Materials Science in Semiconductor Processing xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Synthesis of $ZnFe_2O_4$ nanoparticles in presence and absence of Tween-20: Optical property, adsorption and photocatalytic activity

E. Aghabeikzadeh-Naeini, M. Movahedi, N. Rasouli*, Z. Sadeghi

Department of Chemistry, Payame Noor University, P.O. Box 19395-3697, Tehran, Iran

ARTICLE INFO

Keywords:
Zinc ferrite
Photocatalyst
Tween-20
Nanoparticles
Visible light

ABSTRACT

In this work, the zinc ferrite nanoparticles was synthesized via a chemical precipitation approach in presence and absence Tween 20. The samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDX) and fourier transform infrared (FT-IR). The optical property of the samples was evaluated by UV–vis spectrophotometer. The photocatalytic activity of the samples was evaluated by decolorization of congo red (CR) dye in aqueous solution. A 100 W filament tungsten lamp was used as a visible light source. Furthermore, the ability of the samples for CR dye removal via adsorption was examined. The adsorption and photocatalytic decolorization results for the $ZnFe_2O_4$ synthesized in present of Tween- 20 indicated that the > 90% of CR dye solution was removed and decolorized after 120 and 30 min, respectively. The samples demonstrated the good removal ability after five utilizations. The Langmuir-Hinshelwood model for decolorization kinetic data was examined.

1. Introduction

Photocatalyst has been widely applied for treatment of dye pollutants in wastewater [1–5]. Until now, many efforts have been made to develop efficient visible light photocatalyst [6–8]. In recent years ferrites as a visible light driven photocatalyst has received increasing attention [9–12]. Ferrites as a stable spinel-type material, has potential applications in field of gas sensors, biomedicine, hydrogen production, pigments and photocatalyst [13–17]. Many researchers reported that the different synthetic methods has significant effect on the particle size, specific surface areas, geometrical shapes and properties of materials [18–21]. To date, various procedures such as coprecipitation rout, sol-gel method using agar in reaction media, hydrothermal synthesis without using surfactant, hard template method using mesoporous silica KIT-6, succinic acid-assisted hydrothermal rout, glycine and larginine assisted microwave irradiation, reduction- oxidation method, bio-template method using kapok fibers, non aqueous rout, microwave-assisted ball milling, mechanical ball milling, PEG-assisted rout, combustion synthesis and coprecipitation air oxidation method have been reported to synthesize zinc ferrite [18,22–34]. Despite the fact that $ZnFe_2O_4$ with different methods has been synthesized, it is still great challenge to develop synthetic methods, which will strong effect the properties of the materials. Therefore, the synthesis of the $ZnFe_2O_4$ sample is still attractive. Herein, synthesis of the zinc ferrite in presence and absence of Tween-20 was carried out. The optical property and photocatalytic activity of the samples for decolorization of congo red dye in aqueous solution were examined. Furthermore, the ability of the samples for dye removal via adsorption was tested in dark condition.

2. Experimental procedure

2.1. Materials

Congo red (C.I. Direct Red 28), Tween- 20, $Fe(NO_3)_3{\cdot}9H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ and NaOH were purchased from Merck Company.

2.2. Synthesis of $ZnFe_2O_4$ samples

The $ZnFe_2O_4$ samples were synthesized in presence and absence of Tween-20 in reaction medium, which are named $ZnFe_2O_4$-ST and $ZnFe_2O_4$-S samples, respectively. In a typical procedure, 0.5 mL of Tween-20 was dissolved in 150 mL distilled water (solution 1). 10 mmol of $Fe(NO_3)_3{\cdot}9H_2O$ and 5 mmol of $Zn(NO_3)_2{\cdot}6H_2O$ was dissolved in 50 mL distilled water (solution 2). Then, the solution 2 was added into the solution 1 under constant stirring. After that, 15 mL of the NaOH 4 M solution was added drop wise into the above solution. After stirring the mixture for 4 h at 80 °C, the product was separated and washed with distilled water several times and dried at 60 °C. Finally, heat treatment of the product was carried out at 600 °C for 1 h. Moreover, the $ZnFe_2O_4$ sample was synthesized in absence of Tween-20 by the same procedure.

