Proceedings of the 3rd International Conference on Green Energy, Environment and Sustainable Development (GEESD2022), X. Zhang et al. (Eds.)

doi:10.3233/ATDE220343

Fe-Cu Bimetallic Oxide Quantum Dots Coupled with g-C_3N_4 Nanosheets for Efficient Photo-Fenton Degradation of Phenol

Jingpeng LUO[1], Weiying PANG, Qingying YE and Dong FU
Department of Environmental Science and Engineering, North China Electric Power University, Baoding 071003, Hebei, China

Abstract. Graphitized carbon nitride (g-C_3N_4), as a simple and green photocatalytic material, has been widely used in photocatalytic degradation. However, the photocatalytic activity of g-C_3N_4 was inhibited by poor visible light absorption and high photocarrier recombination rate. Metal quantum dots (Qds)/g-C_3N_4 nanosheets coupled catalysts have attracted more and more attention in the Fenton advanced oxidation process due to their high charge mobility and more active sites. In this work, heterogeneous photocatalysts of Fe-Cu bimetallic oxide quantum coupled with g-C_3N_4 nanosheets were prepared. It shows high activity in Fenton and photocatalytic system. Under the optimal conditions, the removal efficiency of 50 ppm phenol reached 99% after 60 min. The removal efficiency of the catalyst for phenol did not decrease significantly after four cycles of experiments, and the catalyst had good stability. The experimental results show that the synergy between g-C_3N_4 semiconductor photocatalytic oxidation technology and heterogeneous Fenton advanced oxidation technology has great practical significance.

Keywords. Graphitized carbon nitride, metal quantum dots, Fenton, phenol

1. Introduction

With the rapid development of industry and the organic pollutants produced by human activities, water pollution has become increasingly serious. Advanced oxidation technology (AOP) is widely concerned in the field of water treatment because it can produce reactive oxygen species with strong oxidation ability and degrade most organic pollutants [1]. Fenton reaction is a kind of advanced oxidation technology, which is widely used in the field of organic wastewater treatment [2]. However, the traditional Fenton technology has the disadvantages of narrow pH value adaptation range and easy to produce a large amount of iron sludge precipitation in the reaction process. Consequently, the preparation of heterogeneous Photo-Fenton reaction catalyst with wide pH adaptation range, low iron dissolution after reaction and fast reaction rate has a good application prospect [3].

[1] Corresponding Author, Jingpeng LUO, Department of Environmental Science and Engineering, North China Electric Power University, Baoding 071003, Hebei, China; Email: ljpluoljp12@qq.com

Semiconductor photocatalysis technology has been used on a large scale in the field of environmental catalysis because of its green and low energy consumption. A large number of studies have shown that all kinds of semiconductor nanoparticles have certain light response ability. However, the application of photocatalytic technology is difficult to efficiently and completely remove organic pollutants. Therefore, the combination of semiconductor photocatalytic technology and heterogeneous Fenton advanced oxidation technology can significantly improve the treatment effect [4].

The layered structure of g-C_3N_4 is similar to graphene. It is ideal structural unit is mainly heptazine ring. In the layered structure, both C and N atoms are in the sp2 hybrid form. Among them, the six lone electron pairs of N can coordinate with transition metals, making them a good support for stable ultrasmall metal clusters and single atoms [5]. However, g-C_3N_4 prepared by simple calcination often has serious polycondensation, resulting in its small specific surface area, high photocarrier recombination rate and severe coating of coordination metals, resulting in low photo-Fenton reaction rate [6].

In order to maximize the number of catalytic active centers, improve the reaction efficiency, and reduce metal leaching during the reaction process, Fe-Cu bimetallic oxide (Fe-CuO) quantum dots coupled g-C_3N_4 ultra-thin nanochip catalyst was prepared in this paper. The catalyst expresses the synergistic effect of g-C_3N_4 photocatalytic technology and heterogeneous Fenton-like advanced oxidation technology, greatly improving the reaction rate. The effects of Fe/Cu ratio and pH value on the degradation of phenol were discussed. At the same time, the mechanism of synergistic degradation of Fe-CuO Qds/g-C_3N_4 catalyst by photocatalytic technology and heterogeneous Fenton technology was summarized.

2. Experiment Section

2.1. Preparation of Ultrathin g-C_3N_4

5.0g urea was added to the crucible and heated in a Muffle furnace to 550°C (2.5°Cmin^{-1}) for 4 h, afterwards cooled naturally to room temperature. Then, the yellow particles were ground into powder in an agate mortar to prepare g-C_3N_4.

