

ZnFe₂O₄ nanoparticle: Synthesis and photocatalytic activity under UV-Vis and visible light

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Abstract

In the present work, the ZnFe₂O₄ nanoparticle has been successfully synthesized. The obtained sample was characterized by X-ray diffraction (XRD) and emission scanning electron microscopy (FE-SEM) and its optical property were examined by UV-Vis spectrophotometer. FE-SEM revealed that the particle size of the ZnFe₂O₄ of about 47 nm was synthesized. The photocatalytic performance under UV-Vis and visible light was evaluated by decolorization of congo red (CR) anionic dye solution. The UV-Vis and visible light irradiation source consist of a high pressure mercury lamp 400 W and filament tungsten lamp 100 W respectively. The photocatalytic results show that the ZnFe₂O₄ sample can degrade (CR) dye solution up to 100% after 30 and 120 min under UV-Vis and visible irradiation respectively.

Keywords: ZnFe₂O₄; photocatalyst; visible light; congo red.

Introduction

Magnetically separable photocatalysts have been widely applied in the treatment of dye pollutants in wastewater [1-5]. Spinel ferrite with a general formula of MFe₂O₄ is a magnetic material. Many methods such as

refluxing [6] hydrothermal [7-9], thermal decomposition [10], mechanochemical [11] and microwave-hydrothermal assisted ionic liquid [12] have been reported for the synthesis of zinc ferrite. Obviously, fabrication of zinc ferrite *via* a simple

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approach and, further, exploring its novel properties continue to be a challenge. The photocatalytic reaction, based on UV-Vis irradiated semiconductor provides electrons in the conduction band and holes in the valence band. These charge carriers can recombine, or the holes can be scavenged by oxidizing species and electron by reducible species in the solution, finally, led to the destruction of many organic substances to CO_2 , H_2O and corresponding mineral acids [13-17]. Organic dyes have been extensively used for textile application. During textile manufacturing processes, a large quantity of wastewater containing dyestuffs is introduced into the aquatic system. It is necessary to find an effective, visible light driven photocatalyst for wastewater treatment. Until now, efforts have been made to develop efficient visible light and magnetically separable photocatalyst [18-22]. Various spinel ferrites have been used for degradation of contaminants [23-25]. Many researchers have been reported zinc ferrite alone or as composites efficiently degrade dye pollutants [26-29]. In this work, new synthesis for the ZnFe_2O_4 nanoparticle was presented and the ability of ZnFe_2O_4 to degrade congo red dye solution under UV-Vis and Visible light was examined.

Experimental

Materials

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NaOH and cethyl trimethyl ammonium bromide (CTAB) were used to prepare the zinc ferrite sample. All the analytical chemicals were purchased from Merck.

Synthesis procedure for preparing ZnFe_2O_4

In this procedure, 6 mmol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 3 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 40 mmol of NaOH, 0.548 mmol of (CTAB) and 15 mL distilled water were used. Above, chemical materials were stirred vigorous using magnetic stirrer for 2 hours at room temperature; the product was washed with double distilled water several times and dried at room temperature. Then, the product was annealed at $500\text{ }^\circ\text{C}$ for 1 h.

Evaluation of photocatalytic activity

A High pressure mercury lamp 400 W manufactured by Philips, Holland, and filament tungsten lamp 100W manufactured by Pars Shahab, Iran, were used as the UV-Vis and visible light source, respectively. In the mercury lamp, the light produced is lines 404.7, 453.8, 546.1 and 577.6 nm, plus ultra-violet (UV) energy and to the filament tungsten lamp it is (500-700) nm in the visible region. The dye solutions of congo red 5 and 20 ppm were prepared as an environmental pollutant model. Air was blown into the dye solutions by an aquarium

pump to maintain the solution saturated by oxygen. In each photocatalytic experiment, the amount of the prepared catalyst 0.5 g/l was used. During irradiation, agitation was maintained by a magnetic stirrer to keep the suspension homogeneous. The suspension was sampled at regular intervals and immediately centrifuged to completely remove catalyst particles. Then, the degree of photo decolorization (X), as a function of time, is given by $X = (C_0 - C)/C_0$ where C_0 is the initial concentration of dye, and C the concentration of dye at time t. The disappearance of peak at $\lambda = 498$ nm was chosen for monitoring dye decolorization for congo red.

