



# Nanoscale-confined precursor of $\text{CuFe}_2\text{O}_4$ mediated by hyperbranched polyamide as an unusual heterogeneous Fenton catalyst for efficient dye degradation

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## ABSTRACT

Dye effluent causes a serious problem to the environment and is of a great concern worldwide.  $\text{CuFe}_2\text{O}_4$ -based heterogeneous Fenton oxidation is considered as a promising approach for efficient dye effluent treatment. However, the high-temperature calcination of  $\text{CuFe}_2\text{O}_4$  makes this technique less applicability. In this study, nanoscale-confined precursor of  $\text{CuFe}_2\text{O}_4$  (NCFOH) was fabricated via a facile coprecipitation method with the confinement of hyperbranched polyamide (MHP) and characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and BET measurement. Its catalytic performance for dye degradation was also tested. Despite of its amorphous structure, NCFOH possesses a much stronger catalytic performance than the precursor of  $\text{CuFe}_2\text{O}_4$  (CFOH) and calcined  $\text{CuFe}_2\text{O}_4$  (CFO) without the mediation of MHP. In addition, NCFOH even shows a similarly catalytic ability with the corresponding calcination (NCFO). The results reveal that particle size and specific surface area may play more important roles than crystalline structure in the catalytic performance. Furthermore, the cycling experiments suggest the high stability and applicability of NCFOH as a reusable catalyst for dye effluent treatment. This work demonstrates that the NCFOH has a potential of widespread commercialization as an excellent heterogeneous Fenton catalyst, and also provides deeper insights into the novel nanoscale-confined approach for fabricating low-cost and efficient catalysts.

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## 1. Introduction

As a major class of contaminants in the textile effluent, the organic dyes are extremely hazardous to the eco-environment and public health because of its high toxicity and low biodegradability (Aguilar et al., 2017; Hu et al., 2016a, 2016b). Therefore, it is necessary to eliminate these dyes before they are released to surrounding aquatic environment.

The development of economical and effective dye effluent treatment is a goal that has long been pursued. Numerous

technologies have been applied to treat dye effluent, including coagulation/adsorption (Angelova et al., 2016; Lee et al., 2006a, 2006b; Moawed et al., 2017; Shi et al., 2007), biodegradation (Kalyani et al., 2009; Khan et al., 2013; Pereira et al., 2014) and advanced oxidation processes (AOPs) (Chakma and Moholkar, 2013; Oturan and Aaron, 2014; Sirés et al., 2014). The AOPs include ozone oxidation (Ledakowicz et al., 2017; Nawrocki and Kasprzyk-Hordern, 2010), sonochemical oxidation (Liang et al., 2017; May-Lozano et al., 2017; Sathishkumar et al., 2016), electrochemical methods (Brillas and Martínez-Huitle, 2015; Turcanu and Bechtold, 2017; Yang et al., 2017), Fenton oxidation (Du et al., 2016; Meng et al., 2016; Rodríguez et al., 2016; Xu et al., 2016; Zhang et al., 2017a; Zhu et al., 2013), semiconductor-based photocatalysis (Lv et al., 2016; Ma et al., 2018; Safardoust-Hojaghan and Salavati-Niasari, 2017) and others (Bai et al., 2017; Lee et al., 2016). Owing to the recalcitrant nature of dye and operation cost, the

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conventional techniques including coagulation/adsorption and biodegradation fail to remove dyes effectively (Vaiano et al., 2017). In that sense, Fenton oxidation, involving the generation of hydroxyl radicals ( $\cdot\text{OH}$ ), has emerged as a promising approach because of its high efficiency and environmentally benign feature (Deng et al., 2017; Wang et al., 2014). However, the conventional homogeneous Fenton reaction has some significant limitations: (i) a narrow range of operating pH (<4); (ii) the generation of large amounts of iron-based sludge, which is difficult to be removed and greatly increases the operation cost (Liu et al., 2017; Ma et al., 2017; Rache et al., 2014; Wang et al., 2017; Zang et al., 2017; Zhang et al., 2014). Thus, heterogeneous Fenton oxidation has been developed to overcome these shortcomings.

Recently,  $\text{CuFe}_2\text{O}_4$ , one of the spinel ferrite particles, have received intensive attention in heterogeneous Fenton oxidation due to its excellent magnetic property, and chemical stability. Besides,  $\text{CuFe}_2\text{O}_4$  exhibits high reactivity in catalysis of oxidants such as  $\text{H}_2\text{O}_2$  and peroxymono-sulfate (PMS) as well as ozone for eliminating the refractory organic pollutants (Li et al., 2017; Qi et al., 2016; Xu et al., 2016; Zhang et al., 2016, 2017b; Zhu et al., 2013). However, the number of active sites in bulk  $\text{CuFe}_2\text{O}_4$  is limited, which potentially hinders the catalytic activity and applicability (Wang et al., 2014; Zhang et al., 2016, 2017b). To improve its catalytic efficiency, some strategies have been proposed. For example, Zhang et al. creatively used multi-walled carbon nanotube as a functional substrate to confine the size of  $\text{CuFe}_2\text{O}_4$  particles to expose more active sites (Zhang et al., 2016, 2017b). Additionally, Wang et al. firstly fabricated mesoporous  $\text{CuFe}_2\text{O}_4$  with high surface area and large pore size using KIT-6 as the template. It was found that highly enhanced imidacloprid degradation was realized with the mesoporous  $\text{CuFe}_2\text{O}_4$  (Wang et al., 2014). But the high-temperature calcination is always necessarily performed to ensure the catalytic activity of  $\text{CuFe}_2\text{O}_4$ . This process is highly energy-intensive and requires special equipment, eventually making the wastewater treatment expensive.

