The structure of copper ferrite prepared by five methods and its catalytic activity on lignin oxidative degradation

Zhihui Ye, Zaixing Deng, Lin Zhang, Jienan Chen, Guiwu Wang and Zhiping Wu

School of Materials Science and Engineering, Central South University of Forestry and Technology, Changsha 410004, People’s Republic of China

E-mail: wuzhiping02@163.com

Keywords: Lignin, Copper ferrite, Preparation methods, Oxidative degradation

Abstract

Effects of copper ferrites with different prepared methods on the catalytic degradation of lignin with hydrogen peroxide as oxidant is studied. The microstructure, spectral properties and magnetic properties of copper ferrites prepared with five methods were characterized. The results showed that the microcosmic appearance of the catalysts prepared by the five methods was nanoparticles or irregular blocks. All the samples have strong magnetic properties. However the magnetic saturation intensity, residual magnetic intensity and coercivity of copper ferrite prepared by different methods are distinct. The degradation rate and the content of benzene-ring substances were the highest when lignin decomposed under the catalyst of copper ferrite prepared by ethylene glycol assisted sol-gel process, while the content of open-ring substances was the highest when lignin decomposed under the catalyst of copper ferrite made by co-precipitation. Compared with Fenton catalyst, The copper ferrite catalyst easily be separated and good repetitive catalytic performance when used in the lignin degradation. In addition, the crystal structure of copper ferrite play an important role on the catalytic degradation properties of lignin.

1. Introduction

Lignin, as the second most abundant aromatic compound resource in the world, has attracted extensive attention from academia and industry [1]. However its utilization rate is low owing to its complex structure, no more than 2% of lignin was used for commercial products and the rest is burned for heat and power, which lead to the waste of resource and endanger of environment. Degradation of lignin into high-value aromatic chemicals is an effective way to valorize lignin [2]. The degradation methods of lignin are mainly divided into oxidation and catalytic hydrogenation [8]. The reaction conditions of lignin catalytic hydrogenation are harsh, especially most of the catalysts are precious metal catalysts, which are expensive and difficult to recover.

Oxidation degradation of lignin is performed by oxidants under certain conditions [9]. Oxidants used for lignin degradation mainly include hydrogen peroxide, oxygen, potassium permanganate and so on [10]. The treatment of lignin with hydrogen peroxide can break the β-O-4 ether bond under alkaline condition, which leads to the oxidative degradation of lignin [11].
2. Materials and methods

2.1. Materials
Lignin was obtained from Fuchen (Tianjin, China) Chemical Reagents Co., Ltd, Cu(NO3)2·3H2O, Fe(NO3)3·9H2O, NaOH, Cu(CH3COO)2·H2O, NH3·H2O, ethylene glycol, ethanol, HCl and CuCl2·2H2O were analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd, (Shanghai, China).

2.2. Preparation of copper ferrite

2.2.1. Co-precipitation
Cu(NO3)2·3H2O (0.01 mol) and Fe(NO3)3·9H2O (0.02 mol) was dissolved in 100 ml deionized water. The NaOH (4 mol L⁻¹) solution was added dropwise to adjust pH value (9 ~ 10) under magnetic stirring and continued stirring for 30 min. The solid was separated from water and dried at 80°C. The filter residue was calcined at 600°C for 2 h.

2.2.2. Cu(CH3COO)2 co-precipitation
Cu(CH3COO)2·H2O (0.01 mol) and Fe(NO3)3·9H2O (0.02 mol) was dissolved in 100 ml deionized water. NH3·H2O (28%) solution was used to adjust pH till the viscous substance generated. The water was evaporated in a water bath at 80°C. The residue was calcined at 850°C for 3 h.

2.2.3. Hydrothermal process
Cu(NO3)2·3H2O (0.01 mol) and Fe(NO3)3·9H2O (0.02 mmol) was added into 150 ml ethylene glycol and dissolved under magnetic stirring at room temperature. The pH was adjusted to around 10 by adding NaOH (4 mol L⁻¹) solution, the reaction was performed at 180°C for 24 h in the hydrothermal reactor, with mechanical stirring. And the copper ferrite particles were centrifuged and washed with deionized water for 5 times and dried at 60°C.