Results and discussion

The morphology and structure of the sample were characterized by using field emission scanning electron microscope (FE-SEM), Hitachi S-4160 with gold coating and XRD (Holland Philips Xpert, X-ray diffractometer with Cu-K α radiation) respectively. Figure 1 shows that the morphology of the ZnFe₂O₄ sample is nanoparticle and particle size is of about 47 nm.

The crystallite size and phase characteristic of the product were determined by using the XRD pattern. The XRD result (Figure 2) shows that the ZnFe₂O₄ with cubic phase was obtained (JCPDS No. 82-1049).

The crystallite size (D) of the ZnFe₂O₄ sample was estimated using Scherrer's equation as follows [7, 30]:

$$D = \frac{(0.9)\lambda}{\beta \cos\theta} \quad \text{Eq. (1)}$$

where λ , θ , and β are the X-ray wavelength (0.154056 nm for Cu-K α), Bragg diffraction angle, and the full width at half maximum of the diffraction peak (FWHM), respectively. In this calculation, we took the highest intensity peak (311). According to Eq (1), the crystallite size of the synthesized ZnFe₂O₄ was calculated about 17.7 nm. Figure 3a illustrates UV-Vis spectra of the ZnFe₂O₄ sample. To have a quantitative estimate of the sample optical band gap, the Tauc Equation was employed (Eq. 2) [7, 31, 32].

$$\alpha h\nu = A(h\nu - E_g)^\gamma \quad \text{Eq. (2)}$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical band gap, A is a constant which does not depend on the photon energy and γ has four numeric values ($\frac{1}{2}$ for the allowed direct transitions, 2 for the allowed indirect, 3 for the forbidden direct and $\frac{3}{2}$ for the forbidden indirect optical transitions). In this work, the direct transition band gap (E_g) of the sample was determined by plotting $(\alpha h\nu)^2$ versus $h\nu$ curve with the extrapolation of the linear region to $(\alpha h\nu)^2 = 0$. Figure 3b shows that the value of band gap

for the synthesized ZnFe_2O_4 is found to be 2.3 eV. Until now, band gap energy of zinc ferrite was reported about 2.0, 1.9, 1.7 and 1.6 eV. by many researchers [33-35].

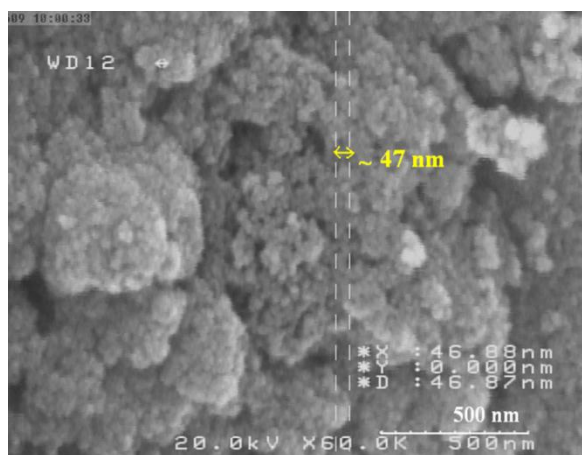


Figure 1. FE-SEM image of the ZnFe_2O_4 sample

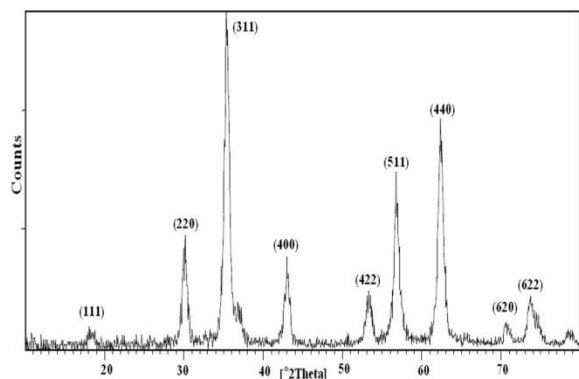


Figure 2. XRD pattern of the ZnFe_2O_4 sample

The photocatalytic activity of the prepared sample was evaluated by the decolorization of the CR solution under the UV-Vis and visible irradiation. Figure 4a and 4b show that the ZnFe_2O_4 sample can degrade congo red dye solution (5ppm) after 30 and 120 min under UV-Vis and visible irradiation respectively. Controlled

