Enhanced visible-light driven photocatalytic property of g-C₃N₄/ZnAl₂O₄ nanocomposites

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Abstract. ZnAl₂O₄ spinel nanoparticles and g-C₃N₄/ZnAl₂O₄ nanocomposites were successfully synthesized by co-precipitation method. The influence of g-C₃N₄ loading contents on structural, morphological and optical properties was investigated by powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-Vis diffuse reflectance spectroscopy (DRS), respectively. The peak intensity of g-C₃N₄ increased as a function of g-C₃N₄ loading contents. The optical band gap values of g-C₃N₄/ZnAl₂O₄ nanocomposites were 3.10, 2.84, 2.82 and 2.80 eV when g-C₃N₄ loading contents were increased from 0 to 10, 20 and 30%, respectively. The photocatalytic activity increased as a function of g-C₃N₄ loading content. The 30% g-C₃N₄/ZnAl₂O₄ nanocomposites exhibited highest MB degradation of about 100% under visible light irradiation for 360 min.

1. Introduction
Metal oxide spinels are important in several application fields due to their high thermal resistance, good catalytic and optical properties [1]. Among metal oxide spinel structures, zinc aluminate (ZnAl₂O₄) with normal spinel (AB₂O₄) structure and band gap of about 3.8 eV has attracted much attention as one of the most promising materials for widely using as a catalyst or catalyst support in many catalytic reactions due to its wide band gap, high chemical and thermal stability [2]. Recently, ZnAl₂O₄ has been synthesized by several methods such as sol-gel [3], hydrothermal [4] and co-precipitation [5]. Among these methods, the co-precipitation method has many advantages such as homogeneity, small particle size and high purity obtained [6] and low-temperature preparation [7].

Graphitic carbon nitride (g-C₃N₄) is a metal-free polymeric semiconductor material that has received considerable interest due to its optical band gap of about 2.7 eV, low-cost, non-toxicity, excellent chemical stability, easy availability and environmental friendly material [2, 8-9]. The g-C₃N₄ can be synthesized from various substances such as ammonium thiocyanate and melamine [10]. Among many strategies for improving the photocatalytic activity, the composite formation is one of the popular ways that was used to enhance the photocatalytic activity. In this work, g-C₃N₄/ZnAl₂O₄ nanocomposites with different loading contents have been synthesized by co-precipitation method. The photocatalytic activity was evaluated using methylene blue (MB) solution under the irradiation of visible light.
2. Experimental

2.1. Materials
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), potassium hydroxide (KOH, Emsure®, Germany), melamine (C$_6$H$_6$N$_6$, Sigma-Aldrich, Germany), methanol (CH$_3$OH, RCILabscan, Thailand), polyethylene glycol (PEG, Sigma-Aldrich, Germany) and methylene blue (C$_{16}$H$_{18}$ClN$_3$S, Emsure®, Germany) were used as received.

2.2. Synthesis of ZnAl$_2$O$_4$ spinel
The ZnAl$_2$O$_4$ spinel nanoparticles were synthesized by a co-precipitation method. 0.005 mol of Zn(NO$_3$)$_2$·4H$_2$O and 0.01 mol of Al(NO$_3$)$_3$·9H$_2$O were added in 100 mL distilled water and stirred for 10 min. Then, an aqueous KOH solution (0.04 mol of KOH in 100 mL distilled water) was added slowly into previous precursor solution. The white precipitates formed in the solution and they were stirred continuously at 70 ºC for 1 h. The precipitates were washed with distilled water several times, filtered, dried at 80 ºC for 24 h and finally calcined at 800 ºC for 1 h.

2.3. Synthesis of g-C$_3$N$_4$/ZnAl$_2$O$_4$ nanocomposites
The g-C$_3$N$_4$ powders were synthesized from the literature [2], 2 g of melamine was put in an alumina crucible and heated at 540 ºC for 3 h. The yellow g-C$_3$N$_4$ powders were obtained 1 g of ZnAl$_2$O$_4$ and different g-C$_3$N$_4$ loading contents (10, 20 and 30%) were added in a mixture of 25 mL of methanol and 5 mL of PEG. Then, ZnAl$_2$O$_4$ and g-C$_3$N$_4$ were mixed and stirred for 5 h. The precipitates were washed with distilled water, filtered, dried at 80 ºC for 12 h and finally calcined at 500 ºC for 1 h.