2.2.4. Ethylene glycol assisted sol-gel process
Cu(NO3)2·3H2O (0.01 mol) and Fe(NO3)3·9H2O (0.02 mol) was dissolved with 40 ml ethylene glycol in a round bottom flask. The flask was placed in a water bath at 80°C for 4 h and reddish brown sol was generated. Brown dry gel was obtained by drying reddish brown sol at 120°C for 8 h and fully ground. The powder was dried in a muffle furnace at 400°C for 1.5 h to remove organic compounds. The precursor was calcined at 800°C for 4 h. The copper ferrite particles were washed by deionized water and ethanol respectively and dried at 80°C for 2 h.

organic solvent lignin. The oxidation degradation of lignin in water conforms to the redistribution mechanism of phenols [12].

There are many oxidative degradation methods for lignin, among which Fenton reagent is the most widely used [13, 14]. However the disadvantage of Fenton catalyst is obvious, such as easy loss of iron ions and environmental pollution. Heterogeneous iron catalyst can make up for the disadvantages [15–17]. A water-soluble heterogeneous catalyst (CuFe2O4@starch) was prepared which has high efficiency and magnetic separation, and can be used to synthesize 1,2,3-triazole in water [18]. Heterogeneous iron catalysts are commonly used in the degradation of dyes. Cobalt ferrite nanoparticles substituted by copper can degrade Congo red more effectively than cobalt ferrite particles under photocatalysis [19]. CuFe2O4 prepared by improved sol-gel method, which did not contain any surfactant and organic solvent, can be applied to degrade methyl orange under ultraviolet photocatalysis [20]. The addition of copper ferrite particles could significantly increase the decomposition of hydrogen peroxide to form hydroxyl radicals, and make the rhodamine B fade and degrade [21]. Copper ferrite particles have good magnetism, which provides a good condition for recovery and reuse of catalysts.

The main methods to prepare copper ferrite are co-precipitation, hydrothermal process, solid reaction process and sol-gel process. Solid reaction process has long reaction time and poor dispersion. The precursors of hydrothermal process is mild and can be used to synthesize 1,2,3-triazole in water [22]. The addition of copper ferrite particles could significantly increase the decomposition of hydrogen peroxide to form hydroxyl radicals, and make the rhodamine B fade and degrade [21]. Copper ferrite particles have good magnetism, which provides a good condition for recovery and reuse of catalysts.

The main methods to prepare copper ferrite are co-precipitation, hydrothermal process, solid reaction process and sol-gel process. Solid reaction process has long reaction time and poor dispersion. The precursors of co-precipitation are difficult to filter. The precursors prepared by sol-gel process tend to cause hard agglomeration and shrinkage after drying. However its crystalline structure is perfect. The reaction condition of hydrothermal process is mild [22–26]. Although the prepared methods of copper ferrite have been reported recently, the systematic study the effect of preparation method on its microstructure and properties have not been reported, especially the application of copper ferrite on the degradation of lignin is scarcely reported.
2.2.5. Solid reaction process
CuCl$_2$$\cdot$2H$_2$O (0.01 mol), Fe(NO$_3$)$_3$$\cdot$9H$_2$O (0.02 mol) and Tween 80 was added into an agate mortar. Solid NaOH was used to raise pH (9 ~ 10) of the system. The mixture was ground for 30 min and washed by ultrasonic with deionized water or ethanol. The residue was calcined at 500 $^\circ$C for 2 h.

2.3. Characterization
X-ray powder diffractometer (XRD) with Cu K$\alpha$ radiation (Panacol Empyrean sharp shadow x-ray diffractometer) was used to identify the crystalline phase. The scanning angle was from 10 – 80° and the scanning speed was 10°/min. Particle morphological feature was imaged by scanning electron microscope (Zeiss Sigma HD). Vibrating sample magnetometer (MPMS XL-7) was used to investigate the particle magnetic property at room temperature with an applied magnetic field of 12 kOe to reach saturation values. X-ray Photoelectron Spectroscopy (EscaLab Xi+) was used to characterize the elemental composition and chemical valence of the catalyst.

2.4. Lignin oxidative degradation by copper ferrites
Puriﬁed lignin (1 g, $m_0$) was added into a ﬂask with 20 ml pH buffer solution ($p$H = 6) and a certain ratio of copper ferrite with hydrogen peroxide. The mixture reacted in a water bath of 80 $^\circ$C for 3 h. After the reaction, the pH of the solution was adjusted to 3 by hydrochloric acid (1 mol l$^{-1}$). After standing for 24 h, the residue and ﬁltrate were separated. The residue was dried, weighted ($m_i$) and the degradation rate ($w$) was calculated, according to equation (1). GC-MS (GCMS-QP2010 SE) was used to analyze the types of lignin degradation products. The HP-5 column was used in this analysis. The initial temperature was 50 $^\circ$C and held for 2 min, then increased to 170 $^\circ$C at 10 $^\circ$C/min, then to 300 $^\circ$C at 10 $^\circ$C/min, and then held for 7 min. Carrier gas was high purity helium gas and flow rate was 1.0 ml min$^{-1}$. The inlet temperature was 270 $^\circ$C. Injection mode was no shunt injection. Ionization mode was EI source and ionization energy was 70 eV. Ion source temperature was 300 $^\circ$C. Scanning mode was select ion scanning (SIM).

