Ag/Fe₃O₄/ZrO₂ Composite: Ternary Magnetically Separable UV-light-driven Photocatalyst for Removal Methylene Blue Dyes

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Abstract. In this research, we demonstrate the preparation of ternary Ag/Fe₃O₄/ZrO₂ composites as a novel magnetically separable UV-light-driven photocatalyst. The Fe₃O₄/ZrO₂ composites were successfully synthesized by using two-step methods, that is, sol-gel followed by ultrasonic-assisted method. Furthermore, the Fe₃O₄/ZrO₂ composites were coupled with silver through ultrasound-assisted method. The prepared samples were fairly characterized by using X-Ray Diffraction and UV-Vis DRS spectroscopy. The photocatalytic activity of this composite was tested to degrade methylene blue dyes under UV-light irradiation. The influence of catalyst dosage, initial concentration, and scavengers of active species were investigated and the results were discussed. Compared with Fe₃O₄/ZrO₂ sample, the Ag/Fe₃O₄/ZrO₂ composite with three weight ratio (5%, 15%, and 25%) of Ag to Fe₃O₄/ZrO₂ display higher photocatalytic activity. Among three variations of the weight ratio of Ag to Fe₃O₄/ZrO₂, 15% weight ratio of Ag in Ag/Fe₃O₄/ZrO₂ exhibits the superior photocatalytic performance followed by weight ratio of 25% and 5%. Moreover, the composite was found to be a reusable catalyst.

Keyword: Ag/Fe₃O₄/ZrO₂, photocatalyst, UV driven, reusable

1. Introduction

In recent years, wastewater treatment from industrial organic dyes has attracted particular attention because of an environmental hygiene-related. Persistent organic pollutant, such as methylene blue (MB) has a complex aromatic structure that causes it is not degraded easily by biological decomposition [1]. Moreover, the presence of organic dyes in the water system can cause serious damage to human health.

To overcome this issue, several methods, such as membrane filtration, coagulation, electrochemical oxidation, adsorption and advanced oxidation process (AOPs) have been established for wastewater treatment. Among these methods, AOPs has received much attention due to the excellent performance for mineralization of many non-biodegradable organic pollutants [2,3].

Many metal oxide semiconductors (MOS), such as TiO₂, SnO₂, ZrO₂, have been frequently employed as a supportive catalyst. Zirconium dioxide (ZrO₂) as a photocatalyst has attracted considerable attention due to its several advantages such as its low cost, non-toxicity, environment-friendly, and high stability [4,5]. However, the main drawback of ZrO₂ is the low catalytic performance because of fast recombination of electron-hole pairs.
Combining MOS with noble metal catalyst, such as Ag, has been carried out as an effort to improve the photocatalytic performance by diminishing the recombination of the photoexcitation electron-hole pairs by trapping electron in conduction band [6].

Much effort has been focused on the incorporation of magnetic components, like Fe$_3$O$_4$, into MOS photocatalyst, which can be easily separated from the treated solution by an external magnetic field. This technique is very useful in reusability for practical applications. Herein, the as prepared ternary Ag/Fe$_3$O$_4$/ZrO$_2$ composites were employed as a highly UV light-driven photocatalyst towards the degradation of MB. The physical and optical characteristics of the samples were examined by using XRD and UV-Vis spectroscopy. We also report that the prepared samples stable and recyclable for the degradation of MB.

2. Experimental Method

2.1 Materials

All the chemical reagents were of an analytical grade and were used without further purification. Iron(II) sulfate heptahydrate (FeSO$_4$·7H$_2$O, 99%), silver nitrate (AgNO$_3$), sodium dodecyl sulfate (SDS), sodium carbonate (Na$_2$CO$_3$), ethylene glycol (EG), zirconium(IV) chloride (ZrCl$_4$) and sodium hydroxide (NaOH) were purchased from Merck. NGP and graphene were purchased from Angstrom Materials.

2.2 Preparation of Fe$_3$O$_4$ nanoparticle

The Fe$_3$O$_4$ nanoparticles were synthesized by using the same method as described previously [7].

2.3 Preparation of ZrO$_2$ nanoparticle

The ZrO$_2$ nanoparticles were synthesized by using the sol-gel method. Briefly, ZrCl$_4$ and NaOH were dissolved separately in distilled water through magnetic stirring. Then, the ZrCl$_4$ solution was added to the NaOH solution slowly, followed by magnetic stirring for 3 h, which allowed a homogenous solution to be achieved. The temperature of solution was maintained at 80 °C during the stirring process. The mixed solution was then centrifuged to separate the products that were precipitated from the solution. The precipitates were rinsed with distilled water and ethanol several times to remove the impurities. The product was heated at 120 °C for 12 h. Then, it was calcined at the temperature of 550 °C. Calcination took place in the air for 5 h, at a heating rate of 10 °C min$^{-1}$.

