Diclofenac degradation based on shape-controlled cuprous oxide nanoparticles prepared by using ionic liquid

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ABSTRACT

Persulfate oxidation technology is widely used in wastewater treatment, but there are still many disadvantages, such as high energy consumption, side reaction and narrow pH applicability. Copper oxides can activate persulfate steadily with higher efficiency. In this paper, a novel preparation method of shape-controlled cuprous oxide (Cu$_2$O) nanoparticles featured with high catalytic performance was explored. It was found that adding ionic liquid 1-butyl-3-methylimidazolium bromide ([BMIM]Br) during preparation of Cu$_2$O can improve the degradation rate of diclofenac (DCF). Cu$_2$O nanoparticles possess good stability in consecutive cycling tests, which was confirmed by X-ray photoelectron spectroscopy. The possible mechanism of Cu$_2$O activating persulfate at different initial pH conditions was discussed based on electron paramagnetic resonance spin-trapping experiment. It was found that DCF was efficiently degraded in the Cu$_2$O/persulfate (PDS) system within a broad pH range from 5 to 11. It proved via a quenching experiment that the activation process of PDS mainly occurs on the surface layer of Cu$_2$O nanoparticles. As a result, shape-controlled Cu$_2$O nanoparticles prepared by ionic liquid are expected to be used for in situ chemical oxidation, which is an effective oxidation processes to degrade DCF remaining in surface water and ground water.

Key words: cuprous oxide nanoparticles, diclofenac, in situ chemical oxidation, ionic liquid, persulfate activation mechanism, water treatment

HIGHLIGHTS

• This study provides a novel preparation method of shape-controlled cuprous oxide (Cu$_2$O) particles featured with high catalytic performance to degrade diclofenac (DCF).
• It overcomes the disadvantages of degradation of organic pollutants by the traditional Fe in situ chemical oxidation system to some extent, such as being unrecyclable and having a narrow application range of pH value.
1. INTRODUCTION

DCF is an anti-inflammatory drug used worldwide. It is distributed in various environmental regions, and especially DCF often appears in freshwater environments. It has potential toxicity to several organisms, such as fish and mussels (Sathishkumara et al. 2020), which make DCF an emerging environmental pollutant. Removal rate of DCF in conventional treatment system is only 30%-70% (Yu & Bi 2019), which has brought about potential hazard to both human beings and the environment. Therefore, it is necessary to find a suitable approach for efficient removal of this pollutant.

In situ chemical oxidation (ISCO) is a technique that introduces chemical oxidants into the subsurface to transform groundwater or soil pollutants into less harmful chemical substances. In recent years, the advantages of persulfate advanced oxidation technology in wastewater treatment have become more and more important (Wang & Wang 2018). Multiple approaches, such as ultraviolet light (Kaur et al. 2020), ultrasound (Monteagudo et al. 2018), heat (Zhao et al. 2014), transition metal ions (Li et al. 2020b) and heterogeneous activators (Xian et al. 2019) have been developed for activating persulfate to produce sulfate radicals. These methods are aimed at breaking peroxide -O-O- bonds in persulfate (including peroxymonosulfate (PMS) or peroxydisulfate (PDS)) to form sulfate (SO$_4^{2-}$) radicals and reactive oxygen species (ROS), such as hydroxyl (·OH) and superoxide (O$_2$·) radicals with high redox ability. ROS can degrade and mineralize organic pollutants into harmless compounds (Matzek & Carter 2016). But there are still some key problems that need to be solved urgently. It was found that activation methods represented by thermal activation and light activation are all carried out by external high consuming energy, which is not adapting to large-scale wastewater treatment. Although transition metal ions are more effective for activating persulfate, there are still many problems. Fe$^{2+}$ can activate persulfate without additional energy. However, side reactions usually occur in the process of activating persulfate, causing an unsatisfactory effect on the degradation of organics. The pH conditions of Fe$^{2+}$ activated persulfate are around 3 which further restrict its application. Liu et al. (2012) reported the degradation results of propachlor using Cu$^{2+}$ and Fe$^{2+}$ activated persulfate. The different degradation kinetics and mechanism between two activation systems were studied. Compared with Fe$^{2+}$, Cu$^{2+}$ activated persulfate reveals a longer lasting degradation effect, and shows a proportional greater degradation promotion effect with increasing Cu$^{2+}$ concentration. As a result, more and more scholars have paid attention to copper catalysts.