$$w = \frac{(m_0 - m_i)}{m_0} \times 100\%$$  \hspace{1cm} (1)

3. Results and discussion

3.1. XRD analysis
Figure 1 shows the XRD of copper ferrite samples prepared by ﬁve methods. It can be seen from ﬁgure 1 that the samples can match the peak positions of the standard graph (PDF#34-0425) of inverted spinel CuFe$_2$O$_4$ and have a low diffraction peak intensity, indicating that the prepared CuFe$_2$O$_4$ has low crystallinity. Strong diffraction peaks appeared in 2 theta angles of 18.3°, 29.9°, 34.7°, 35.8°, 43.7°, 57.8°, 62.1° and 63.6°, corresponding to the Miller index of copper ferrite crystal (101), (112), (103), (211), (220), (321), (224) and (400) respectively. The average particle size of samples was calculated with Jade 6.5 software, as shown in table 1.
Among the copper ferrite samples prepared by five preparation methods, the grain size of the samples prepared by co-precipitation method was the smallest, 15.4 nm, while the grain size of the samples prepared by Cu(CH$_3$COO)$_2$ co-precipitation method was 37.4 nm. It may caused by different treatment methods of the solids obtained from precipitation. The copper ferrites that prepared by Cu(CH$_3$COO)$_2$ co-precipitation method and ethylene glycol assisted sol-gel process method were obtained by evaporation and grinding while the other 3 treatment methods were centrifugal washing. It can be seen from the XRD in figure 1 that the copper ferrite prepared by ethylene glycol assisted sol-gel process and Cu(CH$_3$COO)$_2$ co-precipitation is in the best agreement with the standard card, indicating that the high purity and perfect crystal structure of the catalyst can be obtained by these two methods.

Figure 2 shows the XRD of copper ferrite precursor prepared by four methods except copper ferrite prepared by hydrothermal method owing to its no precursor. The XRD of the precursor could not match the peak of CuFe$_2$O$_4$ standard card (PDF34-0425). Which indicated that CuFe$_2$O$_4$ is not formed in the precursor and can only be formed under long heating or high temperature calcination.

3.2. SEM analysis
The morphology, particle size and dispersion of the copper ferrites were characterized by SEM. The results was shown in figure 3.

It can be seen from figure 3 that all samples showed serious agglomeration. The degree of agglomeration of copper ferrite prepared by hydrothermal process was the highest and that of catalyst prepared by solid reaction process was the lowest. The samples prepared by co-precipitation, solid reaction process and hydrothermal process were particles, while those prepared by Cu(CH$_3$COO)$_2$ co-precipitation and ethylene glycol assisted sol-gel process were irregular blocks. In the latter 2 preparation methods, the precursor and solvent are separated by evaporation and the former three methods are filtered/centrifuged, indicating that the samples morphology is related to the treatment of the precursor before calcining. In addition, the crystal size of the samples obtained by the co-precipitation method is the smallest and that of catalyst prepared by Cu(CH$_3$COO)$_2$ co-precipitation is the largest, which corresponds to the calculated size of XRD analysis.

### Table 1. Average grain sizes of copper ferrite samples prepared by different methods.

| Prepared methods                        | Average particle size (nm) |
|-----------------------------------------|---------------------------|
| Co-precipitation                        | 15.4                      |
| Cu(CH$_3$COO)$_2$ co-precipitation      | 37.4                      |
| Solid reaction process                  | 22.8                      |
| Ethylene glycol assisted sol-gel process| 33.1                      |
| Hydrothermal process                    | 22.9                      |

Figure 2. XRD patterns of copper ferrite precursor prepared by different methods.
3.3. VSM analysis