2.2. Preparation of Fe-CuO Qds/g-C_3N_4 Ultra-Thin Nanosheets

First, 1 g g-C_3N_4 was dispersed in absolute ethanol (100 ml) and stripped for 1.5 hours with the help of ultrasound. Then X mmol $FeCl_3 \cdot 6H_2O$ and Y mmol $CuCl_2 \cdot 2H_2O$ were dissolved in the above solution (X:Y=1:0, 5:5, 7:3, and the total amount of copper and iron precursors was controlled to be 1 mmol). 3 mmol NH_4HCO_3 were added and stirred continuously for 8 h at room temperature. The as-obtained Fe-CuO Qds/g-C_3N_4 precursor was collected by centrifugation, washed several times with ethanol and distilled water and dried at 60°C. Then the precursor was heated to 350°C for 2 h in air with a rate of 5°C min^{-1} to obtain Fe-CuO Qds/g-C_3N_4 [7].

2.3. Photo-Fenton Catalytic Activity

The photo Fenton catalytic reaction was carried out in a jacketed beaker containing a circulating water bath, with 300W Xe lamp. The pH of the solution was adjusted by HCl or NaOH. The 0.05 g catalyst was introduced into 50 ml phenol (50 mgL^{-1}) solution and evenly mixed under shading for 30 minutes to get a balance of desorption and absorption before visible light exposure. Then before starting the photo Fenton reaction, a certain amount of H_2O_2 (30%) was added into the mixture. During the degradation process, a certain amount of water sample was collected every 15 min, and 1ml supernatant was taken to detect the phenol concentration after centrifugation.

3. Results and Discussion

3.1. Materials Characterization

The XRD pattern of catalysts are shown in Figure 1a. There are two obvious diffraction peaks when 2θ = 13.0° and 27.6° in all four groups of catalysts, which belong to (100) and (002) crystal planes of g-C_3N_4, respectively [8]. There is no obvious diffraction peak of Fe or Cu and their oxides in the spectrum, caused by the low content of Fe and Cu in the sample, which exists in a highly dispersed state, or the formation of amorphous composite oxides of Fe-Cu. Compared with pure g-C_3N_4, the characteristic peak attributed to (001) after modification decreased significantly, indicating that the loading of copper and iron reduced its stacking degree, and that the quantum dots did not cause changes in the crystal structure of g-C_3N_4. X-ray photoelectron spectroscopy (XPS) analysis of 7:3Fe-CuO/g-C_3N_4 catalyst shows that the catalyst contains five elements: C, N, O, Fe and Cu (Figure 1b). The orbital binding energies of Fe2p3/2 and Fe2p1/2 correspond to 711.7ev and 725ev, respectively. The orbital binding energies of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ correspond to the characteristic peaks at 932.4 eV and 952.2 eV. This indicates that Fe-Cu oxide is successfully loaded on g-C_3N_4 [9].

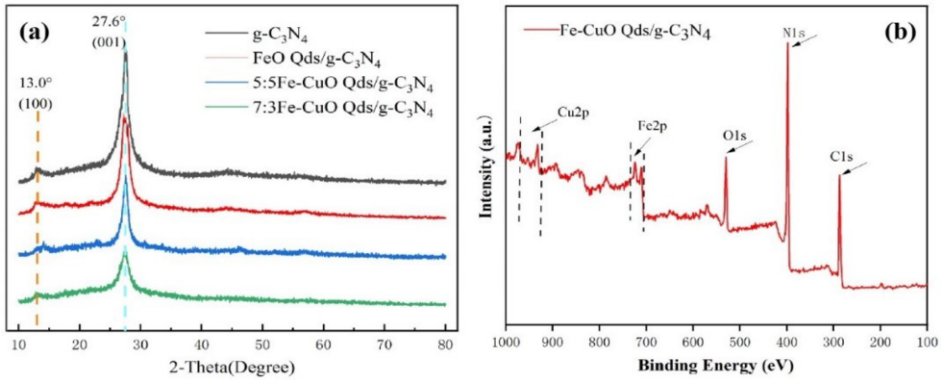

Figure 1. (a): Wide-angle XRD patterns; (b): XPS spectra of 7:3 Fe-CuO /g-C_3N_4.

The scanning electron microscope (SEM) images of 7:3Fe-CuO Qds/g-C_3N_4 catalyst is shown in Figure 2. The catalyst has obvious graphite layered structure, and granular copper iron oxide quantum dots can be observed in the outer layer of g-C_3N_4.