Copper catalyst is a suitable heterogeneous activator for activating persulfate because of its low energy input, low cost of pH regulation and high treatment efficiency under neutral conditions. There have been two different mechanisms proposed recently. Li et al. (2020a) introduced the cuprous oxide (Cu$_2$O) activating peroxymonosulfate (PMS) to decompose organic pollutants. It was shown that exospheric interactions of Cu$_2$O cause the activation of PMS with a higher oxidation capacity to organic pollutants. Furthermore, chemical quenching tests, electron paramagnetic resonance (EPR), solvent exchange and selective oxidation experiments were carried out. It was indicated that Cu$_2$O catalyzing PMS cannot produce free radicals
or singlet oxygen. However, Zhang et al. (2017) synthesized a new type of iron-coupled copper oxide (Fe$_2$O$_3$@Cu$_2$O) catalyst and used it to activate persulfate (PS) for degrading acetaminophen (APAP). By adding methanol and tert-butyl alcohol as free radical trapping agents, it was determined that SO$_4$·/CO$_3$ free radicals were the main free radical species produced in the oxidation process. During the reaction, Cu(I) reacts with Fe(III) to form Fe(II). Fe(II) is the most active phase of PS activation. It should be noted that zero-valent iron (ZVI), pyrite, iron oxides and ferrous ions, especially iron are effective persulfate activators that promote the production of free radicals. In Zhang’s et al. (2017) reaction system, the activation mechanism of Fe$_2$O$_3$@Cu$_2$O/PS is affected by iron species. Therefore, the mechanism of cuprous activated persulfate process still remains controversial.

Room temperature ionic liquid is generally composed of specific organic cations with relatively large volumes and inorganic anions with relatively small volumes (Clare et al. 2010). The structural asymmetry of ionic liquid leads to a series of unique physical and chemical properties. For example, compared with traditional molecular organic solvents, ionic liquid has the characteristics of low vapor pressure, good thermal stability, high ionic conductivity, wide electrochemical window and good solubility, which make ionic liquid suitable for inorganic or organic synthesis reactions. Huang et al. (2020) reported that the catalytic ability of copper oxide depended on not only the dimension, but also on crystalline factors, such as the exposed facets when degrading 2,4-dichlorophenol by Ultrafast O$_2$ activation using copper oxide. Dou et al. (2021) constructed novel 3D nanoflower-like BiOI/Bi$_2$SiO$_5$ heterojunctions using ionic liquid 1-butyl-3-methylimidazolium iodide ([PrMIm]I) that served as a reactant and a soft template. The results showed that the product holds high photocatalytic performance toward abatement of methyl orange (MO), phenol and Cr(VI) under sunlight irradiation. The addition of ionic liquid enlarges the specific surface area, effectively separates photogenerated charge pairs, and constructs step-scheme heterojunctions. Therefore, ionic liquid is a proper template to synthesize well-organized structures for enhancing catalytic performance.

Li et al. (2020a) synthesized different morphologies of Cu$_2$O, including cubic, octahedral and rhombic dodecahedral under different conditions. In this paper, shape-controlled Cu$_2$O nanoparticles with different morphologies were simply prepared based on ionic liquid. The persulfate activation efficiency of resulted Cu$_2$O nanoparticles used for DCF degradation was determined using different approaches. The effects of different pH conditions on the degradation of DCF by Cu$_2$O nanoparticles activated persulfate were also evaluated. Broadening the pH range in homogeneous phase conditions and widening applications of persulfate in the environmental field were also carried out.