2.4. Characterization
The structures of the ZnAl$_2$O$_4$ nanoparticles and the g-C$_3$N$_4$/ZnAl$_2$O$_4$ nanocomposites were characterized by X-ray diffractometer (XRD, X’ Pert MPD, Philips). The morphology of calcined samples was investigated by scanning electron microscopy (SEM, Quanta400, FEI). The optical properties of the ZnAl$_2$O$_4$ spinel nanoparticles and the g-C$_3$N$_4$/ZnAl$_2$O$_4$ nanocomposites were recorded on UV-Vis diffuse reflectance spectroscopy (UV-Vis spectrophotometer 2450, Shimadzu). The concentration of MB solution was estimated using UV-Vis spectrophotometer (UV-Vis spectrophotometer Lambda 25, Perkin Elmer).

2.5. Photocatalytic activity
The photocatalytic activity of the ZnAl$_2$O$_4$ spinel nanoparticles and the g-C$_3$N$_4$/ZnAl$_2$O$_4$ nanocomposites was evaluated by using MB as a dye model under the irradiation of visible light. 150 mg of ZnAl$_2$O$_4$ spinel nanoparticles and g-C$_3$N$_4$/ZnAl$_2$O$_4$ nanocomposites were put in beakers containing 150 mL of 1×10$^{-5}$ M MB solution and placed in the dark for 30 min with moderate stirring to reach adsorption/desorption equilibrium. The suspensions were exposed to a visible light and 3 mL of each solution was withdrawn at regular intervals of time, centrifuged to eliminate the particles. The filtrate was analyzed by UV-Vis spectrophotometer at 664 nm. The percentage of degradation was calculated by following relationship [7].

\[ \text{% degradation} = \frac{C_0-C_t}{C_0} \times 100, \]  

where \(C_0\) is initial MB concentration and \(C_t\) is the concentration at time \(t\).

3. Results and discussion

3.1. Influence of KOH concentration on structural properties
Figure 1. The XRD patterns of ZnAl\(_2\)O\(_4\) spinel and g-C\(_3\)N\(_4\)/ZnAl\(_2\)O\(_4\) nanocomposites with different g-C\(_3\)N\(_4\) loading contents. Figure 1 shows the XRD patterns of ZnAl\(_2\)O\(_4\) spinel and g-C\(_3\)N\(_4\)/ZnAl\(_2\)O\(_4\) nanocomposites with different g-C\(_3\)N\(_4\) loading contents. The diffraction peaks exhibited the hexagonal phase of g-C\(_3\)N\(_4\) (JCPDS No. 87-1526) and the cubic phase of ZnAl\(_2\)O\(_4\) spinel (JCPDS No. 05-0669) without any impurity phase. When the g-C\(_3\)N\(_4\) contents were increased, the peak intensity of g-C\(_3\)N\(_4\) increased whereas the peak intensity of ZnAl\(_2\)O\(_4\) decreased. This could confirm that the g-C\(_3\)N\(_4\)/ZnAl\(_2\)O\(_4\) nanocomposites formed in this study.

The morphology of ZnAl\(_2\)O\(_4\) spinel and g-C\(_3\)N\(_4\)/ZnAl\(_2\)O\(_4\) nanocomposites was investigated by SEM and the results were shown in figure 2. It was found that the pure ZnAl\(_2\)O\(_4\) spinel nanoparticles agglomerated in order to reduce the overall surface energy [11]. The spongy-like structure formed when g-C\(_3\)N\(_4\) loading contents were increased.

Figure 2. SEM images of the ZnAl\(_2\)O\(_4\) spinel nanoparticles and g-C\(_3\)N\(_4\)/ZnAl\(_2\)O\(_4\) nanocomposites with different g-C\(_3\)N\(_4\) loading contents (a) 0 %, (b) 10%, (c) 20% and (d) 30%. 
3.2. Influence of KOH concentration on optical properties

The optical properties of ZnAl$_2$O$_4$ spinel and g–C$_3$N$_4$/ZnAl$_2$O$_4$ nanocomposites were studied by UV-Vis diffuse reflectance spectroscopy (DRS) technique. The absorption spectra of the samples are shown in figure 3(a), the g–C$_3$N$_4$/ZnAl$_2$O$_4$ nanocomposite could more absorb the visible light in the wavelength of 400-800 nm compared with ZnAl$_2$O$_4$ spinel. The absorption edge shifted towards the longer wavelength as a function of g–C$_3$N$_4$ loading contents. The optical band gap was calculated by the Tauc’s relation as following equation [6].

