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CuO Nanoplate Array Supported on Ni foam, a Highly Active Catalyst in the Degradation of Rohdamine B with Hydrogen Peroxide

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Abstract. Removal of organic pollutants from wastewater by catalytic degradation of those organics with hydrogen peroxide has been a hotspot in the field of water environmental protection. In this work, CuO nanoplatelet array supported on Ni foam has been prepared by a facile hydrothermal route. Degradation of Rhodamine B (RhB) with H_2O_2 catalyzed by the as-prepared CuO nanocatalyst was investigated. It is found that RhB can be effectively degraded by H_2O_2/CuO. The large H_2O_2 dosage and high reaction temperature is favourable for the fast degradation of RhB. In addition, the as-prepared CuO nanoplatelet array supported on Ni foam exhibits high stability and good reusability in the RhB degradation reaction.

1. Introduction

Over the past two decades, advance oxidation processes (AOPs) have been regards as one of the most effective ways to remove a number of organic contaminants from wastewater [1, 2]. In AOPs, highly reactive hydroxyl radicals (•OH) are produced by different means, which will oxidatively degrade those organic pollutant without formation of toxic by-products. The applications of nanostructured material in the field of environment have been well documented [3-6]. Recently, degradation of organics with hydrogen peroxide catalyzed by nanosized CuO has received much attention by those researchers from different countries [7, 8]. It has been reported that many organic contaminant can be effectively removed from wastewater by this process. In the traditional CuO/H_2O_2 process, CuO nanocatalysts in the form of powder were used because powdery nanocatalysts possess large specific surface area and can provide more active sites for the catalytic reactions. However, it is hard to recover those CuO powder from the reaction system (generally in the form of a suspension). Considering this fact, the cost CuO/H_2O_2 process is still high. Additionally, if CuO is not separated from the wastewater, it maybe causes secondary pollution. Thus, it is of great importance to fabricate nanostructured CuO catalysts in the form of film. Generally speaking, catalysts in the form film have much higher stability and reusability than that of powdery counterpart [9, 10]. In addition, if the nanostructured films are well designed, they can also have high catalytic activity in degradation of organic pollutants with hydrogen peroxides.

In this work, CuO nanoplate array supported on the Ni foam has been prepared by a facile hydrothermal route. To the best of our knowledge, such CuO nanomaterials have not been reported in the literature thus far. It is found that our CuO nanoplate array has high activity in the degradation of the simulated organic pollutant, rhodamine B. More importantly, our film catalyst has very stability and reusability. After 8 catalytic cycles, its activity is still well maintained.

2. Experimental section

2.1. Preparation of CuO nanoplate array supported on the Ni foam

All the reagents were of analytic grade, and double-distilled water was used throughout the experiments. To prepare Ti sheet supported CuO film, 2.0 mmol $CuSO_4 \cdot 5H_2O$ was dissolved in 20 mL double-distilled water to form a transparent blue solution. At the same time, 6.5 mmol ethylenediamine dissolved in 20 mL double-distilled water. Then, these two solutions were mixed under stirring. After that, 0.1 mol NaOH was dissolved in 40 mL to form a basic solution under intensive stirring. Subsequently, NaOH solution was added dropwisely into the above-mentioned mixed solution. The obtained reaction solution was transferred into a Teflon-lined steel autoclave, in which a piece of 5 cm × 12 cm Ni foam closely attached to the inner wall of the vessel was used as support. The autoclave was sealed and kept in an oven at 160 ^oC for 2.5 h. After reaction, the obtained film was collected and rinsed with double-distilled water and ethanol, and finally dried in a vacuum oven at 65^oC for 3 h.

2.2. Characterization of CuO catalyst

X-ray diffraction (XRD) patterns were obtained by using a Shimadzu XD-3A X-ray diffractometer with Cu Kα radiation (λ = 1.5406Å). The morphology of the samples was investigated by using a Hitachi Su-8010 field emission scanning electron microscope (FE-SEM).

