Synthesis and characterization of noble metal nanocomposites: Ag/Fe₃O₄/ZnO and Ag/Fe₃O₄/CuO/ZnO for better photocatalytic activity under visible light irradiation

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Abstract. Nobel metal such as silver (Ag) nanoparticles have been proven could enhance photocatalytic activity under visible light irradiation and prevent recombination of electron and hole. Fe₃O₄/ZnO and Fe₃O₄/CuO/ZnO has been investigated in our previous study. So in this work, a magnetic Ag/Fe₃O₄/ZnO and Ag/Fe₃O₄/CuO/ZnO nanocomposites were successfully synthesized using sol-gel method. The as-synthesized products were characterized by X-ray diffraction and ultraviolet–visible (UV-Vis) spectroscopy. The results showed that the nanocomposites were the combination of the desired nanoparticles. From the UV-Vis absorption spectra, we found the surface plasmon resonance (SPR) to be around ~440 nm. Under visible light irradiation, the Ag/Fe₃O₄/ZnO and Ag/Fe₃O₄/CuO/ZnO nanocomposites exhibited much higher photocatalytic activity than the Fe₃O₄/ZnO and Fe₃O₄/CuO/ZnO. The effect of catalyst dosage and initial concentration of methylene blue (MB) were also tested. To understand the mechanism in photocatalytic activity, several scavengers were tested. The reusability study suggested that the prepared nanocomposites can still maintain the degradation efficiency after four cycles, showing great potential for water purification.

Keywords: Ag/Fe₃O₄/CuO/ZnO, Ag, photocatalytic, methylene blue.

1. Introduction
In recent years, the use of semiconductor photocatalysts in the field of environmental purification have been intensively studied. Many researchers have found that by using semiconductors, especially metal-oxide semiconductors materials, in photocatalytic experiments, could degrade the organic pollutants efficiently without causing secondary pollutants [1, 2]. Zinc oxide, a II-IV compound semiconductor with a wide band gap, has been widely used in photocatalytic experiments due to its high photocatalytic efficiency, photosensitivity, low cost, high stability, and environmental friendly [3, 4].

However, ZnO as a direct wide band-gap (~3.24 eV [5]) semiconductor is only responsive to ultraviolet (UV) light, which reduces its efficiency in visible light, and ZnO has a high recombination rate of electron–hole [3–5]. Those limitations hinder the practical photocatalytic applications of ZnO. Therefore to overcome these limitations, we could modified ZnO by using several methods such as doping [6], coupled with another semiconductor [7], and deposition of noble metal [5]. Our research group has reported the synthesis and characterization of coupled ZnO with another semiconductor, CuO and Fe₃O₄, which created a Fe₃O₄/CuO/ZnO and also Fe₃O₄/ZnO nanocomposites [8, 9]. We found that
coupling ZnO with another metal oxide could enhance the degradation efficiency of methylene blue (MB) under UV light irradiation [10]. However, the degradation efficiency in the visible light region is still low.

Coupling semiconductors with noble metals such as silver (Ag) has also attracted a lot attention. Silver (Ag) has good physical chemical properties and high electrical conductivity [11]. Furthermore, the presence of Ag nanoparticles in semiconductors could create Schottky junctions, which could hinder the recombination of electrons and holes [12]. Additionally, the surface plasma resonance (SPR) effect of Ag nanoparticles could further increase the degradation efficiency in the visible light region [13].

Herein, we investigate the coupling of Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/CuO/ZnO nanocomposites with silver (Ag) nanoparticles to create Ag/Fe$_3$O$_4$/ZnO and Ag/Fe$_3$O$_4$/CuO/ZnO nanocomposites. The as-synthesized nanocomposites are used as photocatalysts for the degradation of MB under visible light irradiation. The results indicate the increase of degradation efficiency, which may be due to the incorporation of Ag in the nanocomposites.