2. MATERIALS AND METHODS

2.1. Reagents and chemicals

Diclofenac sodium and sodium persulfate (PDS) were obtained from Macklin Co., Ltd (Shanghai, China). 1-Methylimidazole, bromobutane, methanol, tert-butanol and phenol were supplied by Aladdin Chemistry Co., Ltd (Shanghai, China). D-(-)-Glucose, CuCl$_2$·2H$_2$O and NaOH were purchased from Sinopharm Group Chemical Reagent Limited Company (Shanghai, China). All the above chemicals were of analytical reagent grade and used without further purification. All the solutions were prepared with deionized water.

2.2. Preparation of [BMIM]Br

Ionic liquid [BMIM]Br was prepared and purified according to the literature (Rivera-Rubero & Baldelli 2006). 1-Methylimidazole 1 mmol with 1-bromobutane 1.5 mmol was added with stirring and refluxing under nitrogen protection at 80 °C for 12 hours. Then, the product was purified by liquid–liquid extraction using ethyl acetate. Subsequently, the product was dried under vacuum at 60 °C for 24 hours.

2.3. Preparation of Cu$_2$O nanoparticles

Cu$_2$O was obtained according to a chemical precipitation method assisted by ionic liquid procedure described in Qi’s et al. (2017) paper. Firstly, CuCl$_2$·2H$_2$O 1.5 mmol was dissolved in 40 ml deionized water. Then different concentrations of [BMIM]Br (0.4 wt.%, 0.6 wt.%, 0.8 wt.%) were added to the CuCl$_2$ solution under continuous stirring for 10 min. Secondly, D-(-)-glucose 0.1 g was added to the obtained mixture, the mixture was heated to 80 °C. Thirdly, NaOH aqueous solution (0.5 mol·L$^{-1}$) 10 ml was mixed to above-mentioned solution, keeping heating at 80 °C in a water bath and stirring for 15 min. The mixture was then cooled down to room temperature, separated by centrifugation and rinsed with ethanol several times. Finally, the sample was dried in a vacuum oven at 50 °C for 8 h.
2.4. DCF degradation by Cu$_2$O nanoparticles catalyzed PDS oxidation

The catalytic degradation of DCF by Cu$_2$O nanoparticles catalyzing the persulfate oxidation system was carried out in a 150 ml glass batch reactor with constant stirring. DCF 1 mg was dissolved in deionized water 100 ml with PDS 20 mg and Cu$_2$O 0.1 g. At a certain time (every 1 h), 1 ml of the solution was sampled and filtered through a 0.45 $\mu$m membrane to remove the solid catalyst. After that, the filtrate was transferred into a sample bottle that contained 0.1 mL MeOH to quench residual PDS. The initial pH was adjusted by using 0.1 M HCl or 0.1 M NaOH before adding Cu$_2$O and PDS. Other operating steps were the same as the experiments of Cu$_2$O nanoparticles catalyzed PDS oxidation. At the end of each experiment, the insoluble nanoparticles were separated by centrifuge, washed with deionized water and dried thoroughly, then directly used in the next round of experiments under the same conditions. All the degradation experiments were conducted in triplicate.

The degradation efficiency of DCF was calculated according to the following formula:

\[
\text{degradation efficiency (\%) = } \frac{C_0 - C_t}{C_0} \times 100
\]  

(1)

where $C_0$ is the initial concentration of DCF, mg/L; $C_t$ is the concentration at t minutes after the degradation, mg/L.

The pseudo-first order kinetic model used in advanced oxidation processes was applied to explore the kinetics of the degradation of DCF in the Cu$_2$O/PDS system. Pseudo-first-order kinetic model equation is following:

\[
\ln\left(\frac{C_t}{C_0}\right) = -kt
\]

(2)

where $k$ is the pseudo-first-order kinetic rate constant of DCF degradation (min$^{-1}$). $C_0$ is the initial concentration of DCF, mg/L; $C_t$ is the concentration at t minutes after the degradation, mg/L.