* Corresponding author.
E-mail addresses: n.rasooli55@yahoo.com, n.rasouli@pnu.ac.ir (N. Rasouli).

http://dx.doi.org/10.1016/j.mssp.2017.09.024
Received 23 March 2017; Received in revised form 15 September 2017; Accepted 22 September 2017

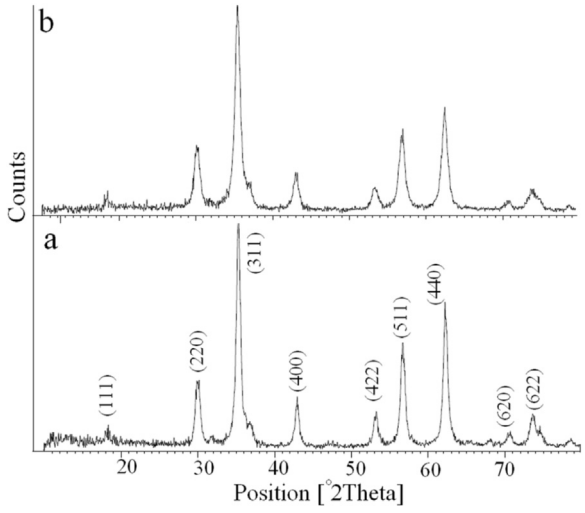

Fig. 1. The XRD patterns of the (a) $ZnFe_2O_4$-S and (b) $ZnFe_2O_4$-ST samples.

2.3. Instrumentation

The products were characterized by using XRD (Holland Philips Xpert, X-ray diffractometer with Cu-Kα radiation), field emission scanning electron microscopy, energy dispersive X-ray spectroscopy (FE-SEM, EDX, Vega 2 Tscan), FT-IR spectrometer (JASCO FTIR-4200) and UV–vis spectrophotometer (Shimadzu-2550).

2.4. Photocatalytic decolorization and adsorption experiments

The photocatalytic activity of the samples was evaluated by decolorization of CR dye solution under visible light irradiation. A 100 W filament tungsten lamp was used as a visible light source. The CR dye solution (5 mg L^{-1}) was chosen as an environmental pollutant model. Air was blown into the dye solution by an aquarium pump to maintain the solution saturated with oxygen. In each photocatalytic experiment, amount of prepared catalyst 0.5 g L^{-1} was used. The suspension was sampled at regular intervals and immediately centrifuged to remove catalyst particles completely. Then, the degree of photo decolorization (X), as a function of time is given by $X = (C_o - C_t) / C_o$, where C_o is the initial concentration of dye and C_t is the concentration of dye at time t. The disappearance of peak at $\lambda = 498$ nm was chosen for monitoring of CR dye decolorization. Furthermore, the adsorption experiment was carried out in dark.