Unfortunately, most studies focus on the improvement of the catalytic efficiency and ignore the most important fact that the successful application of heterogeneous Fenton oxidation is highly determined by its working cost. Therefore, it is imperative to develop a relatively low-cost strategy to fabricate the catalyst with admirable catalytic activity. Lately, the study performed by Xu's group indicated that the precursor of  $\text{CuFe}_2\text{O}_4$  (CFOH) exhibited a higher activity for phenacetin degradation than the corresponding calcined  $\text{CuFe}_2\text{O}_4$  over catalytic ozonation (Qi et al., 2016). This study firstly provided a more easy-access technique to fabricate low-cost catalyst. Besides, utilization of CFOH for Fenton oxidation has remained unavailable by far. In this regard, it is reasonable to suppose that the CFOH may possess the ability to catalyze  $\text{H}_2\text{O}_2$  for dye degradation and enhance the applicability of heterogeneous Fenton oxidation. Meanwhile, developing a novel strategy to reduce the particle size of CFOH may be a significant approach to further enhance its catalytic activity.

Hyperbranched polyamide is one class of dendritic polymers, which has been increasingly used to fabricate metal oxide nanoparticles by the confinement (Manna et al., 2001; Zhang et al., 2013). Inspired by the possibility to enhance catalytic performance and lower the preparation cost of catalyst, we made an effort to fabricate nanoscale-confined heterogeneous Fenton catalyst without high-temperature calcination for dye degradation. In the present study, the nanoscale-confined precursor of  $\text{CuFe}_2\text{O}_4$  (NCFOH) was firstly fabricated via a facile coprecipitation method with the confinement of maleic anhydride modified hyperbranched polyamide (MHP), and then used as a novel heterogeneous Fenton catalyst for dye degradation. By comparison, CFOH, CFO and NCFO were also fabricated. The structure and size of the obtained

catalysts were characterized by several methods such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Brunauer-Emmett-Teller (BET) measurement. Furthermore, the catalytic performance involving the degradation of dyes by  $\text{H}_2\text{O}_2$  was evaluated.

## 2. Material and methods

### 2.1. Chemicals and materials

Diethylenetriamine (99%), methyl acrylate (>99%), maleic anhydride (>99%), methanol (>99%),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (99%),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (99%),  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (25%–28%), KBr (>99.5%) and  $\text{H}_2\text{O}_2$  (30%) were all purchased from Aladdin Industrial Co., Ltd., China. Commercial dyes, including C.I. Reactive Red 2 (defined as RR), C.I. Reactive Yellow 3 (defined as RY), C.I. Basic Red 46 (defined as BR), C.I. Basic Yellow 24 (defined as BY) were obtained from Zhejiang Longsheng Group Co., Ltd. and used directly. The chemical structures and  $\lambda_{\text{max}}$ s (maximum adsorption wavelengths) of selected dyes are shown in Table 1.

### 2.2. Synthesis of MHP

The MHP was synthesized via a previously reported method with modification (Zhang et al., 2007). Typically, 0.2 mol diethylenetriamine (DETA) was firstly added in a 250 ml three-neck round-bottomed glass flask. Then the dropwise addition of methyl acrylate (MA)-methanol solution (0.2 mol in 100 ml) initiated the reaction under  $\text{N}_2$  protection at room temperature with vigorous stirring and reacted for 4 h. After then, 20 ml methanol solution of maleic anhydride (0.5 mol/L) was added into the flask. The mixture contained  $\text{AB}_2$  monomer and modified agent were obtained via the removal of methanol by the vacuum filtration process. After that, the collected mixture was transferred to the oil bath for further reaction at the temperature of 150 °C for another 1 h to synthesize the desired MHP (As a comparison, the hyperbranched-polyamide (HP) was synthesized following the same procedures but without adding maleic anhydride). The pathway of MHP synthesis is described as Scheme S1 in the Supporting Information.

### 2.3. Preparation of CFOH, CFO, NCFOH and NCFO

NCFOH was fabricated by a reported coprecipitation method with some modifications (Kang et al., 1996). Briefly, 100 ml of MHP aqueous solution ( $15 \text{ g L}^{-1}$ ) was added dropwise into 100 ml of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.8 mmol) and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (1.6 mmol) co-dissolved solution at room temperature. The pH of the solution was then adjusted to 9 by  $\text{NH}_3 \cdot \text{H}_2\text{O}$ . After then, the solution was firstly heated up to 65 °C and kept for 90 min, following stand at 80 °C for another 30 min, and then cooled to room temperature. The desired product was obtained by means of centrifugation with following drying at 60 °C for 24 h. CFOH was prepared by the same procedure without the addition of MHP. NCFOH and CFOH were further calcined at 500 °C to form NCFO and CFO, respectively. The pathway of NCFOH preparation is given in Scheme 1.

### 2.4. Characterization

$^1\text{H}$  nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR, FTNMR digital), FT-IR (Vertex70 Bruker, Germany) and UV–Vis spectroscopy (Lambda 35, Perkin Elmer, USA) was employed to determine the composition and chemical structure of a hyperbranched polymer. Crystal phase identifications of NCFOH, CFOH and CFO were

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