2.5. Characterization

The composition and purity of [BMIM]Br was detected by $^1$H NMR spectroscopy (Advance-400 MHz, Bruker, German). The crystalline properties of shape-controlled Cu$_2$O were studied by X-ray diffraction (XRD, D/max-2550VB, Rigaku, Japan) with Cu target at a scanning rate of 8°/min and 2$\theta$ ranging from 20° to 80°. Field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan; prior to SEM imaging, all samples were sputtered with thin layers of gold) and transmission electron microscopy (TEM, JEM-2100FT, JEOL, Japan) were used to determine the morphology and microstructure of the nanoparticles. Fourier transform infrared spectroscopy ( Spectrum Two, PerkinElmer, Germany) was used to determine the chemical bond information of the prepared ionic liquid ranging from 400 to 4,000 cm$^{-1}$. The change of concentration of DCF was analyzed by UV-vis absorption spectroscopy (UV-1800, Shimadzu, Japan) ranging from 200 to 400 nm. Different concentrations of DCF solution were prepared to obtain the standard curve, as shown in Figure S3. The pH values were measured by using a pH meter (pH 100, LiChen, Shanghai, China). The sulfate and hydroxyl radicals were identified on an Electron Paramagnetic Resonance Spectrometer (EPR, A300, Bruker, German) at scanning time 40 s ranging from 3,460 to 3,560 G, center field at 3,502.00 G, sweep width at 100.0 G, microwave frequency at 9.8226 GHz, sweep time at 30.00s, modulation amplitude at 1.000 G and modulation frequency at 100.00 kHz. The concentration of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was 20 mM to capture hydroxyl and sulfate radicals. The surface element chemical states of Cu$_2$O before and after reaction were analyzed on an X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, ThermoFisher, USA) using monochromatized Al K\alpha excitation.

3. RESULTS AND DISCUSSION

3.1. Characterization of [BMIM]Br

The $^1$H NMR spectra of [BMIM]Br are shown in Figure S1 in Supplementary Information. The $^1$H NMR data of the products are as follows: $\delta$ 8.65(1H, s); $\delta$ 7.38(1H, s); $\delta$ 7.32(1H, s); $\delta$ 4.12(2H, t); $\delta$ 3.82(3H, s); $\delta$ 1.77(2H, m); $\delta$ 1.24(2H, m); $\delta$ 0.84(3H, t), which conformed to the structure of [BMIM]Br. Since [BMIM]Br can be easily washed out from Cu$_2$O crystals, as confirmed by FTIR (Figure S2), it cannot affect the subsequent degradation experiments. The vibration bands of other adsorption species (especially [BMIM]Br) were not detected in the FTIR spectra of Cu$_2$O.
3.2. Effect of [BMIM]Br on morphology and crystalline properties of shape-controlled Cu2O

A series of shape-controlled Cu2O nanoparticles was synthesized via adding different concentrations of [BMIM]Br. Morphologies of as-synthesized Cu2O nanoparticles are observed by using SEM. They exhibited octahedral (Figure 1(a)), truncated octahedral (Figure 1(b)) and aggregated sphere (Figure 1(c)) shapes. The size of Cu2O ranged from 500 to 900 nm. When the concentration of [BMIM]Br was 0.4 wt.%, the Cu2O nanoparticles with well defined, smooth, and uniform octahedral shape can be obtained. When the concentration of [BMIM]Br was increased to 0.6 wt.%, the apex of the octahedral was cut off and a truncated octahedral shape was formed, if comparing with the former (octahedral shape). If the concentration of [BMIM]Br increasing to 0.8 wt.%, the Cu2O nanoparticles in regular shape show heavy etched and collapse to assemble spheres bearing many small nanoparticles, as shown in Figure 1(c). It has been reported that oxidative etching plays an important role in the morphologies of Cu2O nanoparticles (Tang et al. 2015). Solubility of oxygen in water at standard temperature and pressure is about 40 mg/L. However, oxygen solubility in ionic liquid solution is up to 800 mg/L (Kumel et al. 2005). The possible reason on the different morphologies of Cu2O nanoparticles prepared by using ionic liquid is that with the increase concentration of ionic liquid, the etching effect of oxygen on Cu2O becomes stronger.

