Physical and Photocatalytic Properties of CeO$_2$/ZnO/ZnAl$_2$O$_4$ Ternary Nanocomposite Prepared by Co-precipitation Method

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ZnAl$_2$O$_4$ spinel nanoparticles and CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposites were synthesized by a co-precipitation method. The structural, morphological, optical properties and chemical compositions of the products were analyzed respectively by X-ray diffraction (XRD), scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS) and X-ray fluorescence (XRF) spectroscopy. The optical band gap of ZnAl$_2$O$_4$ spinel nanoparticles was 3.220 eV. When 1.0 mmol Ce(NO$_3$)$_3$·6H$_2$O was added to the synthesis reaction, the optical band gap of the obtained ternary nanocomposite was 3.170 eV. The influence of phase composition, optical band gap, oxygen vacancy and specific surface area on photocatalytic activity over CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposites was investigated. The CeO$_2$/ZnO/ZnAl$_2$O$_4$ nanocomposite prepared with 1.0 mmol Ce(NO$_3$)$_3$·6H$_2$O showed the lowest recombination rate of photoexcited electron-hole pairs, the narrowest optical band gap (3.170 eV) and the highest oxygen vacancy concentration or highest Urbach energy (0.299 eV). These parameters produced the best photocatalytic activity toward methylene blue (MB) under UV irradiation. The CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposites exhibited better photocatalytic performance than pure ZnAl$_2$O$_4$ spinel nanoparticles and 100% degradation of aqueous MB solution was achieved within 60 min when using the CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposite photocatalyst synthesized with 1.0 mmol Ce(NO$_3$)$_3$·6H$_2$O.

**Keywords:** nanocomposite; chemical synthesis; optical properties; photocatalytic properties.

1. Introduction

In recent years, the paper, textile, leather and cosmetic industries have developed rapidly worldwide. These industries attract customers by coloring their products with a range of synthetic organic dyes. When the use of synthetic organic dyes increases, the amount of wastewater produced also increases. To reduce pollution, factories must remove synthetic organic dyes in wastewater before they are discharged into natural waterways. The elimination of synthetic organic dyes from wastewater is accomplished by biological, coalescence and adsorption methods. However, since these methods cannot completely get rid of the synthetic organic dyes in a single step, further treatment is necessary. The photocatalytic process is another popular method of eliminating dyes. Removing the remaining dye in wastewater by photocatalytic degradation has several advantages; for example, photocatalytic conditions are mild, the use of chemical reagents is reduced, and synthetic organic dyes can be degraded to small non-toxic molecules. In photocatalytic degradation, the photocatalyst used is very important to the process. Therefore, the choice of photocatalyst is the primary consideration and a summary of the many different photocatalysts that have been used is presented in Table 1.

Recently, AB$_2$O$_4$ spinel oxides, in which A is a divalent metal ion and B is a trivalent metal ion, have gained attention from many research groups. This interest has led to their applications in water splitting, gas sensing, transparent conducting materials and photocatalysis. Zine aluminate (ZnAl$_2$O$_4$), a spinel oxide with a wide band gap of about 3.8 eV, is an important member of the AB$_2$O$_4$ spinel oxides. Applications of ZnAl$_2$O$_4$ include dosimetry, opto-electronic devices, gas sensing, ceramic support and photocatalysis. The unique properties of ZnAl$_2$O$_4$ spinel nanoparticles depend on various parameters and researchers have improved these properties by doping with divalent or trivalent metal ions, and loading with secondary metal oxide powders. ZnAl$_2$O$_4$ spinel nanoparticles have been synthesized by vibrational ball milling, hydrothermal synthesis, sol-gel synthesis, combustion and co-precipitation. The advantages of the co-precipitation method include low temperature preparation, high purity products, simple procedure and easy scalability.

The present work proposes a co-precipitation synthesis of CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposites using KOH solution as the precipitating agent. This process has not, to our knowledge, been reported previously. The synthesized nanocomposites were used in the photocatalytic degradation of MB. The chosen dye model enabled the assessment of the
suitability of the photocatalyst for applications in several industries. Photocatalytic activity over the CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposites was characterized to determine its dependence on structural, morphological and optical properties of the photocatalyst.

