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Research article

Characterization of microstructural and optical $CoFe_2O_4/SiO_2$ ferrite nanocomposite for photodegradation of methylene blue

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Abstract: In this research, the $CoFe_2O_4$ and $CoFe_2O_4/SiO_2$ nanocomposites have been synthesized using the co-precipitation method, and the microstructural properties of the samples were characterized using X-ray diffraction methods (XRD). The photodegradation activity of methylene blue for both nanocomposites were also investigated. The XRD pattern of $CoFe_2O_4/SiO_2$ nanocomposites revealed that the sample was polycrystalline and had a spinel crystal structure with group space of Fd3m. The size of crystallite nanoparticle is 29.4 ± 0.2 nm for $CoFe_2O_4/SiO_2$ and 26.8 ± 0.2 nm for $CoFe_2O_4$. The $CoFe_2O_4/SiO_2$ nanocomposites have smaller optical band gap compared to bare $CoFe_2O_4$ due to smaller surface defect and larger particles size. The $CoFe_2O_4/SiO_2$ nanocomposites showed a more energetic photodegradation activity of methylene blue than $CoFe_2O_4$. The encapsulation of the SiO_2 matrix on the surface $CoFe_2O_4$ nanoparticles enhances the photodegradation activity. Based on the result, nanocomposites $CoFe_2O_4/SiO_2$ and $CoFe_2O_4$ are prospective as nano-photocatalyst and nano-adsorbent for organic pollutants.

Keywords: characterization; dye; microstructural; optical; photocatalyst

1. Introduction

Cobalt ferrite ($CoFe_2O_4$) is a ferromagnetic oxide that has attracted considerable attention due to its excellent magnetic properties, such as high coercivity, modest saturation magnetization, high Curie temperature at 520 °C, large magnet crystalline anisotropy (~10^6 erg/cm^3), high mechanical hardness and remarkable chemical stability [1–3]. $CoFe_2O_4$ crystallizes into an inverse spinel structure, where one-half of the Fe^{3+} ions occupy the tetrahedral sites, while the other half are located in the octahedral sites together with Co^{2+} ions [1]. The magnetic $CoFe_2O_4$ nanoparticles retain spherical shapes and size in the 6–35 nm range. The saturation magnetization of the premeditated nanocomposites increases with the increase of cobalt ferrite concentration in the silica matrix [2].

The $CoFe_2O_4$ properties depend on the preparation methods, raw materials, annealing time and temperature [1]. As the synthesis method influences the $CoFe_2O_4$ morphological and structural features, various synthesis methods, i.e., sol–gel, co-precipitation, microemulsion, hydrothermal, combustion, sonochemical, solid-state, complexation, microwave sintering, mechanical alloying, spray pyrolysis, reverse micelle, forced hydrolysis in polyol, pulsed laser deposition and ultrasonic cavitation have been used recently [2,3]. Among all, the co-precipitation method is often exercise in the preparation of nanoparticles dispersed in different matrix due to its high yield and simplicity. Nevertheless, the method is difficult to control particles size and shape [4].

$CoFe_2O_4$ in powder or in dispersed fluid form, has received increasing attention due to its catalytic, electrical and magnetic properties that make it appropriate for a wide range of applications (transformer cores, recording heads, antenna rods, loading coils, memory, microwave devices, catalysts, ferrofluids, magnetic refrigeration, magnetic sensors, drug delivery, gas detectors, sensors, solar energy conversion, stress and biomedical sensors, cellular therapy, tissue repair, etc.). As a ferromagnetic oxide with high magnetic anisotropy and high saturation magnetization, $CoFe_2O_4$ nanoparticles were used for numerous technological applications, such as storage media [2,5], magnetic resonance imaging, hyperthermia treatment, drug delivery [6,7], permanent magnets [8], microwave devices, magnetic refrigeration and solar energy conversion [9]. Most of this application requires specific electrical, optical, and magnetic properties mainly determined by their structure and morphology [2].