The catalytic ability of Cu2O depended on not only the dimension, but crystalline factors, such as the exposed facets. The XRD patterns (Figure 2(a)) of the three cuprous oxides exhibit (110), (111), (200), (220), (311), and (222) reflection peaks that matched the standard patterns of Cu2O (JCPDS No. 05-0667). Compared with the sample prepared by 0.4 wt.% [BMIM]Br, the diffraction intensity ratios of (110)/(111) increased (Figure 2(a)). In addition, the diffraction peaks of aggregated spheres show an obviously broadening, indicating that the crystal size decreased. However, the XRD patterns of all the samples were almost similar, which indicates that adding [BMIM]Br cannot affect the crystal phase of resulted Cu2O nanoparticles. Figure 2(b) depicts the TEM image of the Cu2O crystals prepared with 0.6 wt.% [BMIM]Br. It is shown that the shape of

![Figure 1](image1.png) **Figure 1** | SEM images of Cu2O nanoparticles prepared at different concentrations of [BMIM]Br: (a) 0.4 wt.%; (b) 0.6 wt.%; (c) 0.8 wt.%

![Figure 2](image2.png) **Figure 2** | (a) XRD patterns of Cu2O nanoparticles prepared at different concentrations of [BMIM]Br. (b) HRTEM images of synthesized truncated octahedral. (c) Corresponding SAED pattern of synthesized truncated octahedral.
the sample is a truncated octahedral. Figure 2(c) reveals the corresponding selected area electron diffraction (SAED) pattern of the synthesized truncated octahedral. It was demonstrated that the sample is well defined single crystals. Therefore, the (110) surface of the Cu$_2$O was protected by using [BMIM]Br. Then the subsequent selective oxidative etching by oxygen (Qi et al. 2017) can bring about different morphologies of Cu$_2$O nanoparticles.

### 3.3. DCF degradation by shape-controlled Cu$_2$O catalyzed PDS oxidation

#### 3.3.1. Effect of initial pH

Figure 3(a) presents the degradation of DCF by using the Cu$_2$O/PDS system under neutral conditions (pH $= 7$). It is shown that the DCF/PDS/Cu$_2$O system reaches its maximum DCF degradation (46.2%). DCF can almost not be removed in the PDS/DCF system without the activation process of Cu$_2$O to PDS. In order to figure out the adsorption of DCF by Cu$_2$O nanoparticles, the DCF/Cu$_2$O system without PDS was conducted. It was found that only 13.9% of DCF was removed in the DCF/Cu$_2$O system, indicating that a small amount of DCF was adsorbed by Cu$_2$O nanoparticles. Therefore, Cu$_2$O nanoparticles can enhance the oxidation ability of persulfate. Sulfate radicals (SO$_4$$^{-}$) were generated by the activation process of persulfate. Meanwhile, hydroxyl (·OH) radicals were formed by the further reaction of SO$_4$$^{-}$ and H$_2$O. The reaction equation is shown in Equation (3). As is shown in Figure 3(b), the structural and surface morphology of the as-synthesized Cu$_2$O plays the main influence on the degradation of DCF. After 240 minutes of catalytic degradation, the removal rate of octahedral sample reached 11.9%, while the truncated octahedral sample is 50.8%, and the aggregated sphere sample is 25.4% (Figure 3(b)). In addition, adding [BMIM]Br can improve the catalytic degradation performance of the Cu$_2$O:

$$\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \cdot\text{OH} + \text{H}^+ \tag{3}$$

In the experiments of the effect of initial pH on the DCF degradation, the initial pH was adjusted by H$_2$SO$_4$ or NaOH before adding Cu$_2$O nanoparticles and PDS. The results are shown in Figure 4. The DCF degradation curve was fitted by pseudo-first-order linear fitting. Under acidic conditions (pH $= 5$), the removal rate of DCF is 5.4%, 46.3% and 27.6% after 240 min and rate constants are $2.2 \times 10^{-4}$ min$^{-1}$ ($R^2 = 0.980$), $2.6 \times 10^{-3}$ min$^{-1}$ ($R^2 = 0.976$) and $1.3 \times 10^{-3}$ min$^{-1}$ ($R^2 = 0.982$). Therefore, the potential activation pathways of the persulfate may be by copper ions dissolved from Cu$_2$O. Meanwhile, comparing the degradation rate of DCF under acidic conditions (pH $= 5$), it can be found that the removal rate of DCF is higher as well as the reaction rate constant under neutral conditions (pH $= 7$). Therefore, Cu$^{2+}$ was dissolved from Cu$_2$O under acidic conditions due to the increase in hydrogen ion concentration. Then persulphate was activated by

