Technical Note

Efficient degradation of crystal violet in magnetic CuFe$_2$O$_4$ aqueous solution coupled with microwave radiation

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HIGHLIGHTS

▶ 90% of crystal violet could be fast degraded in 90 s with copper ferrite.
▶ Two pathways for the variant of surface Fe/Cu are proposed.
▶ Important microwave absorption and non-thermal effects in degradation.
▶ Microwave induced holes are attributed to the efficient degradation.

ARTICLE INFO

ABSTRACT

Nanoscale copper ferrite was prepared by co-precipitation method, while citrate acid assisted method was used as reference. Microwave-induced degradation of crystal violet was performed with synthesized copper ferrite, and the behavior of copper ferrite in this process was studied by X-ray photoelectron spectroscopy, SEM/EDS and vector network analyzer. Microwave radiation could greatly enhance the activity of copper ferrite in organic oxidation. The variant of copper and iron on the surface and in the inner core of copper ferrite was studied here. Copper ferrite presents relatively low dielectric loss. Meanwhile, microwave radiation makes a faster degradation than conventional heating process, indicating an indispensable non-thermal effect of microwave with copper ferrite in the process. Microwave induced holes could be responsible for the efficient degradation. The effect of annealing on crystallization and degradation process was considered here, and the intermediates and products were studied by GC–MS and LC–MS to provide a comprehensively evaluation of degradation.

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1. Introduction

Microwave-induced reaction is very attractive in chemical application for its high activity, especially coupled with appropriate microwave absorbent (de la Hoz et al., 2005). This process has promising potential for the efficient degradation of refractory biodegradable organic pollutants. The effects of microwave in this process can be concluded in two major ways (Horikoshi et al., 2003). First, solid material placed in microwave field with greater dielectric/magnetic loss than solvent can form micro/nanoscale 'hot spots' and activate the reaction on surface of material (thermal factor). Secondly, the electromagnetic field of microwave increases the probable contact between molecules and atoms of the reacting substrates, which sometimes considered as pre-exponential factor

changing in the Arrhenius equation (Binner et al., 1995). We can conclude all the explanations without heat energy involved directly as non-thermal factor.

Ferrite, which derived from iron oxides, has attracted great interest for its strong absorption ability of microwave. Ferrites have been used as absorbing walls for radio waves (Naito and Suetake, 1971). Recently, Chen et al. (2010) provided a new method to produce ferrites from industrial wastes, which made it more suitable for application. Nanoscale ferrites are also used as microwave absorption fillers (Peng et al., 2004). However, the performance of nanoscale ferrites in microwave-induced degradation process is still needed further research. Copper ferrite is one of the most common ferrites studied, and copper ferrite nanopowder has been studied as a catalyst in organic synthesis (Liu et al., 2009; Liu and Fu, 2010). It has also been used in pollution control as thermal decomposition material for regeneration (Zhang et al., 2007). In this work, nanoscale copper ferrite was chosen here as representative ferrite with crystal violet (CV) as target compound to investigate the behavior of ferrites in microwave-induced degradation of CV.

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2. Material and methods

2.1. Preparation of CuFe₂O₄

Copper ferrite ($CuFe_2O_4$) nanoparticles were prepared by co-precipitation method (Tao et al., 2000), and the sol–gel combustion method based on citrate acid complexation (Tanaka et al., 2005a,b; Faungnawakij et al., 2008) was also applied for comparison. The details for the methods of preparation and characterization are provided in Supplementary Material (SM). The reagents and material used are also listed in SM.

2.2. Microwave-induced reaction experiment

The microwave device refitted from domestic microwave oven was supplied by Huiyan Microwave System Engineering (Nanjing, Jiangsu, China). More details about the device were provided in our previous study (He et al., 2010). Relative temperature variance during reaction was recorded in Fig. SM-1.

Fifty mililiter of CV solution was set in the microwave device, after 30 min continuous stirring in the dark at room temperature for ensuring adsorption/desorption equilibrium. If no specific instructions are given, the concentration of $CuFe_2O_4$ was $1\,g\,L^{-1}$, and the initial concentration of CV was 0.049 mM (initial pH 9). 10 mL of sample was withdrawn and separated magnetically to remove $CuFe_2O_4$ before analysis. As a reference, common heating degradation experiment was also carried out in a Wolff bottle connecting with a thermocouple and a reflux condenser. Before experiment, CV solution was pre-heated and kept at a uniform temperature with boiling water in an electric-heated thermostatic water bath. The other conditions are the same as that in microwave-induced reaction experiment.

A modified method was used here to detect hydroxyl radicals in the processes, where salicylic acid was used as molecular probe. Sodium oxalate and benzoquinone were used as hole-scavenger and O_2^--scavenger to investigate the effect of microwave-induced holes or superoxide radicals. The messages about analytical methods are provided in SM.