Recently, much attention has been absorbed on ferrite nanocomposites due to their capability to improve optical, electronic, and magnetic properties compared to those of single nanomaterial component [10]. Nanoparticles dispersion in hybrid matrices is an effective method to reduce particle agglomeration, less energy demand, and environmentally friendly use of nontoxic and biocompatible reagents which leads materials to possess superior properties [1]. Several kinds of the matrix such as resin, polymer or silica have been used to stabilize and reduce nanoparticles agglomeration. The silica (SiO_2) matrix provides a biocompatible, hydrophilic, nontoxic surface, and may enhance the formation of a single phase and the magnetic properties of nanocomposites [11]. The SiO_2 matrix also acts as a buffer and control the particles size [1].

Ferrite is known for their application in the magnetic and electronic fields. However, there are limited studies concerning its application as photocatalysts. The Spinel Ferrite (MFe_2O_4) ability to absorb photons in visible light has attracted considerable attention due to its pros, i.e., low cost and photo-corrosion resistance. The selection of the materials based on their redox activity, especially the mobility of high oxygen in their crystalline lattice. The mobility renders the tendency of materials to generate vacancies of this atom when synthesized under diminishing atmosphere. These vacancies improved their photocatalytic activity [11,12].

Moreover, investigation of microstructural and optical properties of nanocomposites also conducted as a foremost concern defining the photodegradation phenomena. Moreover, this study predominantly focuses on reporting the photodegradation activity of $CoFe_2O_4/SiO_2$ for 20 ppm methylene blue dye with a driven of UV light radiation. The result showed that the photodegradation activity of $CoFe_2O_4/SiO_2$ is higher than bare $CoFe_2O_4$. The photodegradation activity of $CoFe_2O_4/SiO_2$ for methylene blue without UV light radiation also included in the investigation.

2. Materials and method

2.1. Preparation and characterization of $CoFe_2O_4/SiO_2$

The Co-Precipitation method also implemented in the preparation of nanoparticle ferrite $CoFe_2O_4$. While the pro analyst grade Cobalt Nitrate $Co(NO_3)_3$ $6H_2O$ and Ferrite Nitrate $Fe(NO_3)_3$ $9H_2O$ procured from E. Merck. Cobalt Nitrate $Co(NO_3)_3$ $6H_2O$ and Ferrite Nitrate $Fe(NO_3)_3$ $9H_2O$ was mixed and stirred at 90 °C for 60 minutes (Table 1). The mixture then calcined at 95 °C for 4 hours. In this research, the preparation of nanoparticles utilizes the co-precipitation method as reported by [5,6,13], while, the encapsulation process employs the Ströber method as reported by [9]. The microstructural of nanocomposites were characterized using X-Ray Diffraction (XRD), and their optical properties were investigated by using diffuse reflectance UV-visible spectrophotometer.

Table 1. Characteristics of the synthesized precursors.

Reagen	Quantity (mol)
$Co(NO_3)_3$ $6H_2O$	0.02
$Fe(NO_3)_3$ $9H_2O$	0.04
SiO_2	0.02

2.2. Photodegradation testing of $CoFe_2O_4/SiO_2$

The $CoFe_2O_4$ and $CoFe_2O_4/SiO_2$ nanocomposite (66.7% b/v) dissolved in an Erlenmeyer flask and stirred at room temperature with UV radiation for 120 minutes followed by measurement of absorbance level at wavelength 650 nm for 30 minutes. $CoFe_2O_4$ and $CoFe_2O_4/SiO_2$ nanocomposites were used to degradation methylene blue (20 ppm).

3. Result and discussion

3.1. XRD-analysis

The XRD pattern, as shown in Figure 1, depicts the scattering form of the plane of Miller indices (*hkl*): (311), (400), (511), and (533), confirming the formation of well-crystallized single phase $CoFe_2O_4$ (JCPDS card 22-1086) [8]. The nanoparticle has a spinel crystal structure with group space of Fd3m. The highest intensity of the diffraction peak was taken place in (311) with a diffraction angle 2θ of 36.23°. The calculated particles size of $CoFe_2O_4/SiO_2$ derived from Scherrer's equation is 29.7 ± 0.08 nm which is larger than $CoFe_2O_4$ of 26.8 ± 0.08 nm (Table 2).

