



# Lactoferrin-assisted synthesis of zinc ferrite nanocrystal: Its magnetic performance and photocatalytic activity



Xinqing Wang<sup>a, b</sup>, Lin Chen<sup>b</sup>, Qingbo Fan<sup>a, b</sup>, Jiangxia Fan<sup>a, b</sup>, Guangliang Xu<sup>b</sup>,  
Minhao Yan<sup>a</sup>, Mark J. Henderson<sup>c</sup>, Jeremie Courtois<sup>a</sup>, Kun Xiong<sup>a, \*</sup>

<sup>a</sup> State Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, Southwest University of Science and Technology, Mianyang 621010, PR China

<sup>b</sup> School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, PR China

<sup>c</sup> Key Subject Laboratory of National Defense for Radioactive Waste and Environmental Safety, Southwest University of Science and Technology, Mianyang 621010, PR China

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## ABSTRACT

Lactoferrin (LF) was used to assist the synthesis of zinc ferrite ( $\text{ZnFe}_2\text{O}_4$ , ZFO) semiconductor photocatalysts in this study, and superparamagnetic ZFO nanocrystals with an average crystallite size ranging from 11.3 nm to 20.1 nm were successfully obtained via the hydrothermal method. It was found that LF was conducive to fast formation of ZFO nuclei, which resulted in remarkable crystallinity enhancement of the as-prepared ZFO nanocrystals. The saturation magnetization ( $M_s$ ) of the as-prepared ZFO crystals would be greatly improved with increasing the LF content, and the  $M_s$  of the as-prepared ZFO crystals synthesized with 50 mg of LF (ZFO-50LF) could reach 19.9 emu/g, whereas the  $M_s$  of the as-prepared ZFO crystals synthesized in the absence of LF (ZFO-0LF) was only 8.8 emu/g. In addition, although the specific surface area of ZFO-0LF nanocrystals (127.2  $\text{m}^2/\text{g}$ ) was larger than that of ZFO-50LF nanocrystals (101.6  $\text{m}^2/\text{g}$ ), and ZFO-0LF exhibited a higher absorption of methyl orange (MO) molecules in contrast with ZFO-50LF, but ZFO-50LF possessed a larger optical absorption coefficient, smaller band gap and higher photocatalytic degradation efficiency per unit area. After being irradiated under UV light for 3 h, ZFO-50LF almost could make MO molecules completely degrade. Therefore, the LF-assisted synthesized ZFO nanocrystals have a promising application prospect to be used as a new high-efficiency recyclable photocatalyst.

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## 1. Introduction

With the rapid developments of industry, the human living environment is suffering from damage, especially for water resources, which is also contaminated by various dyes and organic pollutants [1–3]. It is well accepted that majorities of organic compounds, such as the phenolic compounds, are quite stable and capable of existing in the environment for a long time. More importantly, most of them are toxic and carcinogenic [4]. Photocatalysis has been considered as an environmentally friendly way to effectively decompose organic pollutants, so the preparation of photocatalysts has received increased attention [5–9].

Besides its photocatalytic ability, there is a growing interest in zinc ferrite ( $\text{ZnFe}_2\text{O}_4$ , ZFO) nanocrystals due to its superparamagnetism [10,11]. Furthermore, it is proved that ZFO nanocrystals have shown great potential to be used as a recyclable photocatalyst [12–16]. However, the magnetic performance of the currently available ZFO nanocrystals remains insufficient, which can greatly affect its recovery efficiency. In addition, the photocatalytic efficiency of ZFO nanocrystals is still not acceptable. In order to solve these problems, various physicochemical methods to control the synthesis of uniform ZFO nanocrystals have been extensively investigated [17–24]. However, in most cases, they required handling of a large amount of organic salts, toxic solvents, or surfactants, which would cause secondary environmental pollution. Therefore, it is necessary to find a pollution-free approach to synthesize high quality ZFO nanocrystals.

Inspired by the biomineralization process of living organisms,

\* Corresponding author.

E-mail address: [quentin\\_xiong@swust.edu.cn](mailto:quentin_xiong@swust.edu.cn) (K. Xiong).

the biomimetic route for the preparation of inorganic nanocrystals has become increasingly popular [25]. The Zn-substituted magnetite nanocrystals with a size ranging from 8.3 to 16.1 nm shows excellent magnetic properties, which are produced through the reduction of Fe(III) compounds containing Zn(II) by the iron reducing bacterium *Geobacter sulfurreducens* [26]. In recent years, more attention has been paid to magnetotactic bacteria [27,28], which is due to the presence of the magnetosome, an organelle made of a lipid vesicle loaded with a single magnetite or greigite crystal about 50 nm in size. However, the complicated bacterial culture process and its high preparation cost will limit its extensive applications.

Lactoferrin (LF) belongs to the transferrin protein family, and it consists of a single polypeptide chain folded into two symmetrical highly homologous lobes (N and C lobes). Each lobe can bind metal ions (such as  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$ ) in synergy with the carbonate ions [29,30]. Moreover, LF has a great iron-binding affinity and it can remain bound to this metal over a wide pH range, including at extremely acidic pH [31]. No study about LF-assisted synthesis of ZFO could be found. In this study, LF is used for controlling the preparation of ZFO under hydrothermal conditions in order to represent geological environment. As reported, the empty protein cages of ferritin are found to be capable of effectively constraining the size of iron oxides [32], therefore, we suggest the N-lobes and C-lobes of LF also have similar effect as the empty protein cages of ferritin. The magnetic performance and photocatalytic activity of modified ZFO is presented in detail.