3. Results and discussion

3.1. Characterization

3.1.1. XRD

XRD patterns of $CuFe_2O_4$ spinel are shown in Fig. 1. The commercial $CuFe_2O_4$ shows a great crystallinity. The peak of CuO could be found in both the as-prepared sample and 673 K annealing sample. However, compared to the as-prepared sample, the sample annealed at 673 K shows similar pattern with the sample purchased, which identified as cubic phase, while copper oxide (JCPDS 44-0706) is also included. When annealing temperature rises to 1073 K, the cubic phase begins to transform to tetragonal phase (Selvan et al., 2003), and the sample annealed at 1173 K presents similar spectrum with the sample prepared by citrate acid complexation method, which is supposed to be totally tetragonal phase with great crystallinity (Faungnawakij et al., 2009). The sample annealed at 873 K should be viewed as the mixture of cubic phase and non-ignorable CuO/α-Fe$_2$O$_3$ (JCPDS 33-0664). According to Scherrer Formula, the patterns in inlet (Fig. 1) indicate that the grain size produced by co-precipitation method is smaller than that by citrate acid complexation method.

3.1.2. Morphology

The morphology of the samples was observed by both TEM and SEM. These images were presented in Fig. SM-2, where the particle
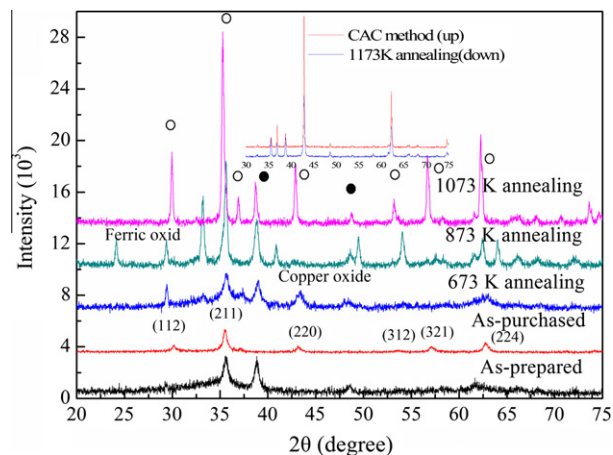

Fig. 1. XRD patterns of the sample as purchased and samples prepared by co-precipitation method: samples as-prepared and annealing in air at three different temperatures (○ for cubic phase and ● for tetragonal phase). The inlet presents curves of samples: prepared by citrate acid complexation (CAC) method and prepared by co-precipitation method (annealed at 1173 K).

sizes could be measured. The sizes of the particle annealed at 673 K are between 10 and 20 nm from Image a in Fig. SM-2, and higher annealing temperatures (873 and 1073 K) lead to aggregation. The sample annealed at 873 K (Image b in Fig. SM-2) involves large particles with irregular outline (ranging from 50 to 100 nm), and smaller rot-like sub-nanoparticles, while the sample annealed at 1073 K (Image c in Fig. SM-2) has a broader dispersity from several tens to several hundreds of nm. Totally speaking, raising annealing temperature leads to fast growth of particles.

If no specific illustration is given, the sample prepared by co-precipitation method and then annealed at 1073 K was chosen for degradation experiment.

3.1.3. Hysteresis measurements

Fig. SM-3 shows magnetic characterization of the nanoparticles. Copper ferrite annealed at 1073 K has a specific saturation magnetization of $36.7\,emu\,g^{-1}$. The synthetic sample is a type of soft magnetic material with small coercivity, which is suitable for recovery. Increasing annealing temperature could form stronger magnetism.

3.1.4. Infrared spectra

The surface groups of copper ferrite annealed at 1073 K are shown in Fig. SM-4. The broad peak from 3000 to 3700 cm^{-1} is in accordance with hydrogen-bond in OH groups. In aqueous solution, these polar groups are covered by water molecules, keeping organics from approaching. The annealed sample with smaller peak indicates that weak polar surface forms after annealing, which accelerates the mass transfer of organic pollutant during degradation. The sample after degradation experiment presents smaller absorption than the one before use. It implies copper ferrite connecting with surface hydroxyl group, is partly reduced during the degradation. The two peaks at ca 1380 and 1639 cm^{-1} correspond with symmetric stretching vibration and asymmetric stretching vibration of N–O in NO_3^{3-} respectively. Annealing cannot fully remove NO^{3-} on surface, for its short annealing time, however it can be removed in microwave-induced degradation process. The peaks with wavenumbers below 800 cm^{-1} relate with metal oxide or ferrite.

3.1.5. Complex electromagnetic parameters

Complex electromagnetic parameters (ε', ε'', μ', μ'', the real part and the imaginary part of permittivity ε and permeability μ) of the