Figure 4 shows hysteresis loop diagram of copper ferrites prepared by different methods. The magnetic parameters such as saturated magnetic intensity ($M_s$), residual magnetic intensity ($M_r$) and coercivity ($H_c$) are shown in Table 2. The hysteresis loops of the samples prepared by the five methods are of typical ‘S’ type, showing obvious ferrous magnetism. Under the action of external magnetic field, the samples can be easily separated from the solution. However, the magnetic strength of the samples varies with different preparation methods. Among them, the saturated magnetic strength of the samples prepared by hydrothermal method is 51.54 emu g$^{-1}$. The residual magnetic intensity and coercivity of copper ferrite samples prepared by co-precipitation and hydrothermal methods indicated that the samples are superparamagnetic and composed of fine magnetic particles. This may be related to the superfine structure of the catalyst, when the size of particles is below critical value, its crystal structure is no longer a complete ‘normal’ spinel ferrite, and part of the positions of Fe$^{3+}$ and Cu$^{2+}$ are exchanged, so that short-range interactions occur in the crystal, resulting the non-magnetic copper ferrite to magnetism [27].

| Prepared methods                        | $M_s$ (emu/g) | $M_r$ (emu/g) | $H_c$ (Oe) |
|----------------------------------------|--------------|--------------|-----------|
| Co-precipitation                       | 27.35        | 0            | 0         |
| Cu(CH$_3$COO)$_2$ co-precipitation     | 27.37        | 15.28        | 473.35    |
| Solid reaction process                 | 20.93        | 2.03         | 78.37     |
| Ethylene glycol assisted sol-gel process | 33.24      | 17.15        | 473.35    |
| Hydrothermal process                   | 51.54        | 0            | 0         |

3.4. XPS analysis

To better understand the effects of preparation methods on the structure of copper ferrites, the elemental composition and chemical valence of the catalyst were characterized by XPS. Figure 5 a shows the full spectrum of the sample. The figure implied that CuFe$_2$O$_4$ is composed of Cu, Fe, O indicating that the catalysts prepared by the five methods have high purity and C comes from the C reference added in the measurement process. The
XPS of Fe 2p regions can be fitted into six contributions (figure 5(b)). All Fe 2p spectra show the main peak around 710 eV, and the presence of the peak around 710.1, 712.3, 723.9, 725.0 eV and 732.5 eV are confirmed as Fe$^{3+}$ and a small amount of elemental iron (718.0 eV) on the catalyst surface. The presence of 710.1 and 712.3 eV indicates that Fe$^{3+}$ exists in two coordination environments, with higher binding energy at site A and lower binding energy at site B. For the XPS of Cu 2p regions (figure 5(c)), they can be fitted into 5 contributions while the XPS of copper ferrite prepared by ethylene glycol assisted sol-gel process can be fitted into 6 contributions. The characteristic peaks at binding energy of 932.95 and 952.85 eV which are assigned to Cu$^{2+}$ on octahedral sites for the Cu 2p$_{3/2}$ lines and Cu 2p$_{1/2}$ lines respectively. And the minor one at 934.95 eV can be assigned to Cu$^{2+}$ on tetrahedral coordination site. And the remaining peak of copper ferrite prepared by ethylene glycol assisted sol-gel process at 954.25 eV can also be assigned to Cu$^{2+}$ on tetrahedral coordination site.

### 3.5. The catalytic activity of copper ferrite

The prepared copper ferrite was used to catalyze the oxidative degradation of lignin by hydrogen peroxide. The FTIR and $^1$H-NMR characterization of lignin was illustrated in figure S1 and table S1, figure S2 and table S2 respectively is available online at stacks.iop.org/MRX/7/035007/mmedia. The degradation rate was shown in figure 6. After methanol extraction, the degradation products were analyzed by GC-MS. The results of GC-MS was illustrated in figure S3 and table S3.

Hydroxyl free radical can accelerate the degradation of lignin, the role of catalyst on the hydroxyl free radical formation is illustrated in figure S4. It implied from figure 6 that degradation rate of lignin is between 54% and 61%, the degradation rate is highest when lignin catalyzed by copper ferrite prepared by ethylene glycol assisted sol-gel process.

The products of lignin degradation under different catalyst obtained from five methods are distinct. The degradative product can be roughly divided into straight-chain/branched alkane, olefin, single-ring substance and multi-ring substance. Among them, there are 4 kinds of substances contained benzene ring, as shown in table 3. The content of contained benzene ring substances produced by catalytic degradation of lignin with copper ferrite prepared by ethylene glycol assisted sol-gel process is the highest, accounting for 24.43% of the degradation products. Dibutyl phthalate is only present in degradative product of lignin catalyzed by copper ferrite obtained from co-precipitation. The contents of 2,4-Di-tert-butylphenol and 1,3-Di-tert-butylbenzene in degradative products when lignin was catalyzed by copper ferrites obtained from ethylene glycol assisted sol-gel process and Cu(CH$_3$COO)$_2$ co-precipitation were the highest. Therefore, copper ferrite prepared by ethylene glycol assisted sol-gel process is more efficient in catalyzing lignin to produce benzene-containing ring substance.

