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Preparation of Polyhedral Copper Oxide Nanoparticles by Molten-salt Method and Their Catalytic Performance

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Abstract: Polyhedral copper oxide (CuO) nanoparticles were successfully prepared by a molten-salt method without any surfactant or template. Scanning electron microscopy images of the copper oxide samples demonstrated that the as-prepared nanoparticles have a polyhedral structure. The catalytic performances of copper oxide on the degradation of Rhodamine B in the presence of hydrogen peroxide were investigated. The results show that the polyhedral copper oxide nanoparticles exhibited much better catalytic performance in the degradation of Rhodamine B with hydrogen peroxide than commercial nano particles, even with smaller specific surface area. The possible reason can be attributed to the synergistic effect of high crystallinity and the exposed facets formed by polyhedral structure.

Key words: CuO; polyhedral; catalyst; nanomaterials

Over the years, more and more attention has been paid to environment problems[1], such as eliminating organic pollutants from wastewater. In the past decade, Advanced Oxidation Processes (AOPs) in which highly reactive hydroxyl radicals (•OH) are formed and result in the oxidative degradation of organics[2], have been considered as promising alternatives for the treatment of organic pollution[3-4].

Among AOPs, CuO/H_2O_2 system has received special attention due to its high efficiency[5-6]. In CuO/H_2O_2 system, the degradation rate of contaminant is highly related to morphology and shapes of the CuO nanocatalysts. So, it is a feasible way to obtain CuO nanocatalysts with high catalytic performance by controlling their morphology during synthesis. According to reports, a number of differently shaped CuO nanomaterials have been successfully prepared[7-8]. However, as far as we know, there is no report about the synthesis of polyhedral CuO nanoparticles and their catalytic applications in the degradation of organic pollutant with H_2O_2 until now. On the other hand, in the synthesis of CuO nanostructures with special morphology, the usages of capping agents will remarkably increase the expenditure of the synthesis. Besides, these capping agents will tightly bind on surface and occupy the active sites of the nanocatalysts, which may bring adverse impact on catalysis. In this regard, preparation of CuO nanocatalysts free of any capping agent is much more attractive. However, to the best of our knowledge, synthesis of CuO nanomaterials with specific morphology free of any capping agents has been seldom documented.

In this study, polyhedral CuO nanoparticles were prepared without the assistance of capping agents by a molten-salt method for the first time. The particle size could be controlled by adjusting the calcination temperature. It was found that the as-prepared CuO nanomaterials show excellent catalytic performance in the degradation of Rhodamine B with H_2O_2, which was much higher than that of recently reported CuO nanocatalyst[6-7].

1 Experimental

In a typical procedure, 0.1 mol $Cu(NO_3)_2{\cdot}3H_2O$ was dissolved in 200 mL distilled water. Then, $NH_3{\cdot}H_2O$ (15wt%) was added to precipitate Cu^{2+} until the pH value of the mixed solution reached in a range from 6.0 to 8.0. With the addition of $NH_3{\cdot}H_2O$, blue precipitation was gradually formed. The resulting mixed solution was fur-

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ther heated at 60℃ for 1.5 h under vigorous stirring. The precipitation was collected and washed successively for several times. After being dried in vacuum oven at 80℃, the blue precipitation was obtained and used as a precursor. The precursor was mixed with KNO_3-$NaNO_3$ at a weight ratio of 45: 55. Herein, the weight ratio of KNO_3-$NaNO_3$ is 1: 1. The above mixture was calcined for 2 h at different temperatures: 450℃, 550℃, 650℃. Then, the resulting products were washed and dried at 80℃ overnight.

In a typical process, 20 mg CuO catalysts were added into 100 mL RhB solution (10 mg/L) under stirring, followed by addition of 2.5 mL H_2O_2 solution (30wt%). Then thermostatic waterbath was used to maintain the reaction temperature at 35℃. During the catalytic process, reaction solution is sampled at different time intervals and its absorption intensity at λ=550 nm was determined using a UV-visible spectrophotometer. To investigate the effect of reaction temperature, the catalytic degradation of RhB was also carried out at 25℃, 45℃, 55℃.

The X-ray diffraction (XRD) pattern was recorded on a Bruker D8 Advance diffractometer using Cu Kα radiation. The morphology of the CuO samples was observed using a JEM-2100F scanning electron microscope. The Brunauer-Emmett-Teller (BET) surface area was determined on a Gemini VII 2390 surface area analyzer.

2 Results and discussion

Figure 1 shows the XRD patterns of the CuO nanoparticles calcined at different temperatures. All of the diffraction peaks of CuO samples can be indexed to monoclinic phase of CuO (ICSD 48-1548). No other possible impurities were detected, indicating the high purity of the as-prepared polyhedral CuO nanomaterials. Notably, the intensity of the peaks increases slightly as the increase of the calcination temperature, giving a hint that the crystallinity of the sample rises when elevating the calcination temperature.