![Figure 3](https://example.com/figure3.png)  
**Figure 3** (a) Degradation curve of three reaction systems; Cu$_2$O/DCF, PDS/DCF and Cu$_2$O/PDS/DCF. (b) Degradation curve of DCF catalyzed by as-prepared Cu$_2$O catalysts. Conditions: [DCF] = 10 mg/L, [PDS] = 0.2 g/L, [Cu$_2$O] = 1 g/L, initial pH = 7.0, terminal pH = 7.0, temperature: 25 °C.
Cu$^{2+}$ to form sulfate (SO$_4^{2-}$) radicals. The reaction equation is shown in Equations (4) and (5):

$$\text{Cu}_2\text{O} + 2\text{H}^+ \rightarrow \text{Cu} + \text{Cu}^{2+} + \text{H}_2\text{O} \quad (4)$$

$$\text{Cu}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Cu}^{3+} + \text{SO}_4^{-} + \text{SO}_4^{2-} \quad (5)$$

Under strong alkaline conditions (pH = 11), as shown in Figure 5, the removal rate of DCF can reach up to 19.9%, 87.2% and 83.2% after 240 min. The rate constants are $9.3 \times 10^{-4}$ min$^{-1}$ ($R^2 = 0.987$), $8.4 \times 10^{-3}$ min$^{-1}$ ($R^2 = 0.982$) and $7.5 \times 10^{-3}$ min$^{-1}$ ($R^2 = 0.985$) respectively. The reason may be that sulfate radicals (SO$_4^{2-}$) can react with hydroxyl radicals (OH$^-$) to form hydroxyl radicals (·OH), for which redox potential is higher than that of the sulfate radical (SO$_4^{2-}$). Alkali-activated persulfate is perhaps the main reason for DCF degradation at pH = 11. The mechanism of alkali activation has been confirmed as Equation (6) (Liang et al. 2013):

$$\text{SO}_4^{2-} + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \cdot\text{OH} \quad (6)$$
3.3.2. Effect of PDS concentration
In order to determine the effect of PDS dosage on degradation rate, DCF was catalytically degraded at different initial PDS concentrations (ranging from 0.05 g/L to 0.50 g/L). The bar chart (Figure 6) shows that with the increasing concentration of PDS, the DCF degradation rate increased too. When the dosage of PDS increased to 0.25 g/L, DCF degradation rate reaches its maximum (0.89). However, further increase in PDS concentrations cannot cause further improvement for DCF removal. Excessive PDS quenched some sulfate radicals (SO$_4^-$), which led to the decrease in sulfate radicals in the system (Guo et al. 2021). When the PDS concentrations increased beyond a quantitative value, the change in DCF degradation rate dropped down.

3.3.3. Stability of shape-controlled Cu$_2$O nanoparticles
To investigate the stability of shape-controlled Cu$_2$O nanoparticles, the consecutive cycling tests of DCF degradation were carried out. As can be seen in Figure 7(a), the degradation efficiency of DCF decreased slightly after the recycling use of shape-controlled Cu$_2$O nanoparticles. The DCF degradation efficiency was 84.1% in the Cu$_2$O/PDS system at the first cycle. Whereas, the removal efficiency of DCF decreased to 79.7% at the second cycle, and it further decreased to 71.2% at the third cycle. The possible reason for the falling degradation rate is the agglomeration of Cu$_2$O nanoparticles (Liu et al. 2017), which reduces the contact opportunity between Cu$_2$O surface and persulfate. XPS survey spectra of Cu$_2$O before and after degrading DCF are shown in Figure 7. It is shown that the copper element on the surface of Cu$_2$O nanoparticles is univalent. The valence state remains the same before and after reaction. It proves that the activation persulfate process of Cu$_2$O is a catalytic degradation of DCF. Therefore, Cu$_2$O nanoparticles can be recycled, which is different from the one-time consumption of ferrous ion, ZVI and pyrite in the common activation persulfate process. In conclusion, shape-controlled Cu$_2$O nanoparticles possess good stability.