It shows that the granular Cu-FeO Qds produced in the process of chemical bath precipitation can be uniformly attached to the surface of g-C_3N_4.

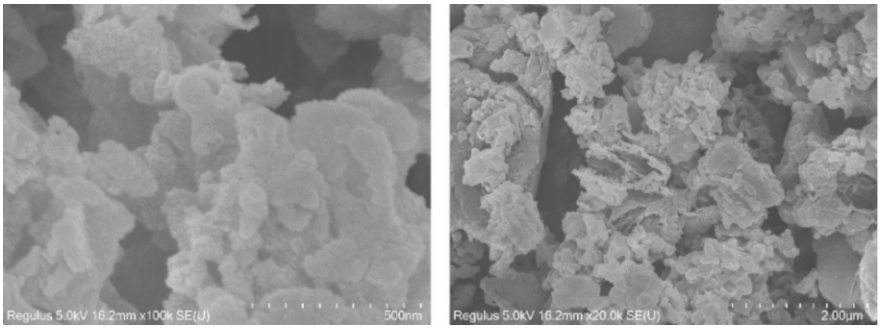

Figure 2. SEM images of 7:3Fe-CuO Qds/g-C_3N_4.

3.2. Photo-Fenton Catalytic Performance for Phenol Degradation

- Degradation effect of catalysts under different doping ratios

The heterogeneous photo-Fenton degradation performance of catalysts with different Fe and Cu doping ratios is shown in Figure 3a. In the composite catalyst, when the ratio of Fe and Cu is 7:3, the phenol degradation efficiency of photo-Fenton system with 7:3Fe-CuO Qds/g-C_3N_4 catalyst achieves 99.2% after 90 min. The efficiency is about 4.5 times that of pure g-C_3N_4, presenting the highest degradation efficiency toward phenol. This is mainly due to the following reasons: (1) Compared with the FeO Qds/g-C_3N_4 catalyst, the Cu site expresses better H_2O_2 adsorption capacity, and Cu^+ can interact with H_2O_2 rapidly to generate •OH in the reaction system; (2) In the meantime, the reaction of Cu^+ and Fe^{3+} accelerates the Fenton cycle of Fe^{3+}/Fe^{2+} on the catalyst surface. The results indicate that there is a synergistic effect between copper and iron, and the dual reaction center can accelerate the photo-Fenton degradation rate.

- Degradation effect of different oxidation methods

The degradation performance of phenol under different systems is shown in Figure 3b. Under the same reaction conditions, the degradation efficiency of phenol by pure g-C_3N_4 photocatalytic oxidation system is only 12.29%. But the photocatalytic oxidation degradation of phenol by 7:3Fe-CuO Qds/g-C_3N_4 catalyst can reach 22.99%. It shows that the loading of copper and iron promotes the photocatalytic performance of the catalyst. At the same time, compared with the Fenton system of 7:3Fe-CuO Qds/g-C_3N_4 (catalyst/H_2O_2), the introduction of visible light not only greatly improves the degradation rate of phenol, but also enhances the phenol removal efficiency. The removal rate of phenol is as high as 99.2% after 90 min. It is indicated that the photocatalytic technology of g-C_3N_4 and Fenton advanced oxidation shows a significant synergistic effect.

- The effect of catalyst dosage

The photo-Fenton degradation performance of 7:3Fe-CuO Qds/g-C_3N_4 for phenol under different catalyst dosages is shown in Figure 3c. The removal efficiency of

phenol can achieve more than 99% when catalyst dosage rises from 0.5 gL^{-1} to 2.0 gL^{-1} after 120 min. However, the catalyst dosage of 2.0 gL^{-1} greatly improved the degradation efficiency of phenol within 15-30 min. The main reason is that the surface of g-C_3N_4 nanosheets provides a large number of copper-iron oxide quantum dots to participate in the Fenton reaction.

- The effect of hydrogen peroxide dosage

The effects of different H_2O_2 dosages on the photo-Fenton degradation of phenol by 7:3Fe-CuO Qds/g-C_3N_4 are shown in Figure 3d. When 0.5 mL of H_2O_2 is added to the system, the removal efficiency of phenol reaches 40.6% after 15 minutes of reaction, greatly improving the response rate of the photo-Fenton reaction. Meanwhile, the photolysis of excess H_2O_2 to generate •OH also accelerates the degradation rate of phenol. The removal rate of phenol is as high as 99% after 90 min. When 0.15 mL and 0.25 mL H_2O_2 are added to the system, the reaction rates are similar in the first 15 min, which may be due to the excess of H_2O_2 reacting with Fe and Cu quantum dots in the system.

