Materials Letters 166 (2016) 247–250

Contents lists available at ScienceDirect

Materials Letters

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

Synthesis of Fe_3O_4 nonoparticles via a fast and facile mechanochemicl method: Modification of surface with porphyrin and photocatalytic study

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ARTICLE INFO

Article history:
Received 11 November 2015
Received in revised form
16 December 2015
Accepted 21 December 2015
Available online 22 December 2015

Keywords:
Semiconductors
Photocatalyst
Porphyrin
Light irradiation
Biomaterials
Fe_3O_4

ABSTRACT

In the present work, the Fe_3O_4 nanoparticles were synthesized via a green and facile mechanochemical method. Then 5,10,15,20-meso-tetrakis(4-carboxyphenyl)porphyrin (TCPP) was immobilized on surface of the Fe_3O_4 nanoparticles. The prepared nonocomposite was characterized by FT-IR, XRD, DRS, VSM and SEM images and their photocatalytic activity was investigated in the removal of methylene blue from aqua media.

1. Introduction

Recently, researchers have focused on the synthesis of the low cost nano-sized metal oxides. Magnetite (Fe_3O_4) nanoparticles have attracted an increasing interest due to the unique and novel physiochemical properties [1,2]. Fe_3O_4 with different structures has been used in nanotechnology, biotechnology and environmental technology [3]. Various methods have been introduced to prepare Fe_3O_4 nanoparticles, such as classical co-precipitation [4], microemulsion technique [5], sol–gel syntheses [6], sonochemical reactions [7], hydrothermal reactions [8] and microwave synthesis [3,9].

Utilization of high-energy ball milling as a mechanochemical process to synthesize magnetic nanoparticles [1,3,10,11] is preferred in comparison with other methods because this way is an effective, environmental friendly, useful, low-cost and a simple technique [12].

In this study, magnetic metal oxide powder of Fe_3O_4 was prepared by using a ball milling technique at different times (10, 30, 50 and 70 min) to obtain optimum time for ball milling. NaCl was applied as dispersing agent. Then the surface of Fe_3O_4 nanoparticles were modified by 5,10,15,20-meso-tetrakis(4-carboxyphenyl)porphyrin (TCPP) for preparation of TCPP/Fe_3O_4 composite. The Fe_3O_4 and TCPP/Fe_3O_4 were applied as photocatalysts to degradation of methylene blue (MB) under LED visible light and their performance to rapidly remove of MB was compared.

2. Experimental

2.1. Materials

All of the Chemicals used in this work were analytical grade reagents and used without further purification. Deionized water was used to preparation of all solutions.

2.2. Methods

The FT-IR analyses were carried out on a Shimadzu FTIR-8400S spectrophotometer using a KBr pellet for sample preparation. The optical characteristics of the samples were evaluated using a UV–visible diffuse reflectance spectroscopy (DRS) from 190 to 900 nm by a MPC-2200 spectrophotometer. The crystalline structure of the prepared Fe_3O_4 nanoparticles was analyzed using an X-ray diffraction method (INEL EQUNOX 3000 diffractometer) with monochromatized Cu-Kα radiation ($\lambda = 1.541874$ Å). The morphology of the nanostructures was depicted by a scanning electronic microscope (SEM, KYKY EM-3200). Magnetic properties of the samples were obtained by using a vibrating sample

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http://dx.doi.org/10.1016/j.matlet.2015.12.087
0167-577X/

