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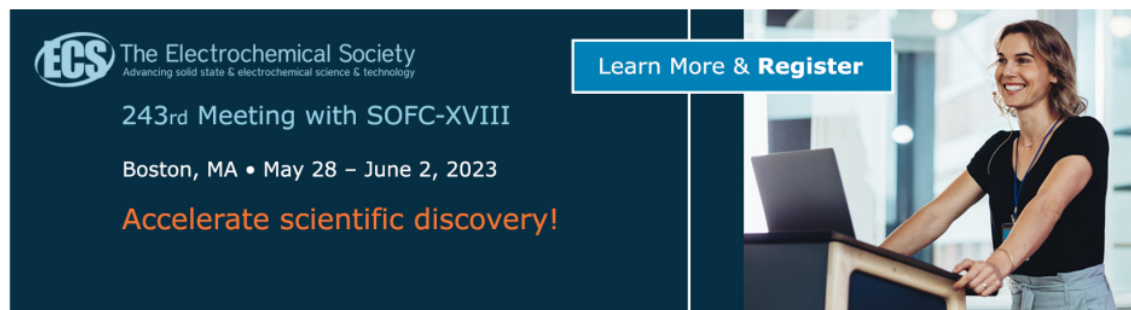
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Photodegradation of Rhodamine B by using ZnFe$_2$O$_4$ Nanoparticles Synthesized through Precipitation Method

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Abstrak. ZnFe$_2$O$_4$ nanoparticles were synthesized through precipitation method from the mixed aqueous solution of ferric nitrate and zinc nitrate. The precipitate was calcined at the temperature of 600, 700, and 800 ºC for 3 hours to obtain crystalline nature. The effects of calcination temperature on the properties of ZnFe$_2$O$_4$ nanoparticles were investigated. The structure, morphology, and optical properties of ZnFe$_2$O$_4$ nanoparticles were characterized by using X-ray diffractometer (XRD), scanning electron microscope (SEM), and UV-vis spectrophotometer, respectively. The photocatalytic activity of ZnFe$_2$O$_4$ nanoparticles was examined to Rhodamine B degradation in water under UV irradiation. The results show that the calcination temperature influences on ZnFe$_2$O$_4$ phase, crystallite size, and the energy gap of ZnFe$_2$O$_4$ nanoparticles. ZnFe$_2$O$_4$ nanoparticles calcined at 700 ºC shows the best photocatalytic activity to Rhodamine B degradation due to smaller crystallite size and higher absorption.

Keywords: ZnFe$_2$O$_4$, Precipitation, Rodhamine B, Photocatalytic

1. Introduction

Considerable research and development in searching for a safe, abundant, and inexpensive photocatalyst have been carried out in several years. Semiconductor photocatalysts show promising photocatalytic activity for the degradation of various dye organic pollutants in water [1,2]. TiO$_2$ powder is the main photocatalyst, which is widely used and developed for dye degradation due to its high photo efficiency and stability under UV light irradiation [3,4]. However, the large band gap energy and rapid recombination of photogenerated charge carriers of that photocatalyst lead limitation in its implementation. The powder photocatalysts were difficult to remove for reuse in aqueous solution. The strategy to overcome its limitation is to investigate the photocatalytic properties of magnetic nanoparticles. ZnFe$_2$O$_4$ nanoparticles are one of the proposed magnetic nanoparticles that can be easily removed from aqueous solution by applying an external magnetic field [5,6]. Moreover, the energy gap of ZnFe$_2$O$_4$ is smaller than TiO$_2$. Thus ZnFe$_2$O$_4$ has attracted attention as semiconductor mediated photocatalysis with wide wavelength spectrum from UV to visible [7].