2. Experimental

2.1 Material

Zinc nitrate tetrahydrate (Zn(NO$_3$)$_2$·4H$_2$O, Emsure®, Germany), aluminium nitrate nonahydrate (Al(NO$_3$)$_3$·9H$_2$O, Sigma-Aldrich, Germany), cerium (III) nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O, Aldrich, China), potassium hydroxide (KOH, Emsure®), Germany), and methylene blue (C$_{16}$H$_{18}$ClN$_3$S, Emsure®, Germany) were purchased and used without further purification.

2.2 Synthesis of ZnAl$_2$O$_4$ spinel nanoparticles

ZnAl$_2$O$_4$ spinel nanoparticles were synthesized by a co-precipitation method. Following stoichiometric calculations, 0.005 mol Zn(NO$_3$)$_2$·4H$_2$O and 0.01 mol Al(NO$_3$)$_3$·9H$_2$O were weighed and dissolved in 100 mL distilled water for 15 min under moderate stirring by a magnetic bar. Then, 0.04 mol KOH dissolved in 100 mL distilled water was added dropwise into the prepared mixture solution of Zn$^{2+}$ and Al$^{3+}$ ions. The white precipitates obtained were continuously stirred and heated at 70°C for 1 h. After the reaction was terminated
and cooled to room temperature, the precipitates were washed three times with 200 mL distilled water, filtered and dried at 80°C for 2 h. Finally, the as-synthesized powders were calcined in air at 800°C for 1 h and the calcined powders were later characterized by various techniques.

### 2.3 Synthesis of CeO$_2$/ZnO/ZnAl$_2$O$_4$ nanocomposites

To enable investigation of the effect of CeO$_2$ and ZnO loadings on the ZnAl$_2$O$_4$ nanocomposites, 0.2, 0.4, 0.6, 0.8 and 1.0 mmol Ce(NO$_3$)$_3$·6H$_2$O were introduced separately into 100 mL mixture solutions prepared, as described in section 2.2, from 0.065 mol Zn(NO$_3$)$_2$·4H$_2$O and 0.01 mol Al(NO$_3$)$_3$·9H$_2$O. The precursor solutions were then precipitated with 0.04 mol KOH dissolved in 100 mL distilled water. The synthesis then proceeded in the same way as the synthesis of pure ZnAl$_2$O$_4$ spinel nanoparticles.

### 2.4 Characterization

Thermal gravimetric analysis (TGA) was used to investigate the thermal behavior of as-synthesized ZnAl$_2$O$_4$ spinel nanoparticles. The TGA thermogram was recorded by thermogravimetric analyzer (TGA 7, Perkin Elmer) under nitrogen gas. X-ray diffraction (XRD) was used to analyze ZnAl$_2$O$_4$ spinel nanoparticles and secondary phases (CeO$_2$ and ZnO). XRD patterns were recorded by powder X-ray diffractometer (XRD, XPert MPD, Philips). X-ray fluorescence spectrometry (XRF, Zetium, PANalytical) was used to analyze the chemical composition of synthesized products. Scanning electron microscope (SEM) was used to observe the morphology of samples. The secondary electron images (SEI) were obtained by scanning electron microscope (SEM, Quanta 400, FEI). Brunauer-Emmett-Teller (BET) surface area analysis was used to determine the specific surface area (SA) of powders. The adsorption isotherm was measured by BET surface area analyzer (Autosorb 1MP, Quantachrome). Diffuse reflection spectroscopy (DRS) was used to study the optical behavior and evaluate the optical band gap of powders. Absorbance spectra were measured by UV-Vis spectrophotometer (UV-Vis 2450, Shimadzu). To evaluate remaining MB concentration, the absorbance of MB solutions was measured by UV-Vis spectroscopy and temporal changes were recorded by UV-Vis spectrophotometer (UV-Vis Lambda 25, Perkin Elmer).

### 2.5 Photocatalytic test

The photocatalytic activity of ZnAl$_2$O$_4$ spinel nanoparticles and CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposites was evaluated by the degradation of aqueous MB solution under UV irradiation (3 parallel blacklight tubes, 15 W). In the typical procedure, 150 mg of photocatalyst were introduced into a 250 mL beaker containing 150 mL of 1×10$^{-5}$ M MB solution. Before irradiation, the suspension was continuously stirred with a magnetic bar for 30 min in darkness to attain adsorption-desorption equilibrium between the MB and photocatalyst. The suspension was then irradiated and 3 mL of the suspension were withdrawn every 30 min and centrifuged at 4000 rpm for 5 min to separate the photocatalyst. The absorbance of the supernatant was recorded between 400 and 800 nm to determine the remaining MB and calculate the percentage of MB degradation.