There are 4 main open ring substances existed the decomposed products of lignin catalyzed by copper ferrite prepared by five methods, the specific contents are shown in table 4. It implied that the content of 13-Docosanamide is considerable, especially for degraded products of lignin by catalyst prepared by co-
precipitation method. Moreover, the total content of 4 kinds open-loop substances in the degradative products of lignin by catalyst prepared by co-precipitation method is the highest.

In order to study the reusability of catalyst, copper ferrite prepared by ethylene glycol assisted sol-gel process was chosen to degrade the lignin. The experimental results showed the recovery of catalyst is 91%–93%. In fifteen trials, the degradation rate of lignin fluctuated between 60%–67% with the constant catalyst dosage through adding new catalyst to compensate the loss (figure 7(a)) The degradation rate present show a slightly downward trend with no new catalyst adding within 6 trials (figure 7(b)), Which indicate the repetitive catalytic performance of the catalyst is satisfied.

4. Conclusions

The differences existed in microstructure and magnetic properties of copper ferrite catalysts prepared by five methods. The smallest particle size of copper ferrite was obtained from co-precipitation method. The catalysts prepared by co-precipitation, hydrothermal and solid reaction methods were particle, while those prepared by the other two methods were irregular blocks. Copper ferrites prepared by hydrothermal method has the highest

![Figure 6. The degradation rate on lignin by H2O2 catalyzed by copper ferrites obtained from different methods. (A-E stand for the copper ferrites prepared by co-precipitation, Cu(CH3COO)2 co-precipitation, hydrothermal process, ethylene glycol assisted sol-gel process and solid reaction process respectively).](image-url)
saturated magnetic intensity, and copper ferrites prepared by co-precipitation and hydrothermal methods are superparamagnetic and composed of fine magnetic particles.

The catalytic properties of copper ferrite catalysts prepared by five methods shows different degradation capacity of lignin with hydrogen peroxide. The catalytic efficiency of copper ferrite catalyst prepared by ethylene glycol assisted sol-gel process was the highest. The degradation rate was 61.76%, and the content of benzene ring substances in the products was the highest, 24.43%. However, the copper-ferrite catalyst prepared by co-precipitation method is more efficient in catalyzing lignin degradation to open-ring substances. It implied that the crystal structure of copper ferrite play an important role on the catalytic degradation properties of lignin. The catalyst is easily separated and possess good repetitive catalytic performance.

Acknowledgments

This work was supported by the National Key R&D Program of China (2017YFD0601004).

Conflict of interest

The authors declared that they have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

ORCID iDs

Zhiping Wu  
https://orcid.org/0000-0001-8022-4837

References

[1] Abdelhamid A M, Solbiati J O and Cann I K O 2013 Insights into lignin degradation and its potential industrial applications—chapter one  *Adv. Appl. Microbio.* **82** 1-28
[2] Deng T S, Lv G Q, Li Y Q, Wang Y X, Jia S Y, Hou X L and Yang Y X 2016 Value-added utilization of the lignin-derived phenol monomer and bioethanol to synthesize ethylphenol and ethyl phenyl ether  *Can. J. Chem. Eng.* **94** 1-7
[3] Prince R C and Stiefel E I 1987 Lignin degradation  *Trends Biochem. Sci.* **12** 334–9
[4] Fisher A B and Fong S S 2014 Lignin biodegradation and industrial implications  *Aims. Environ. Sci.* **1** 92–112
[5] Li J, Yuan H and Yang J 2009 Bacteria and lignin degradation  *Front. Bio. Chem.* **4** 29–38
[6] Dong C J, Shen D K, Hu J, Zhang H Y and Xiao R 2015 The study on the degradation of lignin preparing phenolic compounds by microwave-assisted  *Acta. Energiae Solaris Sinica* **36** 2752–8
[7] Tanahashi M and Higuchi T 1988 Chemical degradation methods for characterization of lignins  *Method Enzymol.* **161** 101–109
[8] Ye Y Y, Zhang Y, Fan J and Chang J 2012 Selective production of 4-ethylphenolics from lignin via mild hydrogenolysis  *Bioresource Technol.* **118** 648–51 (none)
[9] Dai J, Patti A F and Saito K 2016 Recent developments in chemical degradation of lignin: catalytic oxidation and ionic liquids  *Tetrahedron* **74** 4945–51S0040403916312679
[10] Gellerstedt G 1992  *Chemical Degradation Methods: Permanganate Oxidation* (Heidelberg: Springer)
[11] Sun R C, Tomkinson J, Mao F C and Sun F X 2001 Physiochemical characterization of lignins from rice straw by hydrogen peroxide treatment  *J. Appl. Polym. Sci.* **79** 1719–32
[12] Nanayakkara S, Patti A F and Saito K 2014 Chemical depolymerization of lignin involving the redistribution mechanism with phenols and repolymerization of depolymerized products  *Green Chem.* **16** 1897–903
[13] Nanayakkara S, Patti A F and Saito K 2014 Lignin depolymerization with phenol via redistribution mechanism in ionic liquids \textit{Acs. Sustain Chem. Eng.} \textbf{2} 2159–64