ZnFe$_2$O$_4$ nanoparticles have been synthesized by various methods including ball mill [6], hydrothermal [8,9], electrochemical reduction [10], sol-gel [11,12], microwave [13], solvothermal [3] and precipitation [2]. Calcination or sintering improve the properties of ZnFe2O4 nanoparticles. The calcination influencing on optical properties was found on ZnFe$_2$O$_4$ nanoparticles synthesized by sol-gel method [12]. Another research reports the ZnFe$_2$O$_4$ nanoparticles synthesized by sol-gel method with sintering have good properties for catalyst [14]. Comparison to other methods, precipitation is a promising method for producing nanoparticles because of its simplicity and low cost. Usually, the product of precipitate was then calcined to form crystalline nanoparticles. Therefore in this research,

precipitation method was used for producing $ZnFe_2O_4$ nanoparticles followed by calcination to study the effect of calcination temperature on the properties of $ZnFe_2O_4$ nanoparticles. The calcination temperatures of 600, 700, and 800 ºC have been selected based on previous reference [14]. The photocatalytic activity of $ZnFe_2O_4$ nanoparticles was investigated for degradation of Rodhamine B dye under UV light irradiation. Calcination temperature of 700 ºC yields $ZnFe_2O_4$ nanoparticles with good photocatalytic activity.

2 Experimental Method

2.1 Synthesize of ZnFe₂O₄ nanoparticles
$ZnFe_2O_4$ nanoparticles were synthesized through precipitation method by mixing of Zinc Nitrate (Merc, Germany) and Iron (III) Nitrate (Sigma-Aldrich, Germany) with a ratio mole of 1:2 in 100 ml of distilled water. The solution was stirred at 60 ºC, and 3 M ammonia solution was dropwise until pH of 10 to form the precipitate. The precipitated product was filtered and washed with ethanol for several times. The product was then dried at 100 ºC and further calcined at 600, 700, and 800 ºC for 3 hours.

2.2 Characterization
Phase and structure of $ZnFe_2O_4$ nanoparticles were identified by Phillips PW 1710 X-ray diffractometer with Cu Kα irradiation in the scan range from 20 to 70º. The morphology and particle size average were analyzed by scanning electron microscope (JEOL/EO version 1.1, Type: JSM-6360). UV-vis absorption spectrum was recorded by using UV-vis spectrophotometer (SHIMADZU) with a wavelength in the range 200 to 800 nm.

2.3 Photodegradation experiment
Photodegradation of 20 ppm Rhodamine B (RhB) was carried out to evaluate photocatalytic activity of $ZnFe_2O_4$ nanoparticles. 35 mg nanoparticles $ZnFe_2O_4$ was dispersed in 70 ml RhB solution and stirred in the dark for 30 minutes to reach absorption-desorption equilibrium. Then the solution was irradiated by UV lamp for 150 minutes. At given time intervals, 10 ml the solution was sampled and separated by centrifuge to measure the remaining concentration of RhB by using Uv-vis spectrophotometer. The characteristic absorption peak of RhB was at $\lambda = 554$ nm.

3 Results and Discussion

3.1 Structure and morphology of ZnFe₂O₄
Figure 1 shows the diffraction pattern of $ZnFe_2O_4$ nanoparticles calcined at 600, 700, and 800ºC. The peaks of (220), (311), (400), (511), and (440) appear for all samples, indicate the formation of spinel cubic structure (JCPDS No. 22-1012). To confirm that finding, the lattice constant was determined for diffraction peaks of (311) by using Equation 1.

$$a = \frac{\lambda\sqrt{h^2 + k^2 + l^2}}{2\sin\theta} \qquad (1)$$

a is lattice constant, λ is the wavelength of X-ray, θ is the Bragg diffraction angle and *(hkl)* is index miller [5]. The lattice constant was found to be 0.841-0,842 nm. Those results corresponded to a lattice constant of bulk cubic spinel structure of $ZnFe_2O_4$ [5]. Furthermore, increasing calcination temperature from 600 to 700ºC enhanced the crystallinity of $ZnFe_2O_4$ nanoparticles. It is represented by the diffraction peak intensity as can be observed in Figure 1. The diffraction peaks intensity slightly increased at 700ºC. However, the diffraction peak intensity slightly dropped back at the calcination temperature of 800ºC. In addition, a peak of α-Fe_2O_3 phase observed at $2\theta = 33º$ indicates that the single phase of cubic spinel structure $ZnFe_2O_4$ is not yet completely formed. The α-Fe_2O_3 phase that is formed in nanoparticles can be calculated by using peak intensity ratio of phase α-Fe_2O_3 with peak intensity of phase $ZnFe_2O_4$ [15]. The results show the $ZnFe_2O_4$ nanoparticles calcined at a temperature