## 3. Results and Discussion

### 3.1 Thermal analysis

In the experimental procedure, reagents were mixed in distilled water and reacted with each other to form a new compound. The thermal decomposition of representative as-synthesized powders was analyzed to determine an appropriate calcination temperature to obtain a pure ZnAl$_2$O$_4$ phase. The thermal analysis proceeded from room temperature to 1,000°C at a heating rate of 10°C/min under nitrogen gas.

Thermal decomposition comprised three steps (Figure 1). The first weight loss of about 9%, between room temperature and 180°C, was due to the removal of physically adsorbed molecular water. The second weight loss of about 27%, between 180 and 500°C, derived from the elimination of structural water. The third weight loss of about 3%, between 500 and 750°C, was attributed to the removal of nitrates. No weight loss occurred above 750°C. Therefore, before characterization, the powders were calcined at 800°C in air for 1 h.

### 3.2 X-ray diffraction study

The phase formation of nanocomposites was identified from X-ray diffraction patterns of calcined samples (Figure 2). The diffraction peaks of cerium dioxide (CeO$_2$)
appeared at 20 diffraction angles of 28.58°, 33.18° and 79.37° (JCPDS 34-0394). The diffraction peaks of zinc oxide (ZnO) appeared at 20 diffraction angles of 31.80°, 34.47°, 36.30°, 47.58°, 56.59°, 62.95°, 67.95° and 69.36° (JCPDS 36-1451) and the diffraction peaks of zinc aluminate (ZnAlO₂) appeared at 20 diffraction angles of 31.60°, 36.97°, 44.78°, 55.56°, 59.72° and 65.58° (JCPDS 05-0669). A pure ZnAlO₂ spinel phase formed without a ZnO second phase when Ce(NO₃)₃·6H₂O was not present in the precursor solution. Therefore, the chemical reactions that occurred in this process can be expressed as reactions (1−3): 

\[
\begin{align*}
\text{Zn(NO}_3)_2(aq) + 2\text{Al(NO}_3)_3(aq) + 8\text{KOH}(aq) & \rightarrow \text{Zn(OH)}_2(s) + 2\text{Al(OH)}_3(s) + 8\text{KNO}_3(aq) \\
\text{Zn(OH)}_2(s) + 2\text{Al(OH)}_3(s) + 8\text{KNO}_3(aq) & \rightarrow \Delta \rightarrow \text{ZnAlO}_2(s) + 8\text{KNO}_3(aq)
\end{align*}
\]

(1) (2)

On the other hand, when Ce(NO₃)₃·6H₂O was added to the precursor solution, Ce³⁺ ions could not form a substitutional solid solution as ZnAl₂CeCeO₄. They were unable to do so because the ionic radius of the Ce³⁺ ion (101 pm) is significantly larger than that of the Al³⁺ ion (53 pm). Consequently, the Ce³⁺ ions could not replace the Al³⁺ ions at Al sites in the ZnAl₂O₄ spinel structure. According to the Hume-Rothery rule, an extensive substitutional solid solution occurs only if the relative difference between the ionic radius of Al³⁺ and Ce³⁺ is less than 15%. If the difference in ionic radius is more than 15%, a limited substitutional solid solution occurs. In this study, the difference was about 90%. Therefore, the replacement of Al³⁺ ions with Ce³⁺ ions could not occur. However, the Ce³⁺ ions could react with hydroxide ions to form Ce₂O₃ according to reactions (4−6): 

\[
\begin{align*}
\text{Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O}(_3) + \text{H}_2\text{O}(_l) & \rightarrow \text{Ce}^{2+}(_{aq}) + 3\text{NO}_3^{-}(_{aq}) \quad (4) \\
\text{Ce}^{3+}(_{aq}) + 3\text{OH}^{-}(_{aq}) & \rightarrow \text{Ce(OH)}_3(_{s}) \quad (5) \\
\text{Ce(OH)}_3(_{s}) & \rightarrow \Delta \rightarrow \text{Ce}_2\text{O}_3(_{s}) + \text{H}_2\text{O}(_g) + 0.5\text{H}_2\text{O}(_g) \quad (6)
\end{align*}
\]

