ELSEVIER

#### Contents lists available at ScienceDirect

### **Materials Letters**

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



# Facile synthesis of zinc-iron mixed oxide/carbon nanocomposites as nanocatalysts for the degradation of methylene blue



Thanyaphat Techalertmanee <sup>a,b</sup>, Sittikorn Chancharoenrith <sup>a</sup>, Montree Namkajorn <sup>a</sup>, Supavadee Kiatisevi <sup>a</sup>, Laksamee Chaicharoenwimolkul <sup>c</sup>, Ekasith Somsook <sup>a,\*</sup>

- <sup>a</sup> NANOCAST Laboratory, Center for Catalysis, Department of Chemistry and Center for Innovation in Chemistry, Faculty of Science, Mahidol University, 272 Rama VI Rd., Thung Phaya Thai, Ratchathewi, Bangkok 10400, Thailand
- b The Materials Science and Engineering Program, Faculty of Science, Mahidol University, 272 Rama VI Rd., Ratchathewi, Bangkok 10400, Thailand
- <sup>c</sup> School of Chemistry, Faculty of Science and Technology, Suratthani Rajabhat University, 272 Moo 9, Surat-Nasan Rd., Khuntale, Muang, Surat Thani 84100, Thailand

#### ARTICLE INFO

#### Article history: Received 10 November 2014 Accepted 21 January 2015 Available online 28 January 2015

Keywords: Nanocomposites Photocatalysis ZnO ZnFe<sub>2</sub>O<sub>4</sub> Ferrocenium

#### ABSTRACT

Zinc-iron mixed oxide/carbon nanocomposites were synthesized by the pyrolysis of ferrocenium, zinc acetate, and glucose without the assistance of template or surfactant. The as-prepared zinc-iron mixed oxide/carbon nanocomposites exhibited good photocatalytic property over methylene blue under UV light.

© 2015 Elsevier B.V. All rights reserved.

#### 1. Introduction

The rapid industrialization leads to the increasing contamination of chemical compounds in natural water resources in which the detrimental effects on the environment and human health can be observed [1]. To eliminate the chemical pollutants, innovative tools such as advanced oxidation processes [2–6] have been developed to produce highly reactive oxygen species for the treatment of wastewater. Fenton-like reagents [7–9] and photocatalysts (TiO<sub>2</sub>) [10–15] can also generate hydroxyl radicals as reactive oxygen species to eliminate chemical pollutants. Semiconductor-based photocatalytic degradation is a promising method for the degradation of organic pollutants under UV or solar light irradiation [16,17]. ZnO is a semiconductor exhibiting high photocatalytic activity and stability as an alternative photocatalyst to TiO<sub>2</sub> [18]. However, ZnO showed a wide bandgap of 3.2 eV in which visible light irradiation was unfavorable for the photocatalysis [19]. ZnFe<sub>2</sub>O<sub>4</sub> is a class of semiconductor with a spinel structure exhibiting narrower bandgaps with high responses to visible light [19]. The photocatalytic activity of ZnFe<sub>2</sub>O<sub>4</sub> was reported that it was enhanced by high conductive supports such as graphene. ZnFe<sub>2</sub>O<sub>4</sub>/graphene [20] exhibited high photocatalytic performance under visible light irradiation in the presence of H<sub>2</sub>O<sub>2</sub>. However, the addition of H<sub>2</sub>O<sub>2</sub> may be unsuitable

for practical applications due to the excess amount of  $H_2O_2$  may be required. The presence of  $ZnFe_2O_4$  and ZnO in nanocomposites by immobilizing on graphene exhibited enhanced photocatalytic activity under solar light irradiation in the absence of  $H_2O_2$  [19].

Ferrocene ( $(C_5H_5)_2$ Fe or Fc) [21] is a redox active species that can react with hydrogen peroxide to generate hydroxyl radicals for the oxidation of organic compounds [22,23]. In addition, ferrocene has been used as a precursor for the synthesis of iron nanoparticles (or iron oxide nanoparticles) and carbon nanotubes [24-26]. Ferrocene [21] is a nonpolar molecule which is soluble in concentrated sulfuric acid to give a blue viscous solution of ferrocenium ((C5H5)2FeH+ or Fc<sup>+</sup>) [27,28]. The novelty of this work is the preparation of zinc-iron mixed oxide/carbon nanocomposites from the pyrolysis of ferrocenium, zinc acetate, and glucose. Then the photocatalytic activity of zinc-iron mixed oxide/carbon nanocomposites was tested for the decomposition of methylene blue (MB) as a model for the treatment of waste water. Hopefully, the incorporation of carbon derived from ferrocenium, acetate and glucose would tune the photocatalytic activity of the synthesized nanocomposites as demonstrated with the immobilization of graphene to ZnFe<sub>2</sub>O<sub>4</sub> and ZnO [19].