## 2. Experimental

### 2.1. Preparation of ZFO nanocrystals

In this study, zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Sigma–Aldrich) and iron (III) nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Sigma–Aldrich) were used as the sources of Zn and Fe, respectively. Afterwards,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were completely dissolved in 20 mL deionized water, corresponding to a final concentration of 20 mM and 40 mM. For controlling the synthesis of ZFO nanocrystals, different amounts of LF (10 mg, 30 mg, 40 mg and 50 mg), which were produced from bovine milk (Sigma–Aldrich), were added into the mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  with constantly stirring, and the sample without LF was considered as the control group. Meanwhile, ammonia solution (25 wt%) was added to a mixture dropwise with vigorous stirring, and a well dispersed brown emulsion (pH = 10) formed. Subsequently, the brown emulsion was transferred into a 100 mL Teflon autoclave, sealed, and then heated at 170 °C for 6 h. Finally, the brown precipitates were collected for testing.

### 2.2. Characterization of the samples

The phase composition of samples were tested by X-ray diffractometer (XRD, X'Pert PRO, PANalytical, the Netherlands) using a CuK $\alpha$  source ( $\lambda = 1.5406 \text{ \AA}$ ), and their components were ascertained by comparing the diffraction patterns with Joint Committee on Powder Diffraction Standards (JCPDS) cards, respectively. In addition, the size and the morphology of samples were observed by using the high-resolution transmission electron microscope (HRTEM, LIBRA 200FE, ZEISS, Germany) equipped with an energy dispersive X-ray spectrometer (EDS, IETEM100, Oxford, Britain), operated at an acceleration voltage of 10 kV. The magnetic hysteresis (*M-H*) loops of the samples were investigated by vibrating sample magnetometer (VSM, BKT-4500Z, China). The specific surface areas of samples were tested by the Brunauer–Emmett–Teller (BET) method using a Quantachrome NOVA 3000 Analyzer.

### 2.3. Photocatalytic activity measurement

The photodegradation activities of samples were evaluated by measuring the degradation of methyl orange (MO, Sigma–Aldrich) in aqueous solution under UV-light (365 nm). The UV-light source was a 175 W high pressure mercury lamp. Typically, 300 mL of an aqueous solution of MO (20 mg/L) containing 150 mg of the catalyst sample was firstly ultrasonically dispersed in a quartz beaker for 10 min. Before the irradiation, the above suspension was vigorously stirred for 30 min in the dark to reach absorption–desorption equilibrium, and then MO solution was replenished in order to keep its initial concentration in 20 mg/L. The MO solution without the addition of photocatalyst was considered as the control group. Afterwards, the suspensions were irradiated under UV-light, and 9 mL of the suspensions were collected at predetermined intervals. The solid residue was removed from the collected suspension by a magnet, subsequently, centrifuged at 12000 rpm for 5 min to obtain the supernatant liquid. The concentration of MO molecules in the supernatant liquid was determined by absorbance at 464 nm in UV–vis absorption spectrum (UV-3150, Shimadzu, Japan), and UV–vis diffuse reflection measurement was also carried out by using this equipment.

### 2.4. Statistical analysis

Quantitative data were presented as mean  $\pm$  standard deviation, and statistical analyses were performed using a one-way analysis of variance (one-way ANOVA). A comparison between the two means was made using the turkey's test, with statistical significance set at  $P < 0.05$ .

## 3. Results and discussions

As shown in Fig. 1, whether LF is added into the reactant or not, no second phase is detected, and all the diffraction peaks are in good agreement with those of cubic structured ZFO (JCPDS card no. 00-022-1012), but the intensity of the main diffraction peak (along the (311) direction) can be significantly enhanced where LF is a co-reactant, which suggests LF is capable of improving the crystallinity of ZFO. According to the results estimated from the Scherrer formula, the average crystallite size of ZFO along the (311) direction ( $D_{311}$ ) has a slight fluctuation versus the addition of LF. In the absence of LF, the  $D_{311}$  of the as-prepared ZFO crystals is 15.3 nm (ZFO-0LF listed in Table 1). As 10 mg of LF are added, the  $D_{311}$  of the as-prepared ZFO crystals increases to 20.1 nm (ZFO-10LF listed in Table 1), whereas it decreases to 11.3 nm for 30 mg addition of LF (ZFO-30LF listed in Table 1). Nevertheless, on increasing LF to 40 mg, the  $D_{311}$  of the as-prepared ZFO crystals will raise to 15.3 nm (ZFO-40LF listed in Table 1), and it almost has no change for 50 mg addition of LF (ZFO-50LF listed in Table 1).

Commonly, the thermal stability of LF depends on its binding Fe, which results in a change in the molecular conformation of LF. When iron(III) ions ( $\text{Fe}^{3+}$ ) enter into the open interdomain cleft in each N-lobes or C-lobes, it will lead to a more compact structure of LF, so iron-free LF (apo-LF) usually shows lower thermal stability than the iron-saturated LF (holo-LF) [33]. Bokkhim [34] et al., found that holo-LF in aqueous solution had a thermal denaturation temperature of  $91 \pm 0.5 \text{ }^\circ\text{C}$ , but the denaturation temperature of apo-LF is only  $71 \pm 0.2 \text{ }^\circ\text{C}$ . As reported by Ueno [35] et al., holo-LF can maintain its structure stable at 120 °C when presence of soluble soybean polysaccharide. From the above, whether apo-LF or holo-LF, once the heating temperature exceeds 120 °C, its peptide chain will be broken. Accordingly, the structure of LF should be destroyed when they were heated at 170 °C for 2 h. But actually, the nucleation of ZFO has already begun when the reaction

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