3.4. PDS possible activation mechanism
As mentioned above, persulfate can be activated by Cu$_2$O nanoparticles. To further determine whether or not SO$_4^-$ and ·OH radicals over Cu$_2$O/PDS system were produced, EPR spin-trapping experiment was performed under different conditions (pH = 5.0, pH = 7.0, pH = 11.0) (Figure 8). EPR was a technique for detecting substances with unpaired electrons, especially radicals. Hydroxyl and sulfate radicals (·OH and SO$_4^-$) could react with DMPO to form DMPO-OH and DMPO-SO$_4$ adducts, which can be detected by EPR (Zhou et al. 2021). It was shown in Figure 8(a) that after 10 minutes of Cu$_2$O activating PDS, sulfate radical signals improved greatly. It was confirmed that under acidic conditions, the key factor of activating the persulfate is Cu$^{2+}$ dissolved from Cu$_2$O nanoparticles. As can be seen in Figure 8(b) and 8(c) after 10 minutes of Cu$_2$O activating PDS, both sulfate and hydroxyl radical signals improved. It is also shown in Figure 8(b) that few ·OH can be formed by excess SO$_4^-$ under neutral conditions and the intensity of sulfate and hydroxyl radical signals was weaker under alkaline conditions. Therefore, SO$_4^-$ and ·OH were generated by Cu$_2$O nanoparticles under alkaline condition with alkali synergistically.

Figure 6 | Effect of PDS concentration on the degradation of DCF. [DCF] = 10 mg/L, [Cu$_2$O] = 1 g/L, initial pH = 7.0, [PDS] = 0.05–0.50 g/L.
Figure 7 | (a) Recycling use of shape-controlled Cu2O nanoparticles on DCF degradation. [DCF] = 10 mg/L, [PDS] = 1.25 g/L, [Cu2O] = 1 g/L, initial pH = 7.0; full XPS spectra of Cu2O before (b) and after (d) the degradation of DCF; Cu 2p XPS spectra of Cu2O before (c) and after (e) the degradation of DCF.
activating process of persulfate. The EPR analysis verified the generation and participation of ·OH and SO$_4^-$ as active radicals in the DCF oxidation.

It has been reported (Liang et al. 2013) that several scavengers were used to identify sulfate and hydroxyl radicals in solution, such as methanol, ethanol, tert-butanol, nitrobenzene and phenol. In addition, methanol (MeOH), tert-butanol (TBA) and phenol were used as sulfate and hydroxyl radical scavengers (Du et al. 2017). As shown in Figure 9, compared with MeOH and TBA, phenol plays a large inhibitory effect on the degradation of DCF under neutral and alkaline conditions. The dielectric constants of phenol, TBA and MeOH are 9.7, 12.4 and 33.0, respectively, at 20 °C, while water is 80.1 at 20 °C. Therefore, phenol molecules are apt to aggregate on the surface of Cu$_2$O nanoparticles, while MeOH and TBA molecules tend to disperse in solution. Phenol can approach the surface of Cu$_2$O easily and react with sulfate radicals and hydroxyl radicals in a high rate (Liang et al. 2013), which makes phenol completely scavenge radicals on the surface of Cu$_2$O. It is shown in Figure 9 that the degradation rate of TBA is slightly higher than that of MeOH. As the dielectric constant of TBA is less than that of MeOH, TBA can approach the radicals on the surface of Cu$_2$O nanoparticles more easily and quench the radicals. Therefore, the region of radical oxidation of DCF is most likely to occur in the boundary layer on the surface of Cu$_2$O. In addition, MeOH and TBA cannot completely inhibit the degradation of DCF. As a consequence, it is proposed that radicals cannot completely oxidize DCF substances. The result is consistent with the conclusions of literature (Zhang et al. 2014).