of 600, 700, and 800 ºC composed by the α-Fe_2O_3 phase of 12.44%, 13.48%, and 13,36% respectively. The α-Fe_2O_3 phase causes crystallite size reduction of $ZnFe_2O_4$ nanoparticles. The crystallite size average of $ZnFe_2O_4$ nanoparticles was calculated by using the full width at half maximum (FWHM) of the dominant diffraction peak of (311) from the XRD patterns based on Scherrer formula (Equation 2) [2,5].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (2)$$

D is the crystallite size, λ is the wavelength of X-ray, β is FWHM, and θ is the Bragg diffraction angle. These results are presented in Table 1. Generally, the calcination temperature caused an increase in the crystallite size of nanoparticles, however in this research that is not observed. This case is due to the phase of α-Fe_2O_3 formation in the nanoparticles $ZnFe_2O_4$.
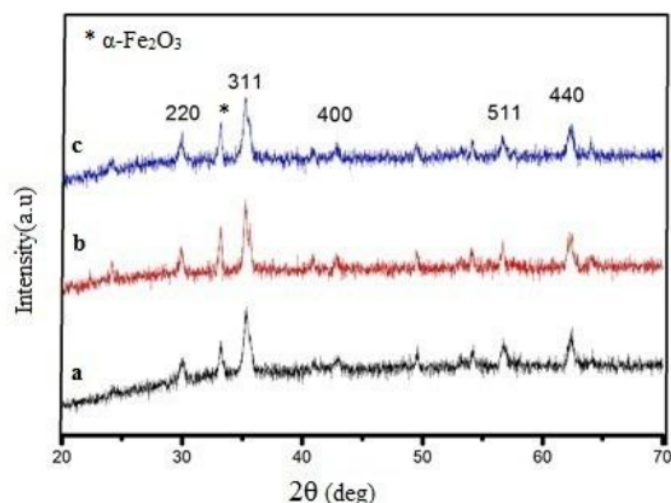

Figure 1. XRD patterns of $ZnFe_2O_4$ nanoparticles (a) 600^{0}C; (b) 700^{0}C and (c) 800^{0}C

Table 1. Crystallite size, lattice constant, and particle size of $ZnFe_2O_4$ nanoparticles

Calcination temperature (ºC)	Crystallite size (nm)	Lattice constant (nm)	Particle size (nm)
600	19.95	0.841	51.8
700	13,80	0.842	84.4
800	15.23	0.842	69.5

The morphological nature of $ZnFe_2O_4$ nanoparticles was identified by using SEM images as presented in Figure 2. The spherical-like morphology with an average size of 51.8, 84.4 and 69.6 nm observed for $ZnFe_2O_4$ nanoparticles with calcination temperature of 600, 700, and 800ºC, respectively. The estimated average size of SEM images is different with the calculated average crystallite size using Scherrer formula indicating the nanoparticles composed by several crystallites as a consequence of polycrystalline nature. Moreover, high agglomeration appears for $ZnFe_2O_4$ nanoparticles calcined at