experiment was performed by exposing a CR solution to the light source without the presence of the ZnFe_2O_4 . Results show that the CR solution cannot be photo degraded in the absence of the ZnFe_2O_4 under UV-Vis and visible light irradiation. Therefore, it is important to know how much CR dye solution is adsorbed on the ZnFe_2O_4 catalyst surface. Hence, the adsorption degree of CR on the surface of the sample was measured in the dark. The adsorption experiment indicates that 64% of CR dye solution (5ppm) was adsorbed on the surface of the ZnFe_2O_4 sample after 120 min (Figure 4c). The amount of (CR) adsorbed on the surface of the catalyst at the time t was calculated *via* the following equation [36]:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad \text{Eq. (3)}$$

where, q_t (mgg^{-1}) is the adsorbed dye amount on the surface of the catalyst, C_0 and C_t (mgL^{-1}) are dye concentration at the initial and any time t , respectively. V is the solution volume (L), and m is the adsorbent mass (g). The maximum adsorption capacity of CR on the surface of the ZnFe_2O_4 was obtained about 6.5 mgg^{-1} after 120 min at 25°C (Figure 5). The comparison of these experiments shows that the ZnFe_2O_4 has good photocatalytic performance under UV-

Vis and visible illumination. For further research, the photocatalytic experiment for decolorization of CR solution with 20 ppm concentration was carried out. The result indicates that ZnFe₂O₄ sample can degrade CR solution (20 ppm) up to 98% during 180 min under UV-Vis irradiation (Figure 4d). Until now, the photocatalytic activity of Zinc ferrite was investigated by many researchers summarized in table 1. As can be seen in table 1, the prepared ZnFe₂O₄, in this work, has good photocatalytic activities for decolorization of the congo red dye solution under UV-Vis and visible light.

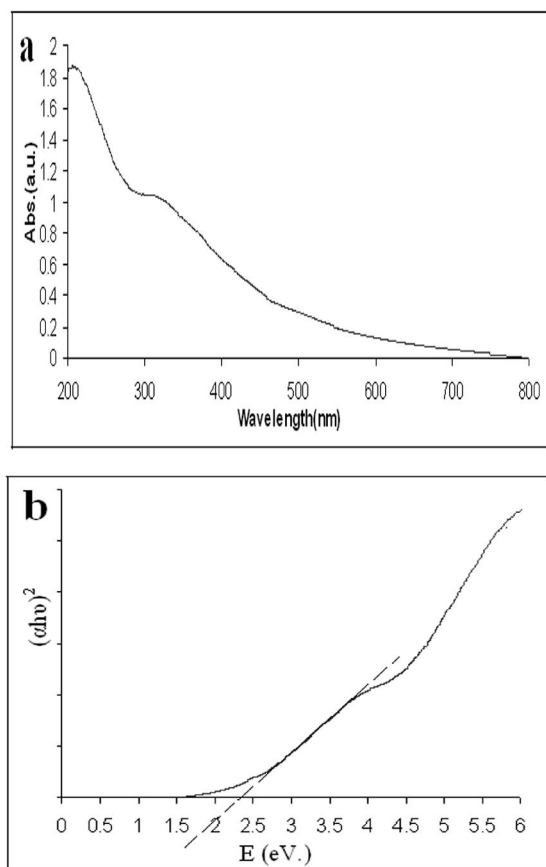


Figure 3. UV-Vis spectra of the ZnFe₂O₄ sample (a), plot of the $(\alpha hv)^2$ versus $h\nu$ (b)