2.4 Preparation of Ag nanoparticle

The Ag nanoparticles were synthesized by using a microwave-assisted method. AgNO$_3$ and SDS were separately dissolved in EG solution through magnetic stirring for 30 min. Meanwhile, Na$_2$CO$_3$ was dissolved in distilled water. Then, Na$_2$CO$_3$ solution was added into the SDS solution followed by adding AgNO$_3$ solution into Na$_2$CO$_3$ and SDS mixture solution. The solution was kept stirred for 10 min. Then it was placed in a microwave oven (800 W) for 1 min followed by magnetic stirring for 30 min. The mixed solution was centrifuged to separate the products that were precipitated from the solution. The precipitates were rinsed with distilled water and ethanol several times to remove the impurities. The product was heated at 120 °C for 5 h to obtain Ag nanoparticles.

2.5 Preparation of Fe$_3$O$_4$/ZrO$_2$ composite

The Fe$_3$O$_4$/ZrO$_2$ composites were synthesized by using ultrasonic-assisted method. Briefly, ZrO$_2$ nanoparticles were mixed with Fe$_3$O$_4$ in aqueous and ethanol mixture. Then, the mixed solution was given ultrasonic for 2 h followed by centrifugation to obtain the product on its precipitation. The obtained product was dried in vacuum condition at 80 °C for 12 h to obtain Fe$_3$O$_4$/ZrO$_2$ composites which were labeled as FZ.
2.6 Preparation of Ag/Fe$_3$O$_4$/ZrO$_2$ composite
The ternary Ag/FZ with various Ag weight percentage (wt%) were synthesized by using the same method and procedure as synthesizing FZ composites.

2.7 Characterization
X-ray Diffraction (XRD) performed on a Rigaku Miniflex 600 diffractometer with Cu K-α radiation ($\lambda$ = 1.5406 Å) was used to obtain the crystal structure of samples. Study on the optical properties of samples was carried out by using UV-Vis spectroscopy (UV-Vis).

2.8 Photocatalytic activity
The photocatalytic activity of samples was investigated via degradation of an MB aqueous solution as a model of organic pollutant at room temperature. In the process, the photocatalyst was dissolved into MB solution. Then, the solution was continuously stirred in the dark for 30 min to ensure that an equilibrium was reached between the adsorption and desorption MB molecules on the catalyst surface. Subsequently, the solution was exposed to UV light irradiation. A small amount of the water sample was collected through centrifugation in every 15 min to measure the MB concentration with UV-Vis spectrophotometer. As a source of irradiation light, two lamps of 40 W UV-C were used.

2.9 Scavenger experiment:
To determine the species involved in photocatalytic activities, the different radical scavengers were added to the solutions of MB. Di-ammonium oxalate, sodium sulfate and tertbutyl alcohol (TBA) were used as scavengers for holes, electrons, and hydroxyl radical, respectively. The same measurements as described above were used.

3. Result and Discussion
As we can see in Figure 1, XRD patterns of Ag/FZ composites with various weight percent of Ag exhibit the series peaks that can be characterized as tetragonal phase of ZrO$_2$ ($2\theta = 30.18^\circ$, 35.03°, 50.36°, and 59.94°, which correspond to the [111], [200], [220], and [311] planes, respectively), cubic spinel phase of Fe$_3$O$_4$ ($2\theta = 30.14^\circ$, 35.49°, 43.28°, 53.76°, 57.20° and 62.83°, which correspond to the [220], [311], [400], [422], [511] and [440] planes, respectively) and cubic phase of Ag ($2\theta = 38.14^\circ$ and 44.26°, which correspond to the [111] and [200] planes, respectively). However, no typical diffraction peaks of Ag were observed within the 5wt% Ag/FZ composites, which probably due to the low content of Ag in sample. Furthermore, there were no others peaks from impurities, suggesting that all prepared samples have good purities. The lattice parameter and grain size of all prepared samples were calculated by using Debye-Scherrer’s formula and Rietveld refinement. The result are tabulated in Table 1.

| Samples | Ag (a=b=c) | Fe$_3$O$_4$ (a=b=c) | ZrO$_2$ (a=b) | <D> (nm) |
|---------|------------|---------------------|--------------|---------|
| FZ      | -          | 8.374               | 3.612        | 5.153   |
| 5wt% Ag/FZ | -          | 8.368               | 3.612        | 5.153   | 42      | 13     |
| 15wt% Ag/FZ | 4.085     | 8.361               | 3.609        | 5.152   | 13      | 41     | 13     |
| 25wt% Ag/FZ | 4.083     | 8.357               | 3.608        | 5.151   | 13      | 40     | 13     |
Figure 1. XRD patterns of Ag, ZrO$_2$, Fe$_3$O$_4$, FZ, 5 wt% Ag/FZ, 15 wt% Ag/FZ and 25 wt% Ag/FZ.