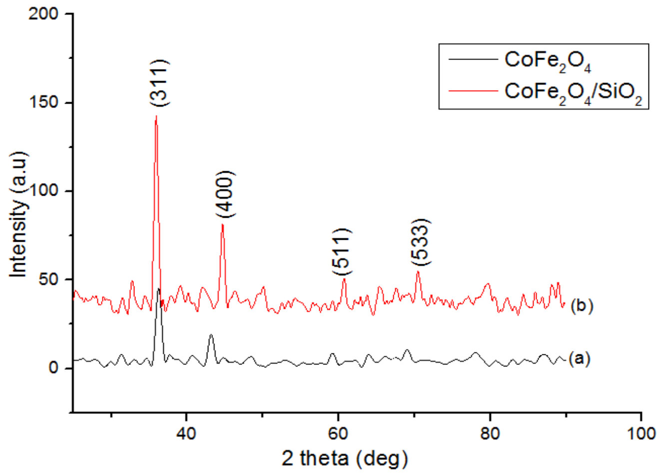


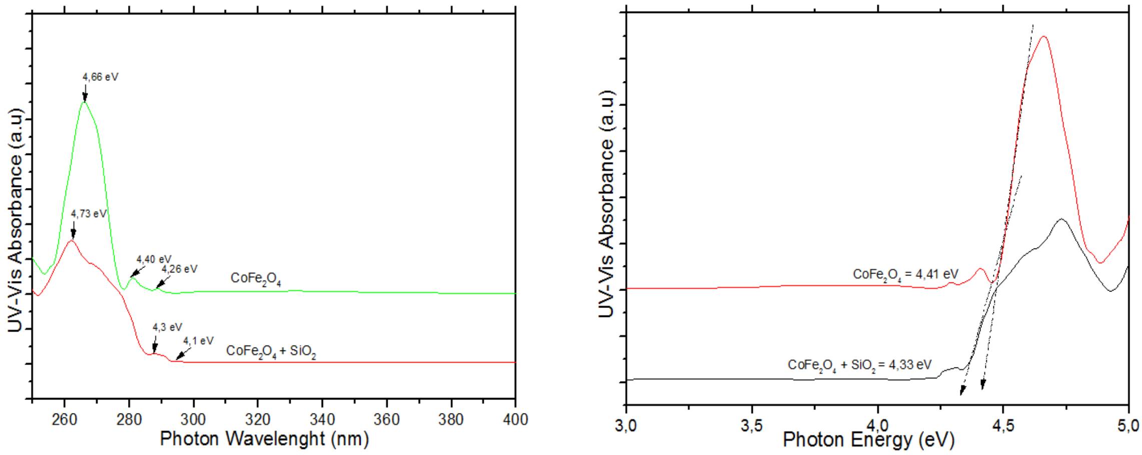
Figure 1. The X-Ray Diffraction Pattern for the (a) $CoFe_2O_4$; (b) $CoFe_2O_4/SiO_2$.

Table 2. Average crystallite size calculated using Scherrer equation.

Samples	2θ (°)	λ (Å)	k	hkl	FWHM (rad)	a (Å)	t (nm)
$CoFe_2O_4$	36.23	1.5406	0.9	311	0.0069	8.2	21.2
	43.17	1.5406	0.9	400	0.0071	8.4	21.1
	59.16	1.5406	0.9	511	0.0052	8.1	30.8
	69.00	1.5406	0.9	533	0.0049	8.9	34.2
$CoFe_2O_4/SiO_2$	36.08	1.5406	0.9	311	0.0054	8.2	27.0
	44.87	1.5406	0.9	400	0.0053	8.1	28.1
	60.59	1.5406	0.9	511	0.0048	7.9	33.4
	70.51	1.5406	0.9	533	0.0056	8.8	30.4

3.2. Optical properties

The optical properties of samples represented by using the diffuse reflectance UV-visible spectra. The calculation of the optical band gap of both sample, $CoFe_2O_4$ and $CoFe_2O_4/SiO_2$, show a different result. Based on the absorbance spectra, the highest elevation of the absorbance takes place between wavelengths of 250 nm and 300 nm (Figure 2a). Physically, this phenomena shows that energy needed by an electron to be excited from the valence band to conduction band ranges between 4.1 eV to 4.70 eV (Figure 2b). The optical gap energy resulted in the research is higher than result discovered by [9]. The excitation type of inter-band on this state could not be determined explicitly into direct-gap or indirect-gap, possibly triggered by the imperfect microstructure and lattice formation of crystallite [6]. Presumably, the crystal defect can be affected the number of the optical gap energy and quantum phenomena.

