytic degradation of MO using BiVO₄ and the favorable photocatalytic degradation induced by the synergistic effect of the ZnO-CuO heterojunction nanocomposite of MB under solar radiation is shown in Figure 5b. The ZnO 50%-CuO 50% was not photocatalytically active under solar irradiation. The pure ZnO and ZnO 95%-CuO 5% have a lower photocatalytic activity than the ZnO 99%-CuO 1%. The lower activity of the ZnO-CuO nanocomposites where CuO was higher than 1% wt. could be associated with the fact that both CuO and ZnO behave as independent photocatalysts rather than as a coupled system, so that the heterojunction could occur in the ZnO 99%-CuO 1% nanocomposite powder, minimizing the chances of charge transfer from one to the other. MB solution degradation by BiVO₄ was also observed.

Figure 5. Degradation of (a) methylene blue using the BiVO₄ powder and (b) methyl orange using the ZnO-CuO heterojunction nanocomposite powder under 3 h solar irradiation.

4. Conclusions
The pure BiVO₄ monoclinic phase was obtained according to X-ray diffraction, and a mixture of ZnO and CuO phases was obtained. Degradation of methyl orange and methylene blue was observed using the obtained powders under solar irradiation. The ZnO 99%-CuO 1% wt. powder has the highest photocatalytic property for MO. The BiVO₄ powder also has good photocatalytic properties for MB after 3 h of solar irradiation.

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