700°C, because its crystallite size was smaller than the other. This finding is similar to $ZnFe_2O_4$ nanoparticles synthesized by sol-gel method [8].
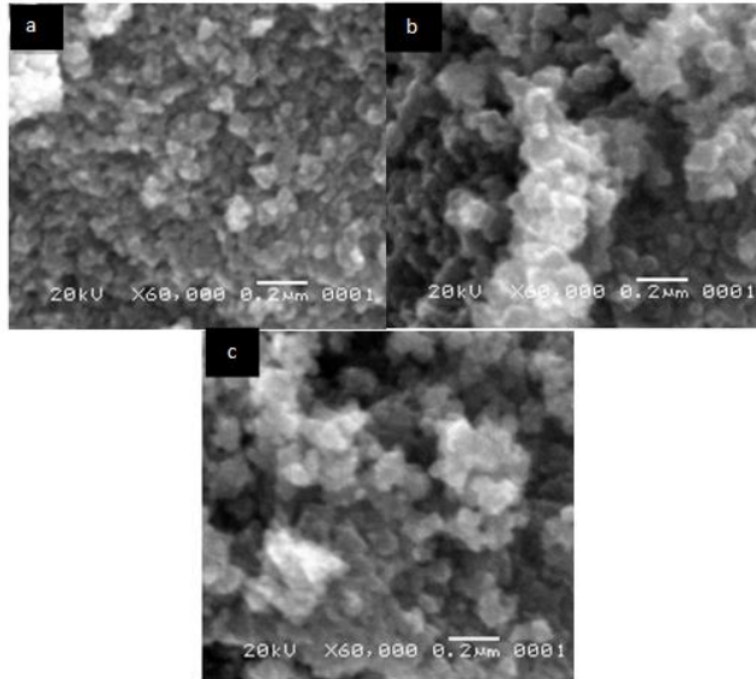

Figure. 2. SEM image of $ZnFe_2O_4$ nanoparticles calcined at (a) 600, (b)700, and (c) 800 °C

3.2 Optical properties of ZnFe₂O₄ nanoparticles

To verify the UV-vis light absorptivity of $ZnFe_2O_4$ nanoparticles, the absorbance spectrum of $ZnFe_2O_4$ nanoparticles was recorded and shown in Figure 3. It can be seen, that $ZnFe_2O_4$ nanoparticles absorb UV-vis light from 200 to 600 nm. The Calcination at 700°C resulted in $ZnFe_2O_4$ nanoparticles with higher absorption in the UV-vis region and its absorption edge exhibited red-shift to higher wavelength compared with other calcination temperature. Thessseee phenomena were due to the phase of α-Fe_2O_3 composed in the nanoparticles was higher than other. It is expected that $ZnFe_2O_4$ nanoparticles can show higher photocatalytic activity.

The band gap energy of $ZnFe_2O_4$ nanoparticles was determined through touc' plot method based on direct transition as expressed in Equation 3 [16]:

$$(\alpha h v)^2 = A(hv - E_g) \tag{3}$$

Where, α is absorptivity constant, h is Planck constant, v is light frequency, A is a constant and E_g is band gap energy. The graph of $(\alpha h v)^2$ vs the photon energy $(h v)$ is shown in Figure 4. The band gap energy of $ZnFe_2O_4$ nanoparticles was obtained to be 2.43, 1.85, and 2.39 eV for calcination temperature of 600, 700, and 800 °C.
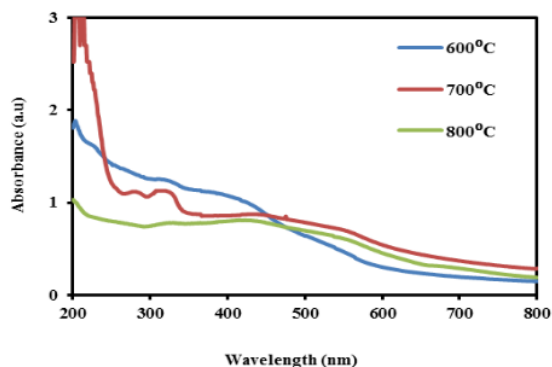
Figure 3. Absorbance spectrum of ZnFe$_2$O$_4$ nanoparticles
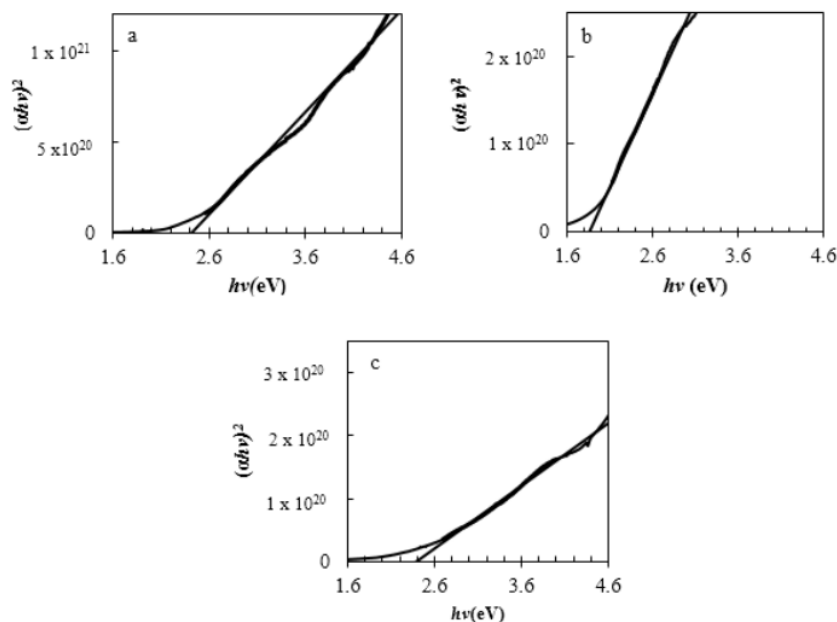