2.3. Catalytic performance testing

The catalytic performance testing was carried out in a batch reactor. In a typical process, a piece of 3 cm × 2.5 cm CuO film was added into 20 mL RhB solution (10 mg L^{-1}) under stirring, followed by addition of 1mL H_2O_2 solution (30 wt.%). The reaction temperature was maintained at 25^oC ± 0.5 ^oC in a thermostated reactor. To investigate the effect of reaction temperature on the catalytic performance of CuO, similar catalytic experiments were also carried out at 15^oC, and 35^oC. During the catalytic process, reaction solution was sampled at different time intervals and its absorption intensity at λ = 550 nm was determined using a UV-visible spectrophotometer.

3. Results and discussion

Figure 1 shows the XRD patterns of CuO nanoplate array supported on Ni foam, as well as Ni foam. In the XRD pattern of Ni substrate, three peaks can be observed at 2θ = 44.8 ^{o}, 52.2 ^{o} and 76.7 ^{o}, which corresponds to the reflection from (111), (200) and (220) plane of face-centered phase of metallic Ni (PDF#700989). In the XRD pattern of CuO nanoplate array supported on Ni foam, besides those three peaks, other two weak peaks in the range from 35 ^{o} to 40 ^{o} are found. It can be seen in the inset in Figure 1 that two peaks of at around of 35.9 ^{o} and 39.1 ^{o} are observable, which can be indexed to the reflection from the (-111) and (111) planes of monoclinic phase of CuO (PDF#895897). This indicates that CuO has been successfully deposited on the surface of Ni foam.

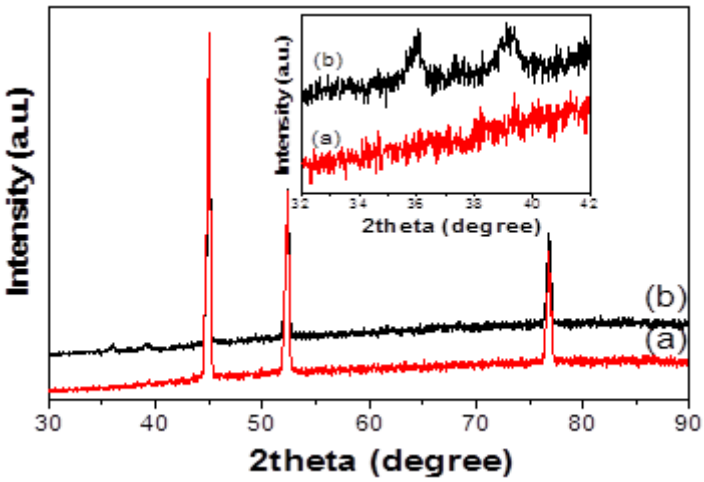

Figure 1. XRD patterns of bare Ni foam (a) and CuO nanoplate array supported on Ni foam (b). Inset shows the enlarged XRD patterns in 2θ range from 32 ° to 42 °