Simultaneously, ZnO could be generated according to reactions (7−10): 

\[
\begin{align*}
\text{Zn(NO}_3)_2 \cdot 4\text{H}_2\text{O}(_3) + \text{H}_2\text{O}(_l) & \rightarrow \text{Zn}^{2+}(_{aq}) + 2\text{NO}_3^{-}(_{aq}) \quad (7) \\
\text{Zn}^{2+}(_{aq}) + 4\text{OH}^{-}(_{aq}) & \leftrightarrow [\text{Zn(OH)}_4 ]^{2-}(_{aq}) \quad (8) \\
[\text{Zn(OH)}_4 ]^{2-}(_{aq}) & \leftrightarrow \text{Zn(OH)}_2(_{s}) + 2\text{OH}^{-}(_{aq}) \quad (9) \\
\text{Zn(OH)}_2(_{s}) & \rightarrow \Delta \rightarrow \text{ZnO}(_s) + \text{H}_2\text{O}(_g) \quad (10)
\end{align*}
\]

Therefore, the products formed as CeO₂/ZnO/ZnAl₂O₄ ternary nanocomposites when they were calcined at 800°C in air for 1 h. In this study, it was observed that the intensity of the principal peaks of CeO₂ and ZnO increased as a function of Ce(NO₃)₃·6H₂O concentration. Therefore, it could be summarized that amounts of CeO₂ and ZnO formed increasingly.

In this study, chemical composition was determined by XRF technique. When the content of Ce(NO₃)₃·6H₂O in the reactions was 0.2, 0.4, 0.6, 0.8 and 1.0 mmol, the CeO₂ content of the products was about 0.92, 2.15, 3.52, 4.30 and 6.06%, respectively, and the ZnO contents were 11.68, 14.41, 16.81, 17.97 and 18.90%. The amount of CeO₂ and ZnO in the product increased as a function of Ce(NO₃)₃·6H₂O concentration. This was in good agreement with XRD results.

3.3 Morphological study

As presented in Figure 3, the morphology of pure ZnAl₂O₄ spinel nanoparticles was an irregular sponge-like structure made up of agglomerated spherical nanoparticles7,39,51 but ZnO particles formed a facet structure in a strongly alkaline solution at pH = 1150. In this study, ZnO particles formed as rod structures along the c-axis, which had the growth velocity in the following order: \(\gamma_{(0001)} > \gamma_{(1010)} > \gamma_{(1011)} > \gamma_{(0001)}\). At the same time, fluffy particles of CeO₂ formed on the surfaces of ZnAl₂O₄ spinel nanoparticles. In agglomerations, many small particles are attracted to one another through chemical bonds and physical forces at interfaces. However, some crystals form a faceted structure due to the different surface energies present at different crystal facets. If particles agglomerated to form a large cluster or a faceted structure, overall surface energy decreased52 and a more stable system resulted.

3.4 Optical properties

Figure 4 shows the UV-vis diffuse reflectance spectra of ZnAl₂O₄ spinel nanoparticles and CeO₂/ZnO/ZnAl₂O₄ nanocomposites. The absorption edge of CeO₂/ZnO/ZnAl₂O₄ ternary nanocomposites shifted towards longer wavelengths or lower energies compared to the absorption edge of pure ZnAl₂O₄ spinel nanoparticles. This shift towards longer wavelengths occurred as a function of the Ce³⁺ ion concentration in the precursor solution and absorption edges shifted to longer wavelengths as the optical band gaps of samples narrowed. Therefore, electrons in valence bands were excited to conduction bands by consuming less photon energy.

The optical band gap of samples was evaluated from Tauc plots via Equation 11:

\[
\alpha h\nu = A(h\nu - E_g)^{\alpha}
\]

(11)

where \(\alpha\) is an absorption coefficient, \(h\nu\) is the photon energy (\(h\) is the Planck’s constant and \(\nu\) is the photon frequency) and \(E_g\) is the optical band gap. The plots of \(\alpha h\nu\) versus \(h\nu\) for all samples are presented in Figure 5. To obtain the optical band gap, the linear region was extrapolated to \((\alpha h\nu) = 0\). The values of the obtained optical band gaps are given in Table 2.