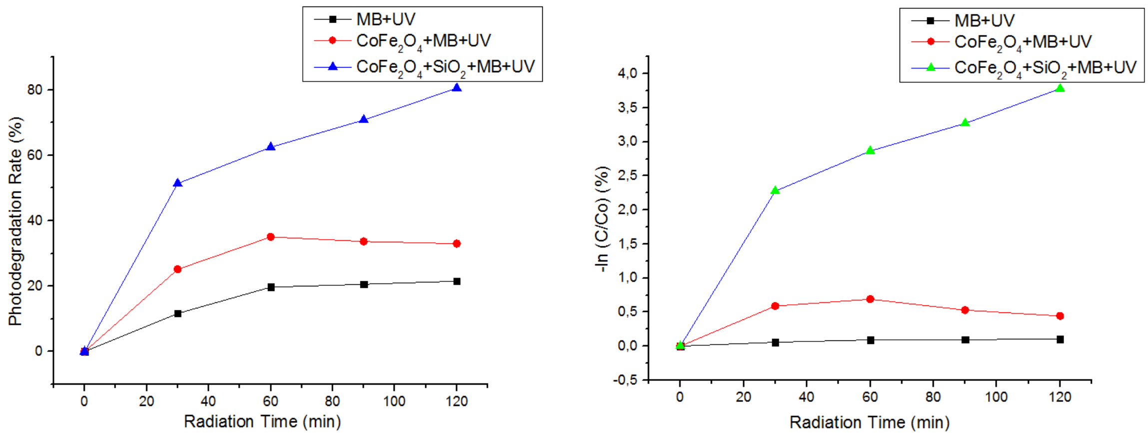


(a) (b)

Figure 2. (a) Absorbance spectra vs. photon wavelength; (b) the Touch's Plot.

3.3. Photodegradation activity

Photodegradation activity of samples was carried out with a variation of irradiation time as shown in Figure 3a,b. The result of the photodegradation activity of methylene blue shows that $CoFe_2O_4/SiO_2$ nanocomposites are higher than $CoFe_2O_4$. The rate of photodegradation of $CoFe_2O_4/SiO_2$ nanocomposites reaches 80.6%.



(a) (b)

Figure 3. (a) Photodegradation rate of $CoFe_2O_4$ and $CoFe_2O_4/SiO_2$ nanocomposites under and without UV-light radiation; (b) Photodegradation kinetic of samples.

As shown in Figure 3a,b, the presence of SiO_2 can amplified photodegradation activity from $CoFe_2O_4$ nanoparticles. Even though, $CoFe_2O_4$ and $CoFe_2O_4/SiO_2$ nanoparticles considered as prospective nano-photocatalyst under UV radiation. Nevertheless, further studies yet require to improve the microstructural properties and optical gap energy of $CoFe_2O_4/SiO_2$ nanocomposites before applying as a photocatalyst.

4. Conclusion

The $CoFe_2O_4$ and $CoFe_2O_4/SiO_2$ nanocomposites have been synthesized using the co-precipitation method successfully. The size of crystallite nanoparticle is 29.4 ± 0.2 nm for $CoFe_2O_4/SiO_2$ and 26.8 ± 0.2 nm for $CoFe_2O_4$. Nanocomposites $CoFe_2O_4/SiO_2$ have smaller optical band gap than $CoFe_2O_4$ due to smaller surface defect and larger particles size. The result of the photodegradation activity of methylene blue showed that $CoFe_2O_4/SiO_2$ nanocomposites are higher than $CoFe_2O_4$. The encapsulation of the SiO_2 matrix on the surface $CoFe_2O_4$ nanoparticles enhances photodegradation activity. Based on the result, nanocomposites $CoFe_2O_4/SiO_2$ and $CoFe_2O_4$ have been potential as nano-photocatalyst and nano-adsorbent for organic pollutants.

Conflict of interest

There is no conflict to declare.

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