2. Experimental

2.1. Materials

Iron (II) sulfate heptahydrate (FeSO$_4$·7H$_2$O, 99%), copper sulfate pentahydrate (CuSO$_4$·5H$_2$O, 99%), zinc sulfate heptahydrate (ZnSO$_4$·7H$_2$O, 99%), silver nitrate (AgNO$_3$), sodium hydroxide (NaOH), ethanol, ethylene glycol (EG), and methylene blue, were purchased from Merck. All chemical reagents (Merck) were of analytical grade and used without further purification.

2.2. Synthesis of nanomaterials

The preparation of Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/CuO/ZnO nanocomposites were discussed in the previous study [8–11]. With slight modification, the preparation of Ag/Fe$_3$O$_4$/ZnO nanocomposites are given as follows: ZnSO$_4$·7H$_2$O and NaOH were mixed in distilled water. This suspension was further stirred well under 80°C using a magnetic stirrer. Then an amount of Fe$_3$O$_4$ and Ag nanoparticles were dispersed into a solution of ethanol and distilled water with particular ratio were added into the suspension. After 2h stirring and heating, the mixed solution was collected, washed, aging, and then dried at 125°C for 1h under vacuum condition. The synthesis method for Ag/Fe$_3$O$_4$/CuO/ZnO is similar to that for Ag/Fe$_3$O$_4$/ZnO but an amount of CuO nanoparticles were added. We vary the amount of Ag in Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/CuO/ZnO by 5 wt.% and 25 wt.%, and the products were denoted as FZ–05 wt.% Ag, FZ–25 wt.% Ag, FCZ–05 wt.% Ag, and FCZ–25 wt.% Ag, where FZ and FCZ represent Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/CuO/ZnO nanocomposites. The materials were structurally characterized using X-ray diffractometer (Rigaku Miniflex 600), additionally the optical property was studied using UV-Vis spectroscopy.

2.3. Photocatalytic experiments

Methylene blue (MB) solution (20 mg/L) was used as a model of organic pollutants. In a typical photocatalytic experiment, 0.03 g of the as-synthesized sample was dispersed with vigorous stirring in 100 mL MB solution for 30 min under dark conditions to ensure adsorption–desorption equilibrium. Then the as-prepared solution was irradiated with visible light for 2 h. In every certain times interval (15 min), the absorbance of the MB solutions were measured using UV-Vis spectroscopy. The degradation efficiency was presented as $C_t/C_0$ versus irradiation time, where $C_0$ = initial concentration of MB before irradiation and $C_t$ = concentration of MB after a certain irradiation time.
3. Results and discussion

3.1. Structural and optical properties

As we can see in figure 1, the XRD patterns of all prepared nanocomposite samples exhibit a series of peaks that can be characterized for cubic spinel Fe$_3$O$_4$ (2$\theta$ = 30.14°, 35.49°, 43.28°, 53.76°, 57.20°, and 62.83°), hexagonal wurtzite ZnO (2$\theta$ = 34.47°, 36.26°, 47.50°, 56.70°, 68.06°, and 69.21°), and monoclinic CuO (2$\theta$ = 38.81° and 48.7°) in the samples coupled by CuO. With the addition of 25 wt.% Ag in Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/CuO/ZnO, new diffraction peaks were found at 2$\theta$ = 38.14°, 44.26°, 64.42°, and 77.44°, which can be assigned to the (111), (200), (220), and (311) planes of face-center-cubic (fcc) Ag. However, no new diffraction peaks could be found on addition of 5 wt.% Ag, which may be due to the low Ag content [14]. Absence of another peaks in the patterns indicated no impurities in prepared samples. The XRD results confirm the presence of Fe$_3$O$_4$, ZnO, CuO, and Ag nanoparticles in the FZ-Ag and FCZ-Ag nanocomposites. The grain size and lattice parameters of all prepared samples were analyzed using the Debye–Scherrer equation and Rietveld refinement model; the results are shown in table 1.