3. Results and discussion

3.1. Characterization

The XRD pattern of the $ZnFe_2O_4$ samples was shown in Fig. 1(a) and (b). All the diffraction peaks are in agreement with the JCPDS file (JCPDS No. 22-1012), which can be indexed as a cubic phase. No additional peak was observed in the XRD pattern of $ZnFe_2O_4$-ST sample, and it confirms that the synthesized product is free from any surfactant. The crystallite size of the samples was calculated using the Scherer's formula [35]:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where λ, θ, and β are the X-ray wavelength (0.154056 nm for Cu-Kα), Bragg diffraction angle, and the full width at half maximum of the diffraction peak (FWHM), respectively. According to Eq. (1) the crystallite size of $ZnFe_2O_4$-ST and $ZnFe_2O_4$-S samples was calculated of about 14 and 20 nm respectively. In this work, Tween-20 was used as a surfactant in reaction medium. Many researchers reported that when, a surfactant is used in the synthesis procedure, and further growth of the crystals was hindered, probably because of the adsorption of surface-active agent on the surface of the crystal nucleus. Moreover, synthesis of magnetic nanoparticles without surfactants easily agglomerate because of the Van der Walls force and magnetic attraction [36]. The FT-IR spectra of the $ZnFe_2O_4$-S and $ZnFe_2O_4$-ST samples were illustrated in Fig. 2(a) and (b). The bands at about ~ (546, 406) and (557, 418) cm^{-1} were observed for the $ZnFe_2O_4$-S and $ZnFe_2O_4$-ST samples, respectively. Generally, FT-IR spectrum of spinel ferrites exhibits two absorption bands in the range of 385–600 cm^{-1}. The vibrational bands present at around 550–600 cm^{-1} and 385–450 cm^{-1} are attributed to stretching vibrations of Fe-O and Zn-O, which are the characteristic of $ZnFe_2O_4$. The bands at ~ 3437 and 1631 $cm^{-1}$are attributed to the absorbed water molecules on the samples [37]. The presence of Tween-20 surfactant molecules as an impurity was not observed by FT-IR spectrum and XRD pattern of the $ZnFe_2O_4$-ST sample. The FE-SEM imagies and results of EDX analysis for the $ZnFe_2O_4$-ST and $ZnFe_2O_4$-S samples were shown in Figs. 3(a)–(c) and 4(a)–(c) respectively. The EDX analysis for the samples confirmed that the prepared sample was composed of Zn, Fe and O. Usually, the sample preparation in FESEM-EDX analysis was performed using thin layer of gold on surface. So, the EDX spectrum showed an Au peak at about 2.2 keV due to gold coating on surface of the sample. According to the FE-SEM images a similar morphology for the samples were observed and size of aggregated nanoparticles of about (16–50) nm was estimated. The UV–vis spectra of the $ZnFe_2O_4$-ST and $ZnFe_2O_4$-S samples were shown in Fig. 5. For the samples the wide visible light absorption range of (~ 400–700) nm was observed. To have a quantitative estimate of the optical band gap, the Tauc Equation was employed Eq. (2) [18,38].

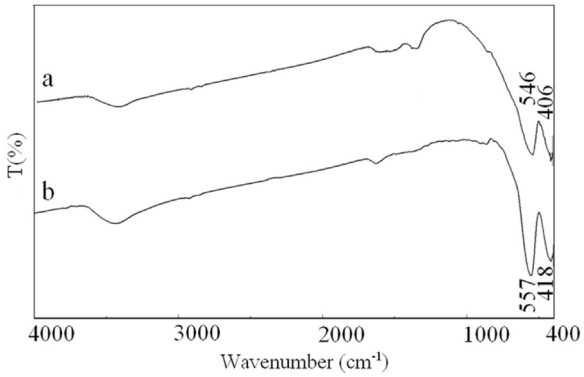

Fig. 2. FT-IR spectra of the (a) $ZnFe_2O_4$-S and (b) $ZnFe_2O_4$-ST samples.

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

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,1/2 for allowed direct transitions, 2 for allowed indirect, 3 for forbidden direct and 3/2 for forbidden indirect optical transitions. In this work, the direct transition band gap (E_g) of the samples was determined by plotting $(\alpha h\nu)^2$ versus E (eV). Until now, band gap energy of zinc ferrite has been reported of about 2.0, 1.9, 1.7 and 1.6 eV [18,38,39].

The optical band gap energy for the $ZnFe_2O_4$-S and $ZnFe_2O_4$-ST samples was found to be 1.7 and 1.9 eV, respectively (Fig. 6(a) and (b)). However, the band gap energy for the $ZnFe_2O_4$-ST sample slightly greater than that the other sample. The result showed that the band gap