- The effect of pH

The photo-Fenton performance of 7:3Fe-CuO Qds/g-C_3N_4 catalyst under different pH conditions is shown in Figure 3e. The photo-Fenton system of 7:3 Fe-CuO Qds/g-C_3N_4 catalyst can remove 99.5% of phenol after 60 min, and when pH=7.3, the degradation efficiency of phenol after 120min is also up to 99.2%. Even when pH=10.0, the degradation rate of phenol in the reaction time reaches 86.3%. It shows that Cu and Fe oxide quantum can be well settled on g-C_3N_4 nanosheets, and the 7:3Fe-CuO Qds/g-C_3N_4 heterogeneous Fenton catalyst system reaches a wider pH adaptability range than the traditional Fenton system.

- Recycling performance of catalyst

After four rounds of recycling, the degradation efficiency of phenol remains above 86% (Figure 3f). It shows that the catalyst still maintains its reusability. The Cu-FeO Qds can be stably supported on the surface of g-C_3N_4 ultrathin nanosheets. It can be significantly observed that the catalyst still maintains a low iron leaching rate after three cycles of use during the reaction. It is indicated that the Fenton system based on Fe-CuO Qds/g-C_3N_4 catalyst has great potential for practical application in wastewater treatment.

3.3. Degradation Mechanism of Phenol by Photo Fenton Reaction

Photo-Fenton mechanism of Fe-CuO Qds/g-C_3N_4 catalyst is shown in Figure 4. Electron-hole pairs are formed in g-C_3N_4 semiconductor under visible light excitation (R1); Photogenerated electrons and H_2O_2 participate in the redox cycle of copper and iron (R2); The reaction between copper and iron and photogenerated electrons accelerates the Fenton reaction rate. In addition, photogenerated electrons have high redox sites, which can reduce O_2 in the system to $•O^{2-}$ and participate in the degradation of phenol (R3). Reactive oxygen species (e.g. $•OH$\$•O^{2-}$) and h^+ in the system degrade phenol (R4).

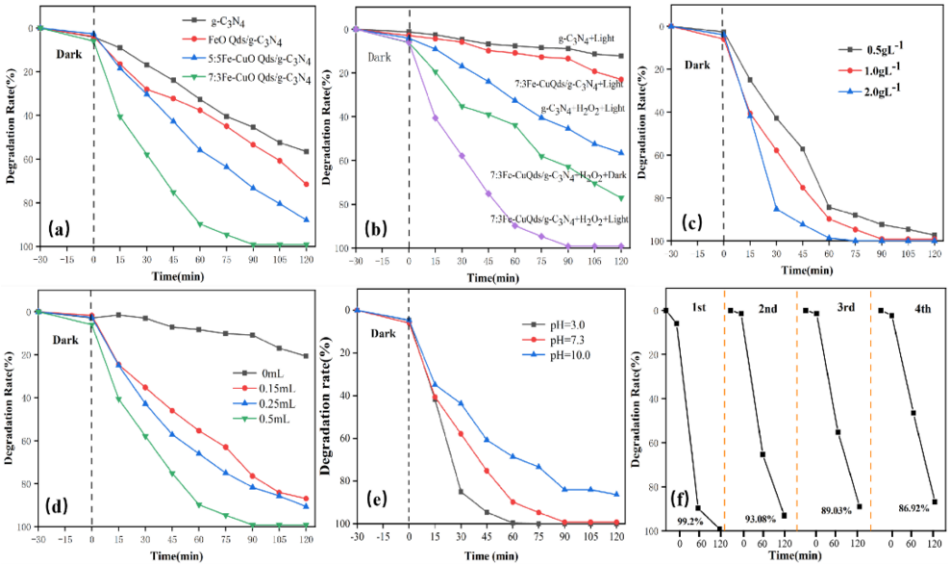

Figure 3. (a): Degradation effect of catalysts with different doping ratios; (b): Degradation effect of different oxidation methods; (c): Influence of catalyst dosage; (d): Influence of H_2O_2 dosage; (e): Influence of pH value; (f): Recycling performance of catalyst [c\d\e\f Initial conditions: cat:7:3Fe-CuO Qds/g-C_3N_4; pH=7.3; H_2O_2=0.5mL; pollutants: 50mgL^{-1} phenol].