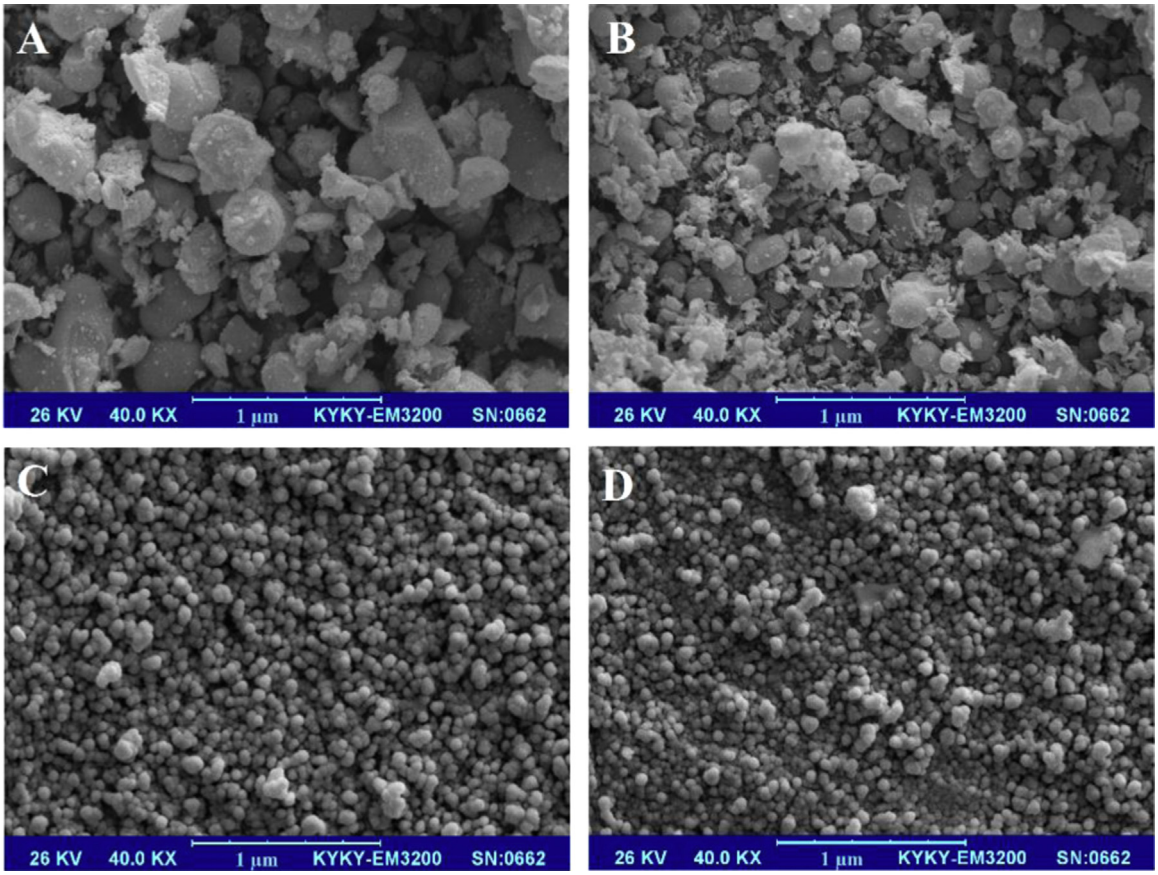

Fig. 1. The SEM images of Fe_3O_4 nanoparticles synthesized by mechanochemical route at different times: (A) 10, (B) 30, (C) 50 and (D) 70 min.

magnetometer (VSM, Meghnatis Daghigh Kavir Company, Iran). Milling was carried out using a high-energy grinding Mixer Mill (Retsch MM-400). The degradation of MB was monitored by measuring the absorbance amount using a double beam UV–Vis spectrophotometer (Shimadzu UV-1700). Bruker 400 MHz NMR spectrometer was used for analyses of the ^{1}H structural environments of TCPP.

2.3. Synthesis of Fe_3O_4 via mechanochemical method

The Fe_3O_4 nanoparticles were synthesized by mechanochemical reaction of $FeCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$ and NaOH. The excess of NaCl powder was added to avoid the aggregation of Fe_3O_4 particles. First, 0.43 g $FeCl_3 \cdot 6H_2O$, 0.3 g of $FeCl_2 \cdot 4H_2O$ and 3 g NaCl were mixed together and were put in a stainless steel cylinder (10 mL) with two small balls of 10 mm diameter by utilizing a mass ratio of 8:1 ball-to-powder. Milling was carried out for 10 min with a rate of 30 Hz (1800 rpm) at room temperature. Then 0.25 g of NaOH was added and the process of ball-milling was repeated for another 10, 30, 50 and 70 min.

The reaction was:

$$FeCl_2 \cdot 4H_2O + 2FeCl_3 \cdot 6H_2O + 8\ NaOH \rightarrow Fe_3O_4 + 8NaCl + 20H_2O.$$

Sampling was carried out at different ball milling time that resulted to three type of Fe_3O_4 nanoparticles, Fe_3O_4-10, Fe_3O_4-30, Fe_3O_4-50 and Fe_3O_4-70.

2.4. Synthesis of TCPP

10 mmol of freshly distilled pyrrole, 10 mmol of 4-carboxybenzaldehyde, 100 mL of propionic acid and 15 mL of nitrobenzene were added together in a 250 mL flask. The mixture was allowed to reflux under stirring at 140 °C for 60 min. After that, the resulting mixture was filtrated under reduced pressure. The crude product was purified by suxhlet with ethanol. A desired purple solid of TCPP was obtained (efficiency: 30%).

^{1}H NMR (400 MHz, CD_3Cl): δ 8.31 (d, 8 H, m-phenyl), δ 8.43 (d, 8 H, o-phenyl), δ 8.87 (s, 8 H, pyrrole).

2.5. Immobilization of TCPP on Fe_3O_4 nanoparticles

First, 2 g of finely grounded Fe_3O_4-50 nanoparticles was dispersed into 50 mL DMF by sonication and then 0.2 g of TCPP was dissolved to this solution. The resulting suspension was stirred under refluxing for 24 h and then the solvent was removed under vacuum at room temperature. Consequently, the product was washed with DMF until no porphyrin could be detected in the supernatant by UV–visible spectrophotometer.

2.6. Photocatalytic procedure

In a typical process, the catalytic reaction was carried out in a 100 mL photoreactor, which contains 50 mL of MB dye solution and 0.05 g of photocatalysts. Before irradiation, the solution was stirred in the dark (30 min) for obtaining an equilibrium point of initial physical adsorption of MB over the surface of photocatalyst samples. Irradiation was carried out using a 5 W LED visible light (5 W). All photocatalytic experiments were accomplished at the same conditions. The photocatalytic performance was indirectly monitored by relating the optical absorbance to the MB degradation amount using a double beam UV–visible spectrophotometer at a wavelength of 664 nm.