Figure 2. UV-Vis absorbance spectra of all prepared samples.

Figure 3. (a) The degradation of MB in the presence of different photocatalyst. (b) Effect of catalyst dosage on the degradation of MB.

Figure 2 shows the UV-Vis absorbance spectra of Ag, FZ, 5wt% Ag/FZ, 15wt% Ag/FZ and 25wt% Ag/FZ. As can be seen, there are broad peaks around 400 - 450 nm in Ag spectra which indicate the surface plasmon resonance (SPR) as a characteristic of Ag [8]. These broad peaks also can be seen at the samples of 5wt% Ag/FZ, 15wt% Ag/FZ and 25wt% Ag/FZ, indicating the presence of Ag on the prepared samples.

The photocatalytic performance was investigated by using pseudo-first-order kinetic model, which expressed:

$$\frac{C_t}{C_0} = e^{-kt}$$

where $C_0$ is the initial concentration, $C_t$ is the concentration at $t$, $t$ is the irradiation time, and $k$ is the pseudo first-order kinetic rate constant. The results of photocatalytic performance are shown in Figure 3 (a). As shown in Figure 3 (a), after 120 min UV light irradiation, the degradation efficiency of MB is reached about 69%, 80%, 95% and 89% for sample of FZ, 5wt% Ag/FZ, 15wt% Ag/FZ and 25wt% Ag/FZ, respectively.
Ag/FZ, respectively, at the condition of 0.3 g/L of catalyst dosage and 20 mg/L of initial concentration. These results indicate that the presence of Ag in samples can increase the photocatalytic performance. The reason is that Ag can form Schottky junction in composite, which can inhibit the rate of recombination of electron-hole pairs [6,9]. The degradation efficiency increased as increasing wt% of Ag until 15wt%, but decreased for 25wt% of Ag. This probably due to the decreased number of active sites brought by ZrO₂ as increasing wt% of Ag.

The effect of catalyst dosage on the degradation of the MB was performed. Catalyst dosages were varied from 0.1 g/L until 0.4 g/L for sample of 15 wt% Ag/FZ with 20 mg/L of MB initial concentration and the result is shown in Figure 4 (b). As can be seen, the degradation efficiency increased as the increase of catalyst dosage from 0.1 g/L until 0.3 g/L. Increasing catalyst dosage means increasing the number of active sites, which consequently increases the population of hydroxyl radicals as a reactive agent to degrade MB. However, when it overdoses, agglomeration of catalyst may occur with increasing turbidity, which turns to a decrease of light penetration and an increase of light scattering [10].

The effects of initial concentration MB were also carried out by varying it from 20 mg/L until 60 mg/L for sample of 15 wt% Ag/FZ with optimum catalyst dosage of 0.3 g/L. The results are shown in Figure 4 (a). This figure shows that the catalytic activity tends to decrease with the increase of MB initial concentration. The reason is that the solution transmittance decreased with increasing initial concentration, resulting in reducing the number of photons that reach the photocatalyst surface [11].

Figure 4. (a) Effect of initial concentration on the degradation of MB. (b) Effect of various scavenger on the degradation of MB

To elucidate the mechanism of photocatalytic, the effect of various active species which participate in photocatalytic activity were studied at optimum condition (0.3 g/L of catalyst dosage and 20 mg/L of initial concentration). The roles of the main active species were investigated by hole, electron and hydroxyl radical trapping experiments and the results obtained are shown in Figure 4 (b). The degradation efficiency of MB furthest decreased upon the addition of hole scavenger. This result demonstrated that the photocatalytic activity was mainly governed by holes, followed by electrons and hydroxyl radicals.

The photocatalytic stability of the 15 wt% Ag/FZ was studied by repeating the photocatalytic process four times at optimum condition. After each reaction finished, the photocatalyst was separated from the solution by an external magnet to be reused with newly MB solution. In Figure 5, we can see that after four-times cycles, the photocatalytic activity did not significantly decrease. The acceptable stability in repeated cycles demonstrated that the 15wt% Ag/FZ photocatalyst composite exhibited good activity for the repeated degradation of MB.
4. Conclusion
In this study, the photocatalyst ternary Ag/Fe$_3$O$_4$/ZrO$_2$ with various wt% of Ag were successfully prepared through ultrasonic-assisted method confirmed by XRD and UV-Vis spectroscopy. The best photocatalytic performance is attained with a 15wt% Ag/FZ composite. To understand the mechanism of the reaction, the Di-ammonium oxalate, sodium sulfate, and tertbutyl alcohol (TBA) were used as scavengers for holes, electrons, and hydroxyl radical, respectively. The result revealed that the hole is the main active species in the photocatalytic process, followed by electron and hydroxyl radical. The catalyst can be reused with no significant loss in photocatalytic activity for the four-times cycles.

5. References
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