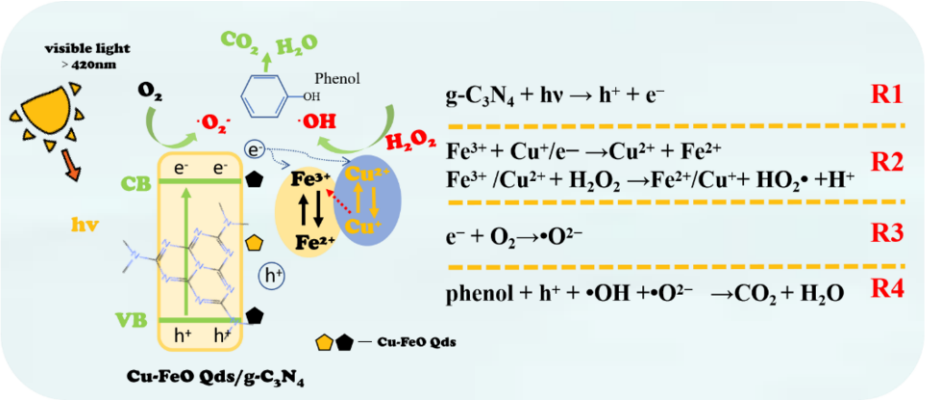

Figure 4. Mechanism for phenol degradation by Fe-CuO Qds/g-C_3N_4/H_2O_2/vis system.

4. Conclusion

In this study, we report a heterogeneous photo Fenton catalyst prepared by a simple method, which couples Fe-Cu bimetallic oxide quantum dots with g-C_3N_4, showing the dual degradation performance of Fenton reaction and photocatalysis. Under the same conditions, compared with FeO Qds/g-C_3N_4 catalyst, the phenol removal efficiency of 7:3Fe-Cu Qds/g-C_3N_4 catalyst is 28.8% higher, indicating that there is a good synergy between copper and iron. In addition, the catalyst still has a good removal efficiency of phenol under a wide pH value. Through three cycles of recovery, the removal rate of

phenol by the catalyst also remained above 80%. The results show that the catalyst is a promising catalyst for heterogeneous photo Fenton degradation of organic wastewater.

References

[1] Deng Y, Zhao R. Advanced oxidation processes (AOPs) in wastewater treatment. Current Pollution Reports. 2015;1(3):167-176.
[2] Pignatello JJ, Oliveros E and MacKay A. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Critical reviews in Environmental Science and Technology. 2006;36:1-84.
[3] Nidheesh PV. Heterogeneous Fenton catalysts for the abatement of organic pollutants from aqueous solution: A review. Rsc Advances. 2015;5:40552-40577.
[4] Luo J, Du X, Ye Q, et al. Graphite Phase Carbon Nitride Photo-Fenton Catalyst and its Photocatalytic Degradation Performance for Organic Wastewater. Catalysis Surveys from Asia, 2022: 1-17.
[5] Sudhaik A, Raizada P, Shandilya P, Jeong DY, Lim JH, Singh P. Review on fabrication of graphitic carbon nitride based efficient nanocomposites for photodegradation of aqueous phase organic pollutants. Journal of Industrial and Engineering Chemistry. 2018;67:28-51.
[6] Ma J, Wang K, Wang C, Chen X, Zhu W, Zhu G, Yao W, Zhu Y. Photocatalysis-self-Fenton system with high-fluent degradation and high mineralization ability. Applied Catalysis B: Environmental. 2020;276:119150.
[7] Liu M, Xia H, Yang W, Liu X, Xiang J, Wang X, Hu L, Lu F. Novel Cu-Fe bi-metal oxide quantum dots coupled g-C3N4 nanosheets with H2O2 adsorption-activation trade-off for efficient photo-Fenton catalysis. Applied Catalysis B: Environmental. 2022;301:120765.
[8] Hu J, Zhang P, An W, Liu L, Liang Y, Cui W. In-situ Fe-doped g-C3N4 heterogeneous catalyst via photocatalysis-Fenton reaction with enriched photocatalytic performance for removal of complex wastewater. Applied Catalysis B: Environmental. 2019;245:130-142.
[9] Zhang S, Gao H, Huang Y, Wang X, Hayat T, Li J, Xu X, Wang X. Ultrathin g-C3N4 nanosheets coupled with amorphous Cu-doped FeOOH nanoclusters as 2D/0D heterogeneous catalysts for water remediation. Environmental Science: Nano. 2018;5:1179-1190.