Figure 2 shows the UV-Vis absorbance spectra of FCZ, FCZ-05 wt.% Ag, and FCZ-25 wt.% Ag. As can be seen, the absorbance spectrum of the sample with the incorporation of Ag nanoparticles displays typical SPR around 400-450 nm [15], indicating the presence of Ag in the prepared samples.

Table 1. Lattice Constant and grain size of FZ, FZ-05 wt.% Ag, FZ-25 wt.% Ag, FCZ, FCZ-05 wt.% Ag, and FCZ-25 wt.% Ag.

| Samples                  | Lattice Constant (Å) | <D> (nm) |
|--------------------------|----------------------|----------|
|                          | Ag a=b=c  | ZnO a=b  | CuO a=b  | Fe$_3$O$_4$ a=b=c | Ag  | ZnO  | CuO  | Fe$_3$O$_4$ |
| Fe$_3$O$_4$/ZnO          | –        | –       | –       | –         | 8.374 | –    | 25    | 42         |
| Ag/Fe$_3$O$_4$/ZnO       | 4.085    | 3.242   | 5.214   | –         | –     | –    | –     | –          |
| Fe$_3$O$_4$/CuO/ZnO      | –        | 3.242   | 5.214   | 4.692     | 3.425 | 5.136| –     | –          |
| Ag/Fe$_3$O$_4$/CuO/ZnO   | 4.085    | 3.242   | 5.214   | 4.692     | 3.425 | 5.136| 8.374  | 13 18 15 42 |

Figure 1. XRD patterns of (a) pure Ag, (b) FZ, (c) FZ-05 wt.% Ag, (d) FZ-25 wt.% Ag, (e) FCZ, (f) FCZ-05 wt.% Ag, and (g) FCZ-25 wt.% Ag.

Figure 2. UV-Vis absorbance spectra of (a) FCZ, (b) FCZ-05 wt.% Ag, and (c) FCZ-25 wt.% Ag.
3.2. Photocatalytic performance

To study the photocatalytic performance of all prepared samples, MB was used as an organic pollutant. The photocatalytic experiment was tested under visible light irradiation. The MB solution containing the catalyst was kept in the dark for 30 min to reach adsorption–desorption equilibrium. As shown in figure 3a, after 120 mins the degradation efficiency of MB reached about 51%, 55%, 60%, 75%, 80%, 86%, and 100%, respectively, for pure ZnO, FZ, FZ–05 wt.% Ag, FZ–25 wt.% Ag, FCZ, FCZ–5 wt.% Ag, and FCZ–25 wt.% Ag. The incorporation of Ag nanoparticles into Fe₃O₄/ZnO and Fe₃O₄/CuO/ZnO nanocomposites was found to enhance the degradation efficiency under visible light irradiation. And with the increased amount of Ag, the degradation was further increased.

The pseudo first-order kinetic rate reaction is expressed by equation (1) bellow:

$$\ln \left( \frac{C_0}{C_t} \right) = kt + A$$

where $C_0$ is the initial concentration at $t = 0$, $C_t$ is the concentration at $t$, $t$ is irradiation time, and $k$ is the pseudo first-order kinetic rate constant. The kinetics of all prepared samples are presented in figure 3b. The $k$ values of FZ and FCZ increased with the addition of Ag nanoparticles. The rate order was determined as follows: FCZ–25 wt.% Ag $\rightarrow$ FCZ–05 wt.% Ag $\rightarrow$ FCZ $\rightarrow$ FZ–25 wt.% Ag $\rightarrow$ FZ–05 wt.% Ag $\rightarrow$ FZ $\rightarrow$ pure ZnO. The FCZ–25 wt.% Ag displays the best photocatalytic performance, with a $k$ value of 0.03261. These results further proof the increased in catalytic performance with the introduction of Ag in the nanocomposites.