#### 2. Experimental section

Ferrocenium was prepared by the addition of concentrated sulfuric acid to ferrocene [27,28].  $ZnFe_2O_4/C$  nanocomposites were

<sup>\*</sup> Corresponding author. Tel.: +66 2 201 5123; fax: +66 2 354 7151. E-mail address: ekasith.som@mahidol.ac.th (E. Somsook).

prepared by the following method. In an aluminum crucible with aluminum-cap, ferrocenium, zinc acetate  $(Zn(CH_3COO)_2)$ , and D-glucose with ratio (1:0.5:1) were mixed and annealed in air at 100 °C for an hour and then the pyrolysis of the mixture was performed in air at the desired temperatures (400, 500, 600, or 800 °C) for 5 hours. After that, obtained solid was collected and stored in desiccators before used.

Photocatalytic experiments were performed in a dark box equipped with UV or visible lamp. A suspension composed of 100 mg of the prepared nanocomposites and  $100 \, \mathrm{cm}^3$  of methylene blue solution (MB)  $(1 \times 10^{-5} \, \mathrm{mol/dm^3})$  was stirred and irradiated with UV light or visible light, or the absence of light for 2 hours. The analytical samples were withdrawn at a specific time of 10, 20, 30, 45, 60, 90, and 120 minutes for the analysis of MB concentration by UV–visible spectroscopy at a wavelength of 662 nm. The percentage of degradation was defined as Eq. (1) where  $A_0$  and  $A_t$  were absorbance at the starting point and a specific time.

$$\%Degradation = \left(\frac{A_t - A_0}{A_0}\right) \times 100 \tag{1}$$

The as-prepared samples were characterized by Powder X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), Thermal Gravimetric Analysis (TGA), UV–visible diffuse reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS), specific surface area and porosity measurements. The UV–visible spectrophotometry was carried out at room temperature on JASCO V-530 in range of 350–700 nm and scan speed of 1000 nm/min.

#### 3. Results and discussion

The synthesis of  $ZnFe_2O_4/ZnO/C$  was readily obtained by the pyrolysis of ferrocenium, zinc acetate and glucose as seen in the XRD patterns, TEM images, TGA Thermograms, UV–visible diffuse reflectance spectra, band gap plotting, elemental analysis, and specific surface area of mixtures pyrolyzed at 400 °C, 500 °C, 600 °C and 800 °C shown in Fig. 1 and Table 1. The sources of carbon were derived from ferrocenium, acetate, and glucose. Characteristic peak of  $ZnFe_2O_4$  and hematite ( $\alpha$ -Fe $_2O_3$ ) were identified in the XRD patterns with the amorphous phase of ZnO. TEM images of prepared Zn–Fe–O mixed oxide/carbon nanocomposites *via* pyrolysis at 400 °C, 500 °C, 600 °C

 Table 1

 Elemental analysis, crystallite size, and BET analysis.

Entry	Pyrolysis temperature (°C)	Carbon content (%) <sup>a</sup>	Crystallite size <sup>b</sup>	Fe/ Zn <sup>c</sup>	Specific surface area (m <sup>2</sup> /g) <sup>d</sup>	Total pore column (cc/g) <sup>d</sup>	Average pore size (nm) <sup>d</sup>
1	400	2.06	35.1	7.39	30.0	0.13	37.7
2	500	0.56	31.1	2.89	34.2	0.13	37.9
3	600	0.09	13.7	1.83	30.8	0.14	19.3
4	800	0.14	63.6	1.13	22.4	0.08	14.3

- <sup>a</sup> measured by elemental analysis.
- b measured by XRD.
- c measured by XPS.
- d measured by BET.

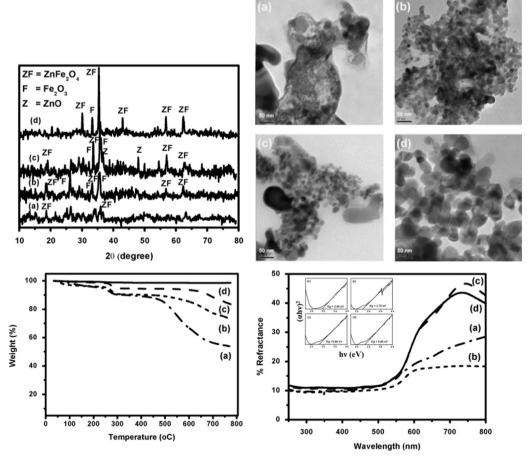


Fig. 1. XRD patterns, TEM images, TGA Thermograms, UV–visible diffuse reflectance spectra and band gap plotting of Zn–Fe mixed oxide/carbon nanocomposites pyrolyzed at (a) 400 °C, (b) 500 °C, (c) 600 °C and (d) 800 °C.

## Download English Version:

# https://daneshyari.com/en/article/1643011

Download Persian Version:

https://daneshyari.com/article/1643011

<u>Daneshyari.com</u>