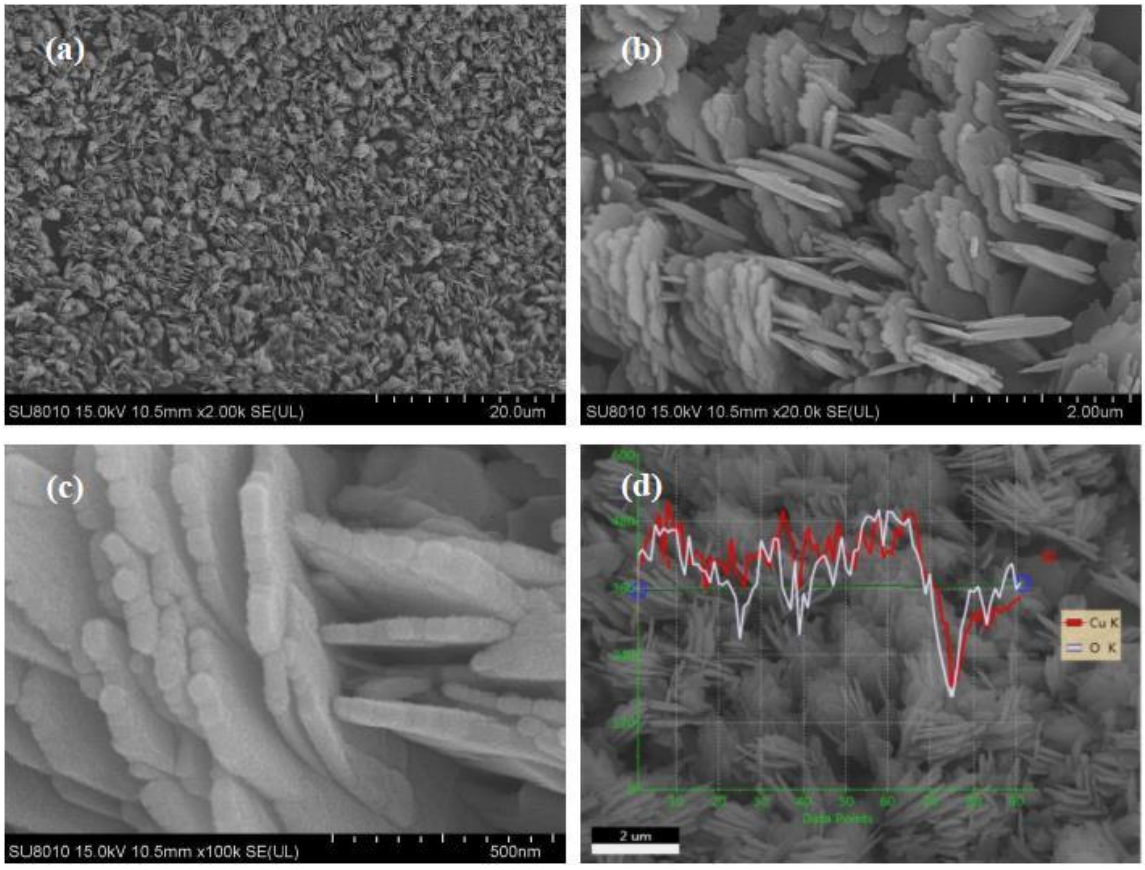

Figure 2. SEM images (a, b, c) and element line-scan of CuO nanoplate array supported on Ni foam

Figure 2a is the low-magnification SEM image of CuO nanoplate array supported on the Ni foam. As can be seen, the surface of the obtained material is very coarse. Figure 2b demonstrates the CuO layer is composed of numerous CuO nanoplates. High-magnification SEM image in Figure 2c reveals that the thickness and the sizes of these nanoplate is about 30-50 nm and 1-2 μm. To analyze the element distribution on the surface of Ni foam, line-scan of elements of Cu and O was carried out on

the surface of the CuO array. Evidently, elements of Cu and O are homogeneously distributed, and the molar ratio is close to 1:1. This further confirms the surface layer on the surface of Ni foam is CuO.

It has been reported that H_2O_2 can significant affect the degradation ratio of organic pollutant by the H_2O_2/CuO process. Figure 3 shows the effects of H_2O_2 dosages on the degradation RhB. In a preliminary experiment, it was found that there is no degradation of RhB in the absence of H_2O_2. This indicates that H_2O_2 plays a crucial role in the degradation of RhB and CuO catalyst itself can not make RhB degraded. In contrast, in the presence of H_2O_2 and CuO, RhB can be effectively degraded. When the H_2O_2 dosage is 0.5 mL in the reaction solution, about 36% degradation ratio can be achieved when the reaction time is 50 min. However, the degradation ratio can reach about 57% at the same reaction time. This demonstrated that a large H_2O_2 dosage is favorable for the degradation of RhB.