Figure 3. (a) DRS spectra and (b-e) the plots between (αhν)$^2$ vs. hν for evaluating the E$_g$ values of the ZnAl$_2$O$_4$ spinel and g–C$_3$N$_4$/ZnAl$_2$O$_4$ nanocomposites with different g–C$_3$N$_4$ loading contents.
\[(ahv)^n = A(hv - E_g)\]  
(2)

Where \(\alpha\) is absorption coefficient, \(hv\) is photon energy, \(A\) is a constant, \(E_g\) is an optical band gap and exponent \(n\) depends on the type of transition, \(n = 2\) for the direct transition. The plots of \((ahv)^2\) vs. \(hv\) are shown in figure 3(b-e), thus the optical band gaps of the ZnAl\(_2\)O\(_4\) spinel and g-C\(_3\)N\(_4\)/ZnAl\(_2\)O\(_4\) nanocomposites were about 3.10, 2.84, 2.82 and 2.80 eV when g-C\(_3\)N\(_4\) loading contents were increased from 0 to 10, 20 and 30%, respectively.

### 3.3. Influence of KOH concentration on photocatalytic property

Figure 4 showed percentages of degradation of MB solution in the presence of ZnAl\(_2\)O\(_4\) spinel nanoparticles and g-C\(_3\)N\(_4\)/ZnAl\(_2\)O\(_4\) nanocomposites under the visible light irradiation. It was observed that the photocatalytic activity of g-C\(_3\)N\(_4\)/ZnAl\(_2\)O\(_4\) nanocomposites were higher than ZnAl\(_2\)O\(_4\) spinel, this could be attributed to a formation of g-C\(_3\)N\(_4\) and ZnAl\(_2\)O\(_4\) heterojunction. When g-C\(_3\)N\(_4\) and ZnAl\(_2\)O\(_4\) powders are coupled together, photons may be absorbed in both g-C\(_3\)N\(_4\) and ZnAl\(_2\)O\(_4\) and resulted in generation of electron and hole pairs. The electrons at the conduction band (CB) of ZnAl\(_2\)O\(_4\) could transfer to the g-C\(_3\)N\(_4\); whereas holes generated from ZnAl\(_2\)O\(_4\) remain at the valence band (VB). Then, the holes at the VB of the g-C\(_3\)N\(_4\) could transfer to the g-C\(_3\)N\(_4\); whereas holes generated from ZnAl\(_2\)O\(_4\) remain at the valence band (VB). Then, the holes at the VB of the g-C\(_3\)N\(_4\) could transfer to ZnAl\(_2\)O\(_4\) [12]. This event could retard the recombination of photoexcited electron and hole pairs. This event led to an enhancement in photocatalytic activity of g-C\(_3\)N\(_4\)/ZnAl\(_2\)O\(_4\) nanocomposite. The plausible mechanism for photocatalytic degradation can be expressed as follows [13].

\[
g\text{-C}_3\text{N}_4/\text{ZnAl}_2\text{O}_4 + hv \rightarrow e^- + h^+ \]  
(3)

\[
h^+ + \text{H}_2\text{O} \rightarrow 'OH + H^+ \]  
(4)

\[
e^- + \text{O}_2 \rightarrow '\text{O}_2^- \]  
(5)

\[
2e^- + \text{O}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 \]  
(6)

\[
'\text{O}_2^- + \text{H}_2\text{O}_2 \rightarrow '\text{OH} + \text{OH}^- + \text{O}_2 \]  
(7)

\[
'\text{OH} + \text{MB} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]  
(8)
4. Conclusion
In summary, the ZnAl$_2$O$_4$ spinel nanoparticles and g-C$_3$N$_4$/ZnAl$_2$O$_4$ nanocomposites were successfully synthesized by co-precipitation method that can confirm by XRD analysis. The optical band gap value of g-C$_3$N$_4$/ZnAl$_2$O$_4$ nanocomposites was narrower than pure ZnAl$_2$O$_4$ spinel and the optical band gap decreased as a function of g-C$_3$N$_4$ loading contents. The 30% g-C$_3$N$_4$/ZnAl$_2$O$_4$ nanocomposite showed the best photocatalytic activity under visible light.

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