# Synthesis, characterization and activity evaluation of visible light responsive CuFe<sub>2</sub>O<sub>4</sub> catalyst

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of Abstract—The photocatalytic activities CuFe<sub>2</sub>O<sub>4</sub> photocatalyst for removing organic dve from wastewater under visible light irradiation have been investigated. Cupper ferrite (CuFe<sub>2</sub>O<sub>4</sub>) nanoparticles have been successfully synthesized via a nitric acid assisted sol-gel method. The photocatalytic evolution of CuFe<sub>2</sub>O<sub>4</sub> has been achieved over the organic dve (Methylene Blue, MB) degradation and the activity is dependent on the synthesis method. The results show that the photocatalytic activity and visible light response to CuFe<sub>2</sub>O<sub>4</sub> is higher than some other photocatalysts used for dye reduction. In addition, it is evident from the literature survey that various low-cost adsorbents are highly potential for the removal of various aquatic pollutants still suffers from drawbacks for commercial application. The present work has been proposed to circumvent these limitations by exploring the organic dye removal from wastewater over CuFe<sub>2</sub>O<sub>4</sub> photocatalyst under visible light irradiation.

Keywords—synthesis;  $CuFe_2O_4$ ; characterization; activity evaluation

#### I. INTRODUCTION

The contamination of water resources by industrial effluents is posing a great problem to the human society. Various methods of treating wastewater such as biotechnology, chemical oxidations and adsorption have been studied for the treatment of organic pollutants in water [1-3]. Adsorption is efficient but once toxic compounds adsorb on the adsorbents, they became hazardous waste that need to be disposed properly [2, 4, 5]. The production of potable water has become a worldwide concern; for many communities, projected population growth and demand exceed conventional available water resources. Over 1 billion people are without clean drinking water and approximately 2.3 billion people (41% of the world population) live in regions with water shortages [6-8]. For most, solutions such as water conservation and water transfer or dam construction are not sufficient methods to cope with increasing demand and, in many cases, decreasing supply. Traditional fresh water resources such as lakes, rivers, and groundwater are overused or misused; as a result, these resources are either diminishing or becoming saline. As countries continue to develop and cities expand, few new water resources are available to support daily fresh water needs. As a result, solutions such as water reuse and salt water

desalination have emerged as the keys to sustaining future generations across the globe [6, 9-11].

Recently, water shortages are becoming an increasing problem due to scientific advances following rapid industrial growth, environmental pollution, depleted water resources, global warming causing abnormal climate changes, and uncontrolled ground-water development [3, 7, 12]. The rapid development of manufacturing technology after the industrial revolution has improved the standards of living significantly but it is becoming a factor that is threatening human health and the environment. Pollutants are changing both quantitatively and qualitatively, and the number of chemicals currently in circulation is 38,000 with more than 300 new materials being synthesized every year due to the diversification of industrial structures and high-tech industry [5, 9, 12]. Some contaminants such as aromatic halides and dyes have adequate resistance to oxidation by bio-degradation and conventional chemical oxidation [13]. Therefore, removal of organic pollutants remains a great challenge [14]. It was reported that about 20% of the total world production of dye is lost during dyeing process and released as textile effluents. Organic dyes produce toxic substance through oxidation and hydrolysis in the wastewater phase [5, 15, 16]. The high concentration of organics and higher stability of modern synthetic dyes makes conventional method ineffective for complete removal and degradation of dyes [3, 17]. Hence, wastewater containing toxic organic dyes have serious problem to the environment [9].