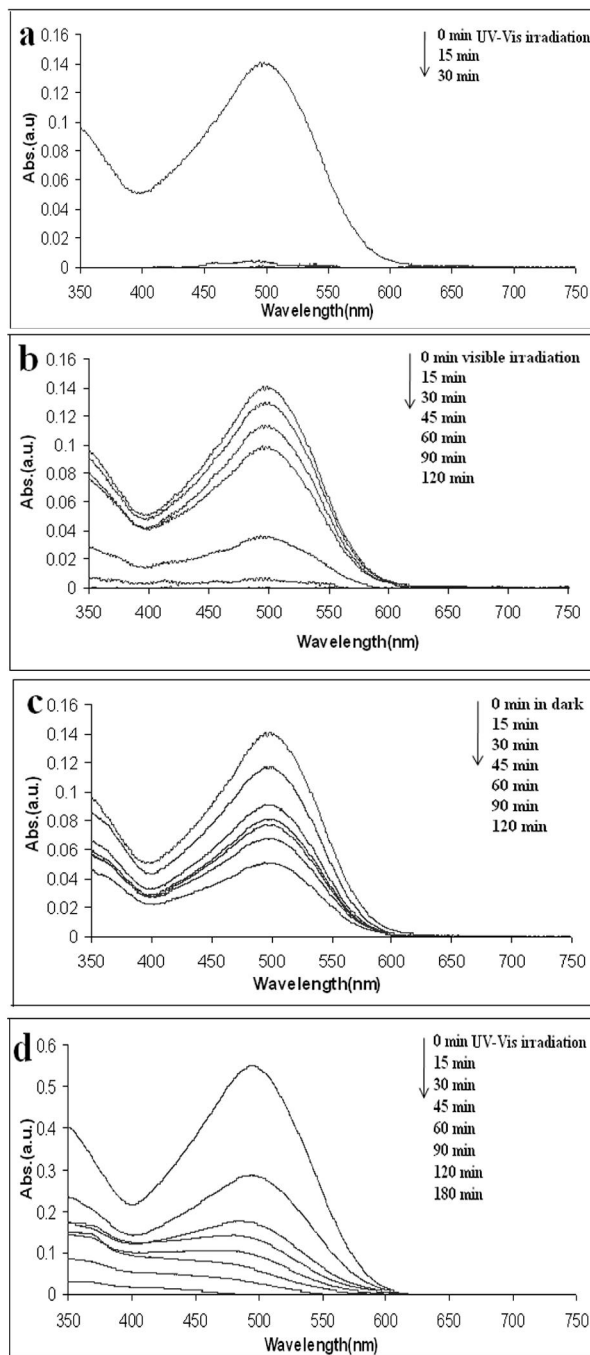


Figure 4. UV-Vis spectra changes of congo red dye solution in presence of the ZnFe₂O₄ sample (a) 5 ppm concentration of (CR) dye, UV-Vis irradiation (b), 5 ppm concentration of (CR) dye, visible irradiation (c),

5 ppm concentration of (CR) dye, in dark (d) and 20 ppm concentration of (CR) dye, UV-Vis irradiation

Table 1. Photocatalytic activity of $ZnFe_2O_4$ for decolorization of various dye solutions in different condition recently published

Name of dye	Dye (mg/l)	Catalyst (mg/l)	Irradiation Source	Irradiation time (min)	Decolorization of dye (%)	Ref.
Rodamin B	20	0.8	Xe lamp (500 W)	300	100	[33]
Methyl Orange	10	0.4	$\lambda < 500$	60	75	[37]
Rodamin B	10	0.75	Xe lamp (300 W)	120	97.5	[34]
Rodamin B	20	0.5	Two 36 W H-type lamps	360	97	[35]
Methylene blue	5	1	Sunlight irradiation	360	85	[38]
Congo red	5	0.5	High presser Hg-lamp 400 W	30	100	In this work
Congo red	5	0.5	Filament tungsten lamp 100W	120	100	In this work
Congo red	20	0.5	High presser Hg-lamp 400 W	180	98	In this work

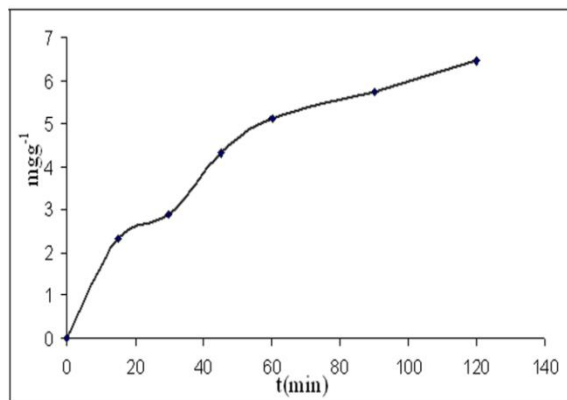


Figure 5. Adsorption capacity of (CR) dye on the surface of $ZnFe_2O_4$, $T=25\text{ }^\circ\text{C}$

Conclusion

In the present work, the $ZnFe_2O_4$ nanoparticle has been synthesized using the simple procedure. Results indicate that the prepared $ZnFe_2O_4$ has high photocatalytic activity under UV-Vis irradiation provided by a high pressure mercury lamp, 400 W and good photocatalytic activity under visible light irradiation provided by the filament tungsten lamp 100 W.

Acknowledgments

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