[14] Huang X Q, Feng B M, Niu Y L, Zhao L and Hu W H 2018 Fenton-reaction-derived Fe/N-doped graphene with encapsulated Fe$_3$C nanoparticles for efficient photo-Fenton catalysis \textit{Catal. Lett.} \textbf{148} 2528–36

[15] Parkhomchuk E V, García-Aguilar J, Sashkina K A, Berenguer-Murcia A, Cazorla-Amoros D, Dralyuk R I, Shestakova D O, Ayupov A R, Danilova I G and Parmon V N 2018 Ferrosilicate-based heterogeneous Fenton catalysts: influence of crystallinity, porosity, and iron speciation \textit{Catal. Lett.} \textbf{148} 3134–46

[16] Chen D Y, Zeng D C and Liu Z W 2016 Synthesis, structure, morphology evolution and magnetic properties of single domain strontium hexaferrite particles \textit{Mater. Res. Express} \textbf{3} 045002

[17] Priya R, Stanly S, Anuradha R and Sagadevan S 2019 Evaluation of photocatalytic activity of copper ferrite nanoparticles \textit{Mater. Res. Express} \textbf{6} 095014

[18] Wang W, He Q, Xiao K and Zhu I 2018 Electrostatic self-assembly of Fe$_3$O$_4$/Go nanocomposites and their application as an efficient fenton-like catalyst for degradation of rhodamine b \textit{Mater. Res. Express} \textbf{5} 035510

[19] Kirankumar V S, Hardik B and Sumathi S 2017 Photocatalytic degradation of congo red using copper substituted cobalt ferrite \textit{Adv. Mater. Sci. Eng.} \textbf{263} 022027

[20] Vosoughifar M 2016 Preparation and application of copper ferrite nanoparticles for degradation of methyl orange \textit{J. Mater Sci-Mater El.} \textbf{27} 10449–55

[21] Flores A, Nespias K, Vitale P, Tasca J, Lavat A, Eyler N and Canizoz A 2014 Heterogeneous photocatalytic discoloration/degradation of rhodamine B with H$_2$O$_2$ and spinel copper ferrite magnetic nanoparticles \textit{Aust. J. Chem.} \textbf{67} 609

[22] Song Y L 2008 Hydrothermal synthesis and adsorption catalysis of copper ferrite nanoparticles \textit{Doctoral dissertation} Southwest University of Science and Technology

[23] Fu J, Shen Y, Cheng G W and Deng Y Q 2011 Preparation and catalytic properties of spinel CuFe$_2$O$_4$ under visible light irradiation \textit{J. Dalian Jiaotong Univ.} \textbf{32} 101–4

[24] Hua L and He Y R 2015 Preparation of CuFe$_2$O$_4$ materials by the hydrothermal method and its electrochemical characteristic researches as anode material for lithium ion battery \textit{J. Huabei Univ. Educ.} \textbf{32} 1–4

[25] Wang B K 2017 Oxidative degradation of methylene blue by copper-ferrite photoassisted fenton system \textit{Doctoral dissertation} Northwest Normal University

[26] Hong W L, Liu J H, Tian D Y, Zhao F Q and Wang F 2003 Synthesis of nanometer-CuFe$_2$O$_4$ and its catalysis on thermal decomposition of RDX. \textit{J. Propul. Technol.} \textbf{24} 560–2

[27] Narentuya S and Moregan T 2009 Preparation and characterization of nano-cadmium ferrite and copper ferrite by combustion \textit{Neimenggu Petrochem. Technol.} \textbf{12} 75–7