The optical band gap of ZnAl₂O₄ spinel nanoparticles obtained from this experiment was narrower than the optical band gap of bulk ZnAl₂O₄ spinel (3.8 eV)53. This may have been due to the formation of a subband between valence and conduction bands caused by the formation of localized energy states of defects such as oxygen vacancies, which
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The concentration of Ce$^{3+}$ ions in the precursor solution. The reduction in the optical band gap could be attributed to increments in the secondary phases. Khan et al.\textsuperscript{10} studied the optical properties of CeO$_2$ and they found that reductions in the optical band gap were due to the presence of Ce$^{3+}$ ions at grain boundaries, which generated localized energy states from oxygen vacancies within the forbidden band. Consequently, electrons in valence bands could be excited to localized energy states with lower photon energy. In addition, Suwanboon et al.\textsuperscript{11} found that the optical band gap of ZnO nanoparticles decreased due to the presence of defects in the ZnO nanoparticles. Band tail energy was created within the forbidden band of ZnO and this event resulted in a reduction in the optical band gap of ZnO nanoparticles. Reports by other research groups\textsuperscript{12,54,55} indicated that the optical band gap of CeO$_2$/ZnO nanocomposites decreased when the mole ratio of Ce to Zn was increased. The reductions were attributed to an increase in the concentration of oxygen vacancies.

In this study, the products formed as CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposites and the augmentation in CeO$_2$ and ZnO secondary phases was in good agreement with the XRD results (Figure 2). The increases in CeO$_2$ and ZnO contents generated more oxygen vacancies in the ternary nanocomposite systems.

**Table 2. Principal characterization data of ZnAl$_2$O$_4$ spinel nanoparticles and CeO$_2$/ZnO/ZnAl$_2$O$_4$ nanocomposites.**

| Ce(NO$_3$)$_3$•6H$_2$O (mmol) | Phase | Shape | $E_g$ (eV) | $E_u$ (eV) | SA (m$^2$/g) |
|-----------------------------|-------|-------|------------|------------|--------------|
| 0                           | ZnAl$_2$O$_4$ | Irregularly agglomerated sphere | 3.220 | 0.120 | 37.78 |
| 0.2                         | CeO$_2$/ZnO/ZnAl$_2$O$_4$ | Rod + Irregularly agglomerated sphere | 3.192 | 0.282 | 27.98 |
| 0.4                         | CeO$_2$/ZnO/ZnAl$_2$O$_4$ | Rod + Irregularly agglomerated sphere | 3.184 | 0.284 | 40.64 |
| 0.6                         | CeO$_2$/ZnO/ZnAl$_2$O$_4$ | Rod + Irregularly agglomerated sphere | 3.180 | 0.287 | 41.45 |
| 0.8                         | CeO$_2$/ZnO/ZnAl$_2$O$_4$ | Rod + Irregularly agglomerated sphere | 3.178 | 0.294 | 39.45 |
| 1.0                         | CeO$_2$/ZnO/ZnAl$_2$O$_4$ | Rod + Irregularly agglomerated sphere | 3.170 | 0.299 | 37.06 |

**Figure 3.** SEM images of CeO$_2$/ZnO/ZnAl$_2$O$_4$ nanocomposites prepared at different Ce(NO$_3$)$_3$•6H$_2$O concentrations.

**Figure 4.** Diffuse reflectance spectra of CeO$_2$/ZnO/ZnAl$_2$O$_4$ nanocomposites prepared at different Ce(NO$_3$)$_3$•6H$_2$O concentrations.
and as a result the optical band gap reduced. To confirm the presence of oxygen vacancies in the samples, the Urbach energy or band tail energy ($E_u$) was taken into account. The Urbach energy was expressed as Equation 12:

$$\alpha = \alpha_0 \left( \frac{E}{E_u} \right)$$

(12)

where $\alpha$ is the absorption constant, $\alpha_0$ is the constant, E is the photon energy and $E_u$ is the Urbach energy. Urbach energy was determined from the reciprocal of the slope in the linear region of the plot of $\ln(\alpha)$ versus E (Figure 6). The values of obtained Urbach energy were presented in Table 2. Urbach energy was greater when the amount of Ce(NO$_3$)$_3$•6H$_2$O in the solution was greater. This behavior was attributed to increments of oxygen vacancy due to increased Ce(NO$_3$)$_3$•6H$_2$O concentration and the resultant reductions in optical band gap value.