TiO<sub>2</sub>, metal ferrite, and other semiconductors are very promising photocatalysts for water purification and removal of different organic elements from industrial waste water. These semiconductors should be stable, inexpensive, non-toxic, and especially capable of harvesting light to get photo-generated carriers for dye or organic compounds removal. With good electronic conductivity, high thermal stability, and excellent catalytic activity, spinel-type compounds have been explored as catalysts, especially photocatalysts. MFe<sub>2</sub>O<sub>4</sub> is typical spinel-type compounds, and exhibit promising photocatalytic activity. So it's of great significance to investigate their photocatalytic activity for dye removal [4, 18-23]. TiO<sub>2</sub> is a promising photocatalyst for water treatment, having a strong resistance to chemical and photocorrosion, low operational temperature, low cost, significantly low energy consumption, led to the relevant applications of the photocatalytic dye reduction. However,  $\text{TiO}_2$  exhibits a relatively high energy band-gap (3.2 eV) and can only be excited by high energy UV irradiation with a wavelength shorter than 387.5 nm. The wide band gap only allows  $\text{TiO}_2$  remains active under UV irradiation. This is not efficient as only 5% of solar energy reaches Earth as UV irradiation while 46% were visible light [3, 24-30].

In this study,  $CuFe_2O_4$  was used as a photocatalyst for photocatalytic dye (Methylene Blue, MB) reduction under visible light irradiation. The  $CuFe_2O_4$  photocatalyst was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet visible spectroscopy (UV-Vis), and energy dispersive X-Ray spectroscopy (EDX) instruments. The photocatalytic activities of the  $CuFe_2O_4$ photocatalysts for reducing organic dye present in wastewater have been investigated under visible light irradiation in detail.

## **II. MATERIALS AND METHODS**

#### A. Materials

The copper nitrate,  $Cu(NO_3)_2.3H_2O$  (99%), iron nitrate,  $Fe(NO_3)_3.9H_2O$  (99%), Nitric acid,  $HNO_3$  (65%), and Agar were obtained from R&M Chemicals. Methylene Blue (MB) dye was obtained from Fisher Scientific for calibration and analysis. All chemicals used in this work were analytical grade and used as received.

#### B. Catalyst Synthesis

 $CuFe_2O_4$  has been prepared through sol-gel method. For the photocatalyst ( $CuFe_2O_4$ ) preparation,  $Cu(NO_3)_2.3H_2O$  and  $Fe(NO_3)_3.9H_2O$  were dissolved in HNO<sub>3</sub> in which 4 g of agar and 400 mL of water were added and retained for 3 h under continuous stirring at room temperature. The solution was then heated under stirring at 90°C for 3 h. The gelatin formation was gradually proceeded until a green gel was obtained, and then dried at 130°C under vacuum for 24 h. Finally, the powder is fired at 900°C with a heating rate of 10°C/min for 16 h [18].

## C. Characterization

The XRD patterns were obtained at room temperature using Rigaku MiniFlex II. The morphologies of the spray/dipcoated photocatalysts were observed by scanning electron microscope (SEM) of the model JEOL JSM-5410LV (JEOL, Japan). Energy dispersive X-ray spectrometer (EDX) (5.0 kV) in connection with SEM was used to identify and analyze the elemental composition of surface composite photocatalysts. The UV-Vis diffuse reflectance spectrum (DRS) in the range of 200–800 nm was measured with a Daojin UV-2550PC diffuse reflectance spectroscope.

## D. Photocatalytic activity

Photocatalytic is process in which light photons are absorbed with energies greater than its bang-gap energy  $(E_g)$ to create electron-hole pairs. The photogenerated electrons (e-) and holes (h+) participate in various oxidation and reduction processes to produce final products [31]. However, if the electrons fail to find any trapped species (e.g.  $CO_2$ ) on the semiconductor surface or their energy band gap is too small, then they recombine immediately and release unproductive energy as heat[18, 32]. Photocatalytic absorption of light photons creates photoelectrons in the conduction band (CB) and holes in the valence band (VB) of the semiconductor, as schematically depicted in Fig. 1a. In the Fig. 1b, the photogenerated electron-hole pairs must separate and migrate to the surface (paths a and b in Fig. 1b) competing effectively with the electron-hole recombination process (path c in Fig. 1b) that consumes the photo charges generating heat. The photoinduced electrons and holes reduce and oxidize adsorbed organic dye (MB) for water purification [31, 33-35].