Figure 4. Tauc's plot of ZnFe$_2$O$_4$ nanoparticles calcined at (a) 600, (b) 700, and (c) 800 °C

3.3 Photodegradation of RhB solution

Photodegradation of RhB solution under UV light irradiation was carried out to evaluate the effect of calcination temperature on the photocatalytic activity of ZnFe$_2$O$_4$ nanoparticle. As depicted in Figure 5, RhB degradation without ZnFe$_2$O$_4$ nanoparticles almost did not appear after 120 min irradiation. Sharp degradation up to 60% occurred after 60 min irradiation, and then the degradation increased slightly. The photocatalytic activity of ZnFe$_2$O$_4$ nanoparticles calcined at 600 and 800°C were almost similar. Whereas, the ZnFe$_2$O$_4$ nanoparticles calcined at 700°C exhibited higher photocatalytic activity than the other. It could be correlated to smaller crystallite size and higher UV absorption of that ZnFe$_2$O$_4$ nanoparticles. Small crystallite size leads large surface area that results in more electron-hole pairs covering the surface of ZnFe$_2$O$_4$ nanoparticles reacting with RhB solution.
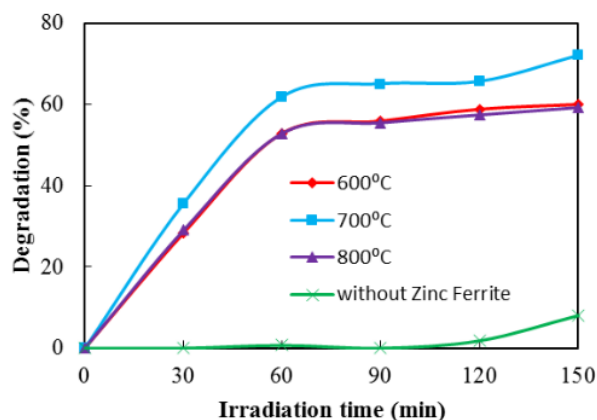
Figure. 5. Photodegradation activity of $ZnFe_2O_4$

Calcination temperature of 700 ℃ yields good photocatalytic activity of $ZnFe_2O_4$ nanoparticles. Similar phenomena was reported for sintered $ZnFe_2O_4$ nanoparticles prepared by the sol-gel method at 700^0C for four h [14]. Photocatalytic of $ZnFe_2O_4$ nanoparticles as described in other research shows the degradation of 10 ppm MG solution under UV irradiation for 60 min was 50% [17], while in this research the degradation of 20 ppm RhB solution was 60%. Therefore comparison to other research, our $ZnFe_2O_4$ nanoparticles show good photocatalytic activity. The degradation of RhB will be improved by prolonging irradiation.

4. Conclusion

$ZnFe_2O_4$ nanoparticles were synthesized by precipitation method with calcination temperature of 600, 700, and 800^0C. The band gap energy of $ZnFe_2O_4$ nanoparticles was obtained to be 2.43, 1.85, and 2.39 eV, respectively. The $ZnFe_2O_4$ nanoparticles at calcination temperature of 700^oC possess high crystallinity, high UV absorption, and good photocatalytic activity.

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