### 3.5 Photocatalytic activity

In this study, an aqueous MB solution was used as a dye model. The degradation of MB molecules over ZnAl$_2$O$_4$ spinel nanoparticles and CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposites was observed under UV irradiation.

The strongest intensity of the absorbance peak of the aqueous MB solution centered at a wavelength of 664 nm decreased as a function of irradiation time (Figure 7) as MB contents in the solution were reduced by the photocatalytic reaction. In this study, the MB molecules completely degraded over CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposites prepared with 0.2 mmol Ce(NO$_3$)$_3$•6H$_2$O within 180 min, whereas they degraded by about 70% over pure ZnAl$_2$O$_4$ spinel nanoparticles at the same irradiation time.

The degradation of aqueous MB solution over all photocatalysts was determined using Equation 13:

$$\%\text{degradation} = \frac{C_0 - C_t}{C_0} \times 100 = \frac{A_0 - A_t}{A_0} \times 100$$

(13)

where $A_0$ is the initial absorbance of aqueous MB solution, $A_t$ is the absorbance of aqueous MB solution at time interval $t$, $C_0$ is the initial concentration of aqueous MB solution and $C_t$ is the concentration of aqueous MB solution at time interval $t$.

The degradation of aqueous MB solution was higher over CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposites than over ZnAl$_2$O$_4$ spinel nanoparticles (Figure 8). After exposure to UV radiation for 1 h, MB molecules were completely degraded over the CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposites prepared with 1.0 mmol Ce(NO$_3$)$_3$•6H$_2$O, whereas only about 54% of MB molecules were degraded over pure ZnAl$_2$O$_4$ spinel nanoparticles. When irradiation time was increased to 2 h, the MB molecules were completely degraded over the CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposites prepared with 0.6, 0.8 and 1.0 mmol Ce(NO$_3$)$_3$•6H$_2$O. At the same irradiation time, the degree of degradation over pure ZnAl$_2$O$_4$ spinel nanoparticles increased from 54% after 1 h to 64%. After irradiation for 3 h, the MB molecules were completely degraded over all the CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposites, whereas only 73% of the MB molecules were degraded over pure ZnAl$_2$O$_4$ spinel nanoparticles. Besides irradiation time, photocatalytic activity is influenced by various other parameters, including the optical band gap, defects concentration and specific surface area.

The photocatalysts with narrower optical band gaps exhibited higher photocatalytic activity. Since electrons in
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with H$_2$O at the surface of the photocatalysts to generate superoxide (•O$_2^-$) radicals and hydroxyl (•OH) radicals, respectively. These reactive species (•O$_2^-$, •OH, h$^+$) were mostly responsible for the degradation of the MB in solution. The CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposites with higher Ce$^{3+}$ concentrations could also adsorb more UV radiation (Figure 4). This result was in good agreement with the higher degradation of aqueous MB solution.

Although the CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposites exhibited narrower band gaps than ZnAl$_2$O$_4$ spinel nanoparticles, the recombination rate of photoexcited electron-hole pairs was retarded because the heterostructure of the CeO$_2$/ZnO/ZnAl$_2$O$_4$ ternary nanocomposite could promote the transfer of photoexcited electrons via the interfaces.
of the heterostructure, as occurred in the heterostructure of ZnO/ NiO/ZnAl₂O₄. This transfer of photoexcited electrons contributed to the superior photocatalytic activity of CeO₂/ZnO/ ZnAl₂O₄ ternary nanocomposites compared to pure ZnAl₂O₄ spinel nanoparticles.

Oxygen vacancy is another important parameter that can enhance photocatalytic activity for dye degradation. During the photocatalytic process, oxygen vacancies accept electrons and recombination rates of photoexcited electron-hole pairs are reduced. Moreover, oxygen vacancies can interact with adsorbed O₂ at the surface of photocatalysts, trapping photoexcited electrons to generate ‘O₂‘ radicals. As a result, the degradation of aqueous MB solution improved as a function of the concentration of oxygen vacancies.