## **III. RESULTS AND DISCUSSION**

## A. XRD Analysis

The XRD pattern of CuFe<sub>2</sub>O<sub>4</sub> is showed in Fig. 2. Fig. 2 depicts the XRD pattern of the CuFe<sub>2</sub>O<sub>4</sub> photocatalyst fabricated via sol-gel approach. It was observed from Fig. 2 that there were three sharp peaks in the patterns of  $CuFe_2O_4$  at 18.56°, 37.31° and 62.25°, respectively. The diffraction lines of these samples can be readily indexed to tetragonal-type CuFe<sub>2</sub>O<sub>4</sub> (JCPDS 34-0425) [18, 20]. Fig. 2 depicts the XRD patterns of the as-obtained photocatalysts calcined at 900 °C. The diffraction lines of the as-obtained CuFe<sub>2</sub>O<sub>4</sub> can be indexed spinel-type CuFe<sub>2</sub>O<sub>4</sub> readily to (JCPDS 101,112,200,202,211,220,303, 224, 400, 422). The diffraction peaks of these samples are narrow and strong, indicating good crystallinity. No impurity phase was detected in the asobtained CuFe<sub>2</sub>O<sub>4</sub> sample, except existing a small amount of CuO (JCPDS 110, 200) and Fe<sub>2</sub>O<sub>3</sub> (JCPDS 104,102,110) impurity phase in the as-obtained CuFe<sub>2</sub>O<sub>4</sub> samples (Fig. 2).

Fig. 1. Principle of photocatalytic water splitting: (a) photoelectron



excitation in the photocatalyst-generating electron hole pairs and (b) processes occurring on photocatalyst particle following photoelectronic excitation



Fig. 2. XRD patterns of the  $\rm CuFe_2O_4$  photocatalyst fabricated via sol–gel approach at 900  $^{\circ}\rm C$ 

# B. UV-Vis Spectroscopy Analysis

The UV–Vis DRS of the as-prepared photocatalyst  $(CuFe_2O_4)$  has been presented in Fig. 3. A band gap of 1.71 eV was obtained from UV-Vis DRS analysis (Fig. 3). The required wavelength to make the photocatalyst active can be calculated according to the following equation [36]:

Wavelength,  $\lambda$  (nm)  $\leq$  1240/ Band gap of semiconductor (eV) (1)

This means that  $CuFe_2O_4$  photocatalyst is active under visible light irradiation up to 725 nm. Therefore  $CuFe_2O_4$ covered a broad range of solar spectrum of visible light which consists of light with wavelength of 390 to 780 nm.



Fig. 3. The UV-Vis DRS of the prepared photocatalyst (CuFe<sub>2</sub>O<sub>4</sub>)

#### C. SEM and EDX Analysis

The morphologies of the photocatalysts were observed by SEM as shown in Fig. 4. The micrograph of  $CuFe_2O_4$  prepared by sol gel method was formed from fine spherical particles with a uniform distribution and well defined natural crystalline faces (Fig. 4). The  $CuFe_2O_4$  particles were almost spherical, and the size was much less than 10 µm, even to several hundred nanometers. EDX analysis confirms the presence of Cu, Fe and O elements in the prepared  $CuFe_2O_4$  catalyst (Fig. 5). The experiments confirm all the elements present in the asprepared samples including some unwanted phases, e.g., Pt and C (Fig. 5). Pt may contaminated from coating and carbon from the carbon paper during the analysis. Table I shows the elemental compositions of Cu, Fe and O in the prepared  $CuFe_2O_4$ .