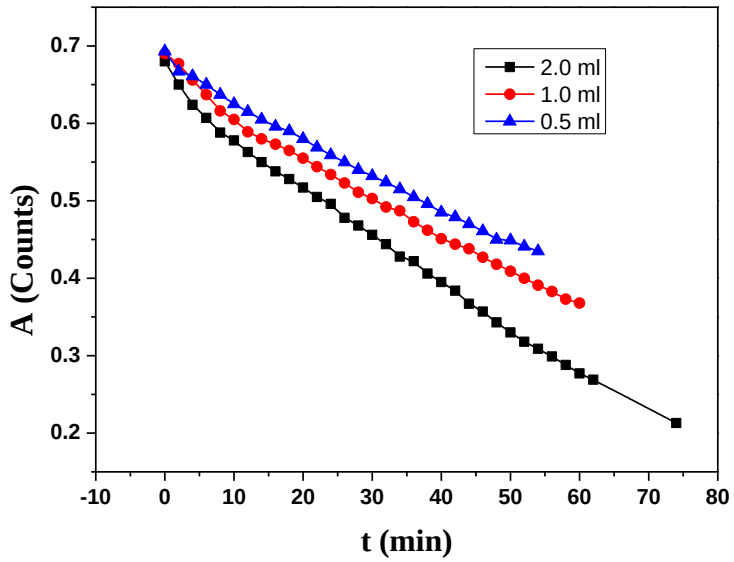

Figure 3. Effects of H_2O_2 dosages on the degradation RhB

Figure 4 shows the degradation of RhB at different reaction temperature. As shown in Figure 4, reaction temperature can remarkably affect the degradation rate of RhB. At temperature of 15°C, the degradation ratio is only about 35% at reaction time of 50 min. In contrast, when the reaction temperature increases to 35°C, about 90% RhB was degraded at the same reaction time. This is understandable because the conversion of H_2O_2 into •OH is accelerated at higher temperature, which is favorable for the degradation of RhB [7].

Considering the practical application, the stability and reusability of the CuO nanostructures are important concerns. In this work, after the catalytic reaction, the CuO nanoplate array supported on Ni foam can be easily separated from the reaction solution. After washing, the recovered CuO film was then re-used in another run of catalytic reaction. In this way, the stability and reusability of the nanostructured CuO film catalyst is investigated. It is found that after 8 catalytic cycles, its activity is almost kept unchanged. The CuO nanoplate array catalyst exhibit significantly improved durability compared with other CuO catalysts in the literature, such as CuO nanopetals (ca. 22% activity decrease after 2 cycles [13]), CuO/activated carbon (ca. 21.5% activity decrease of after 4 cycles [14]), CuO/Al_2O_3 (25.6 % activity decrease after 3 cycles [9]).

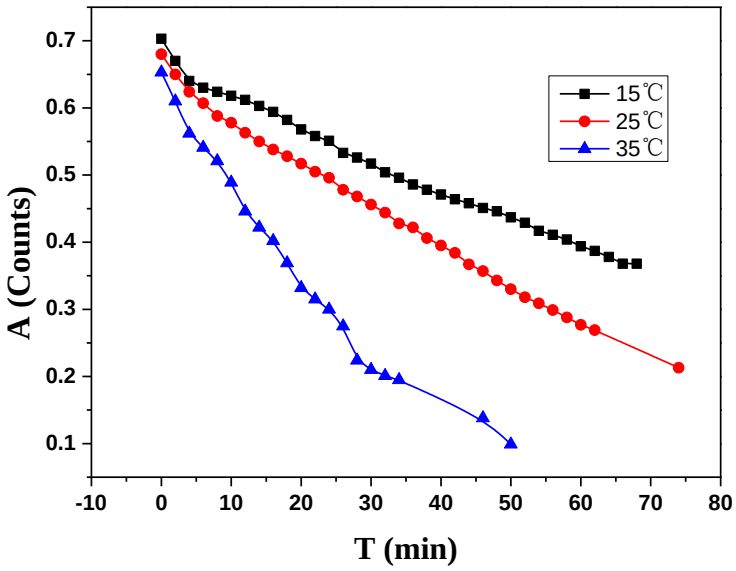

Figure 4. The degradation of RhB at different reaction temperature

4. Conclusions

In summary, CuO nanoplatelet array supported on Ni foam has been prepared by a facile hydrothermal route. Degradation of Rhodamine B (RhB) with H_2O_2 catalyzed by the as-prepared CuO nanocatalyst was investigated. It is found that RhB can be effectively degraded by H_2O_2/CuO. The large H_2O_2 dosage and high reaction temperature is favourable for the fast degradation of RhB. More importantly, our film catalyst has very stability and reusability. After 8 catalytic cycles, its activity is still well maintained.

5. Acknowledgements

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