In order to obtain the optimum catalyst dosage (FZ–25 wt.% Ag and FCZ–25 wt.% Ag), photocatalytic experiments were carried out by varying the dosage of catalyst from 0.01g to 0.04g with the concentration of MB = 20 mg/L. The results are shown in figure 4a; with the increased amount of catalyst from 0.01 g to 0.03 g, the degradation efficiency was also increased, but further increment in catalyst dosage lead to a decrease in degradation efficiency. The increase in degradation efficiency may be due to the increased number of active sites, which increases the formation of oxygen species [13]. However, further increase of dosage could result in severe catalyst aggregation, which leads to light scattering and reduced light penetration through the MB solution [16].
The effect of initial MB concentration on photocatalytic degradation was also examined in the presence of 0.03 g FZ–25 wt.% Ag and FCZ–25 wt.% Ag, varying the concentration of MB from 20 mg/L to 50 mg/L. The results (figure 4b) indicate that with the increase of the MB initial concentration decreased the degradation efficiency. The decreased in degradation efficiency may due to the shielding of light by dye molecules [17].

To further understand the mechanism in the photocatalytic activity process, we controlled the experiment by adding several trapping agents. In this experiment, sodium sulfate, di-ammonium oxalate, and tert-butyl alcohol were used to trap electrons, holes, and OH, respectively. Figure 4c shows that the addition of any trapping agent caused the degradation efficiency of MB to decrease by several percent. With the addition of di-ammonium oxalate (hole scavenger) the degradation efficiency was greatly inhibited; therefore, it can be inferred that the main active species in the photocatalytic experiment with FZ–25 wt.% Ag and FCZ–25 wt.% Ag nanocomposites are holes followed by OH and electrons.

Separation and reusability of the nanocomposite materials are also important issues. To examine reusability, the prepared nanocomposites were separated from the MB solution using an external magnet.

**Figure 4.** (a) The effect of dosage on the degradation efficiency of MB, (b) effect of initial concentration of MB on the degradation efficiency ([Catalyst] = 0.03 g), (c) effect of various scavenger and (d) the recycling experiment.
and reused for a second, third, and fourth photocatalytic cycle. In figure 4d we can see that the degradation efficiency is not significantly decreased after four cycles. This result shows that FZ–25 wt.% Ag and FCZ–25 wt.% Ag show great promise for use in industrial processes.

The enhanced photocatalytic activity of Ag/Fe$_3$O$_4$/ZnO and Ag/Fe$_3$O$_4$/CuO/ZnO nanocomposites under visible light irradiation is may caused by SPR of the Ag nanoparticles [12, 18], which was confirmed using UV-Vis absorbance spectroscopy (figure 2). The obtain main active species, holes, may due to the fact that hole could interact directly to the dyes pollutants whereas the electrons are trapped in metal region (Ag), in which SPR effect taken places [12, 15, 17].

4. Conclusions

Ag/Fe$_3$O$_4$/ZnO and Ag/Fe$_3$O$_4$/CuO/ZnO nanocomposites with different added amounts of Ag (5 and 25 wt.%) were successfully synthesized by using sol-gel method. The XRD pattern exhibited all desired peaks, confirm the existence of Ag, Fe$_3$O$_4$, CuO, and ZnO. UV-Vis spectroscopy could confirm the existence of SPR effect. These prepared samples exhibit highly efficient photocatalytic activity for the degradation of MB in aqueous solution under visible light irradiation. The maximum degradation efficiency and k values follow the order FCZ–25 wt.% Ag > FCZ–05 wt.% Ag > FCZ > FZ–25 wt.% Ag > FZ–05 wt.% Ag > FZ > pure ZnO. The maximum photocatalytic degradation is achieved with a reaction time of 120 min, catalyst dosage of 0.03 g, and initial concentration of 20 mg/L. The main active species follow the order: hole > OH > electron. In addition, the photocatalysts are found to be stable without loss of activity after four cyclic experiments.

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