TABLE I. ELEMENTAL COMPOSITIONS OF PREPARED CUPPER FERRITE

Elements	Weight (%)	Atomic (%)
C K	5.23	16.63
O K	17.29	41.27
Fe K	44.20	30.22
Cu L	13.23	7.95
Pt M	20.05	3.92



Fig. 4. SEM micrograph of CuFe<sub>2</sub>O<sub>4</sub> prepared by sol-gel at 900 °C



#### Fig. 5. Elemental analysis of CuFe<sub>2</sub>O<sub>4</sub> by EDX

## D. Photocatalytic Degradation of Organic Dye (MB)

Effects of photocatalyst loading: Fig. 6, summarizes I. the influence of photocatalyst loading in the range of 0.3 to 1.0 g/L after 5 h adsorption study to ensure equilibrium have been attained. By using CuFe<sub>2</sub>O<sub>4</sub>, a considerable amount of MB degraded, indicating that CuFe<sub>2</sub>O<sub>4</sub> is an effective photocatalyst toward MB degradation under visible light irradiation. With increasing of  $CuFe_2O_4$  loading, the degradation of MB increases. The active sites on the CuFe<sub>2</sub>O<sub>4</sub> particles surface and the light penetration of photoactivating light into the reactor are crucial to photocatalytic degradation of MB [37]. When the photocatalyst loading is below its optimum value, the available active sites on the CuFe<sub>2</sub>O<sub>4</sub> particles surface increases with the increasing of photocatalyst loading, leading to more and more absorption of photons for degradation of MB. However, an excess of photocatalyst may impede the further penetration of incident light into the reactor, and the inner photocatalyst cannot be photoexcited to generate electron/hole pairs (EHP). As a result, less OH will be generated and causes photocatalytic degradation of MB to be decreased. According to Yang et al. [19], photocatalytic activity decreases at extreme high concentration of photocatalyst loading because activated CuFe<sub>2</sub>O<sub>4</sub> can be deactivated by the collision with the ground state CuFe<sub>2</sub>O<sub>4</sub>:

$$CuFe_2O_4^{\#} + CuFe_2O_4 \rightarrow CuFe_2O_4^{*} + CuFe_2O_4$$
(2)

Where  $CuFe_2O_4^{\#}$  is the photoexcited  $CuFe_2O_4$  and  $CuFe_2O_4^{*}$  is the deactivated form of  $CuFe_2O_4$ . Under this situation, the photocatalytic degradation of MB reduces.

*II.* Effects of initial MB concentration: Fig. 7, illustrates the photocatalytic degradation of MB as a function of initial MB concentration  $(C_0)$  after 5 h adsorption study to ensure equilibrium have been attained. The degradation rate is lower for higher initial concentrations as the order decreases. This is because CuFe<sub>2</sub>O<sub>4</sub> had reached its maximum efficiency. At constant CuFe<sub>2</sub>O4 catalyst loading, there will be no additional active sites on the CuFe<sub>2</sub>O<sub>4</sub> particle surface when the dye concentrations are increased. Therefore, degradation of dye decreases as the initial dye concentration increases.



Fig. 6. Normalized MB concentration (C/C $_{o}$ ) plot at various catalysts loading with similar initial MB concentration of 20 ppm



Fig. 7. Normalized MB concentration (C/C<sub>o</sub>) plot at different initial MB concentration with similar catalyst loading of 0.6 g/L

#### **IV. CONCLUTIONS**

The CuFe<sub>2</sub>O<sub>4</sub> photocatalyst was prepared by direct reactions between Cu(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, by dissolving in HNO<sub>3</sub> following sol-gel method. The spinel CuFe<sub>2</sub>O<sub>4</sub> is non toxic, low cost, chemically stable and possesses an optical gap, close to the ideal value required for terrestrial applications. The prepared  $CuFe_2O_4$  is an effective photocatalyst that is able to utilize visible light to perform oxidation processes. Photocatalytic degradation of MB can take place efficiently on the prepared CuFe<sub>2</sub>O<sub>4</sub>. The CuFe<sub>2</sub>O<sub>4</sub> photocatalyst was characterized by XRD, UV-Vis spectroscopy, SEM and EDX. It is found out that the photocatalytic activity and visible light response of CuFe<sub>2</sub>O<sub>4</sub> is higher at low MB concentration. Moreover, the modification of CuFe<sub>2</sub>O<sub>4</sub> can enhance its photocatalytic activity and visible light response. The modified  $CuFe_2O_4$  will be used for  $CO_2$ conversion into hydrocarbons in future detail investigation.

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