Photocatalytic activity was also affected by particle shape. ZnO particles with a rod-like structure could enhance photocatalytic activity. The degradation of the aqueous MB solution was improved as a function of the {0001} surfaces in which the {0001} facets are strongly reactive in the degradation of MB molecules. ZnO rod structures consist of a positively charged Zn-(0001) terminate and a negatively charged O-(0001) terminate that created an internal electric field between the positive and negative planes by spontaneous polarization. Therefore, under the influence of this internal electric field, photoexcited electrons transferred to the positive (0001) plane and holes transferred to the negative (0001) plane. This phenomenon can improve the reduction reaction at the positive (0001) plane and the oxidation reaction at the negative (0001) plane, so the formation of ZnO in a rod structure can promotes the degradation of aqueous MB solution.

The specific surface area of a photocatalyst plays a crucial role in the photocatalytic process. A higher specific surface area provided more active sites; therefore, the photocatalytic reactions involved were accelerated. Considering the specific surface areas listed in Table 2, the specific surface area of the CeO₂/ZnO/ZnAl₂O₄ ternary nanocomposite prepared at 2.0 mmol Ce(NO₃)₃·6H₂O was smaller than that of the pure ZnAl₂O₄ spinel nanoparticle and the specific surface area of the ternary nanocomposite prepared at 1.0 mmol Ce(NO₃)₃·6H₂O was equal to the specific surface area of the pure ZnAl₂O₄ spinel nanoparticle. However, the photocatalytic activity of both those CeO₂/ZnO/ZnAl₂O₄ ternary nanocomposites was greater than the photocatalytic activity of pure ZnAl₂O₄ spinel nanoparticles. Therefore, the specific surface areas of the CeO₂/ZnO/ZnAl₂O₄ ternary nanocomposites did not significantly influence their photocatalytic activity in this study.

The positions of the valence band potential (Eᵥᵥ) and conduction band potential (Eᶜᵇ) were calculated from Equations 14 and 15:

\[ Eᵥᵥ = X - E^* + 0.5E_g \]  
\[ Eᶜᵇ = Eᵥᵥ - E_g \]

where X is the geometric mean of the Mulliken’s electronegativity of CeO₂, ZnO, ZnAl₂O₄ E* is the energy of free electrons on the hydrogen scale (4.50 eV for a normal hydrogen electrode (NHE)) and Eᵥᵥ is the optical band gap energy of CeO₂, ZnO, ZnAl₂O₄. The X, E*, Eᵥᵥ, Eᶜᵇ are listed in Table 3.

Table 3. X, E*, Eᵥᵥ, and Eᶜᵇ of CeO₂, ZnO, and ZnAl₂O₄

| Constituents | X     | E*   | Eᵥᵥ  | Eᶜᵇ  |
|-------------|-------|------|------|------|
| CeO₂       | 5.57  | 2.88 | 0.370| -2.510|
| ZnO        | 5.79  | 3.22 | 0.310| -2.890|
| ZnAl₂O₄   | 5.49  | 3.20 | 0.620| -2.600|

4. Conclusion

CeO₂/ZnO/ZnAl₂O₄ ternary nanocomposites were successfully synthesized by a facile co-precipitation method in which the addition of Ce⁺⁺ ions to the precursor solution disturbed the reaction equilibrium of spinel formation. The degradation of aqueous MB solution was improved as a function of the concentration of oxygen vacancies. The degradation of aqueous MB solution improved as a function of {0001} plane and the oxidation reaction at the negative (0001) plane and holes transferred to the positive (0001) plane. This phenomenon can improve the reduction reaction at the positive (0001) plane and the oxidation reaction at the negative (0001) plane, so the formation of ZnO in a rod structure can promote the degradation of aqueous MB solution.
SEM revealed the different particle shapes of CeO₂ (fluffy particles), ZnO (rod-like) and ZnAl₂O₄ (irregular sponge-like). The optical band gap of CeO₂/ZnO/ZnAl₂O₄ ternary nanocomposites slightly shifted to a longer wavelength compared with ZnAl₂O₄ spinel nanoparticles. The defect concentration of oxygen vacancies increased as a function of Ce⁺ ion concentration. The photocatalytic activity of the CeO₂/ZnO/ZnAl₂O₄ ternary nanocomposites depended significantly on the particle shape of the loading, the optical band gap and the defect concentration.

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