According to above results, sulfate radicals (SO$_4^-$) and hydroxyl radicals (·OH) are reactive oxygen species during the degradation of DCF. Among them, the activated persulfate was dominant and forms heterogeneously from the surface of Cu$_2$O nanoparticles.

**Figure 8** | EPR spectrum for DMPO-OH and DMPO-SO$_4$ obtained in the Cu$_2$O/PDS system. (a) Initial pH = 5.0; (b) initial pH = 7.0 and (c) initial pH = 11.0. Conditions: [DCF] = 10 mg/L, [PDS] = 0.2 g/L, [Cu$_2$O] = 1 g/L$^{-1}$, DMPO = 20 mM. The positions marked by green circle, blue diamond were assigned to sulfate and hydroxyl radicals. Please refer to the online version of this paper to see this figure in colour: [http://dx.doi.org/10.2166/wst.2021.369](http://dx.doi.org/10.2166/wst.2021.369).
Cu$_2$O. Most persulfate is attached to the copper site through exospheric interactions without forming strong bonds or free radicals (Zhang et al. 2014). Subsequently, the surface persulfate oxidizes Cu (II) to Cu (III) and produces sulfate (SO$_4^{2-}$) radicals. The resulting Cu(III) oxidizes the H$_2$O molecule to hydroxyl radicals (·OH). The total possible activation mechanism could be described as follows Figure 10.

4. CONCLUSION

In this paper, a novel and simple method for preparing shape-controlled Cu$_2$O nanoparticles based on ionic liquid [BMIM]Br has been developed. The results show that the resulted shape-controlled Cu$_2$O nanoparticles can activate PDS effectively to degrade DCF over a broad pH range. The high degradation rate of DCF by using truncated octahedron and aggregate sphere of Cu$_2$O nanoparticles is attributed to the protection of active surfaces (100) and (111) by [BMIM]Br. It was found

![Figure 9](image)

Figure 9 | Effects of various quenching agents on DCF degradation. Conditions: [DCF] = 10 mg/L, [PDS] = 0.2 g/L, [Cu$_2$O] = 1 g/L, [MeOH] = [TBA] = 200 mM, [phenol] = 2 mM. Temperature: 25 °C (a) initial pH = 7; (b) initial pH = 11.

![Figure 10](image)

Figure 10 | Mechanism of the activation of Cu$_2$O/PDS combined system at different pH. DCF and DCF$_{ox}$ stand for diclofenac and diclofenac oxidation products, respectively.
that shape-controlled Cu2O possess good stability. When c(PDS):c(DCF) is 125:1, DCF degradation rate reaches its maximum (0.89). According to the EPR spin-trapping experiment, sulfate (SO4·) and hydroxyl (·OH) radicals play the main roles during the degradation process. Under alkaline conditions, SO4· and ·OH were generated by Cu2O nanoparticles and alkali synergistically activating the process of persulfate. Under acidic conditions, the key factor of activating the persulfate is Cu2+ dissolved from the Cu2O nanoparticles. While, under neutral conditions, few ·OH are formed by excess SO4·, which leads to the slight increase in the degradation rate of DCF. Through the analysis of the radical scavenging experiment, it was proved that the region of radical oxidation of DCF is most likely to occur at the boundary layer on the surface of shape-controlled Cu2O nanoparticles. Therefore, the Cu2O/PDS system is a good catalyst for degrading DCF.

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CONTRIBUTIONS

JiaLei Huang: Resources, investigation and data curation. Software, methodology, and carried out the research. Conceptualization, validation and wrote the manuscript.

Yan Luo: Supervision, reviewing and editing and idealized the work.

CONSENT TO PARTICIPATE

All authors have given their consent to participate in this research article.

CONSENT FOR PUBLICATION

All authors have given their consent to publish this research article.

CONFLICT OF INTEREST

The authors declare no competing interests.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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