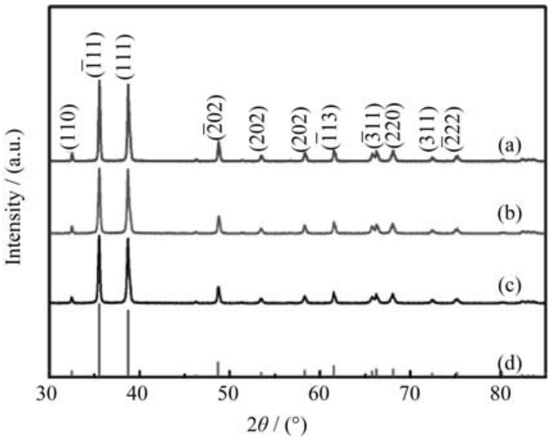

Fig. 1 XRD patterns of the as-prepared CuO nanomaterials calcined at 650℃ (a), 550℃ (b), 450℃ (c) and the standard XRD pattern of monoclinic phase CuO (d)

As shown in Fig. 2, the SEM images of CuO calcined at 450℃ indicate that the particle size is about 100–150 nm. Fig. 2(c) and 2(d) are the SEM images of polyhedral CuO nanoparticles calcined at 550℃. Clearly, the average size of these CuO particles is *ca.* 200 nm, which is larger than that of CuO calcined at 450℃. As can be observed in Fig. 2(e) and 2(f), the particle size of CuO calcined at 650℃ is about 300 nm, which is larger than CuO particles calcined at 450℃ and 550℃. This suggests that the particle size of CuO can be controlled by adjusting the calcinations temperature.

Figure 3(a) demonstrated that the normalized concentration of RhB is *ca.* 0.09, 0.171, 0.325 and 0.65 at the reaction time of 100 min with the CuO calcined at 450℃, 550℃, 650℃ and the commercial CuO nanoparticles, respectively. Obviously, the three samples prepared by molten-salt method exhibit higher catalytic activity than the commercial CuO nanoparticles. As can be seen from Fig. 3, the catalytic degradation reaction follows a pseudo-first-order reaction, the rate constant of the RhB decomposition over CuO (450℃, 550℃, 650℃ and commercial CuO) were estimated *via* the formula

$$\ln(C/C_0) = -\mathrm{k}t$$

In this formula, k is the apparent first order reaction rate constant of RhB degradation. The value of k was obtained by calculating the slope of lines in Fig. 3(b) and the results

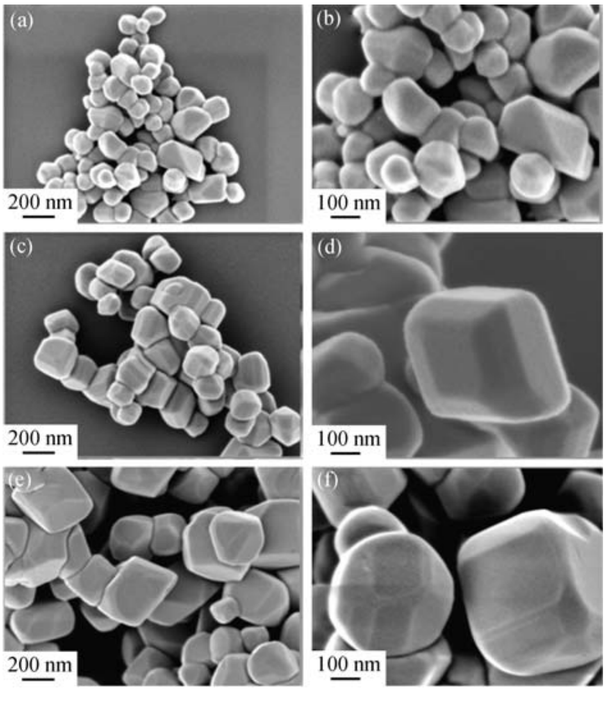

Fig. 2 SEM images of CuO nanostructures calcined at different temperatures

(a) (b) 450℃; (c) (d) 550℃; (e) (f) 650℃

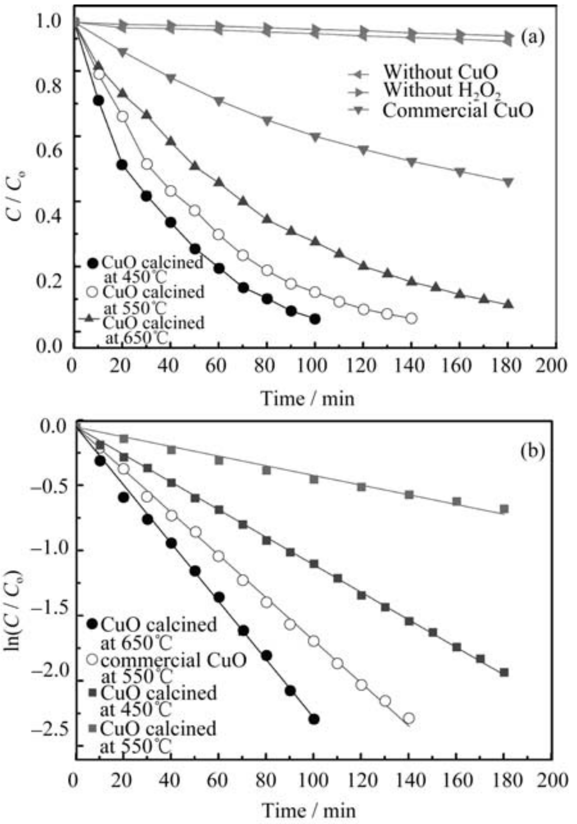

Fig. 3 Normalized concentration of RhB (a) and logarithm of normalized concentration of RhB (b) at different reaction time

are listed in Table 1. For comparison, the BET surface of different CuO catalysts was determined and the corresponding BET surface normalized rate constants was calculated, which are also shown in Table 1.

Clearly, the rate constant of RhB degradation in the presence of the as-prepared CuO as catalyst is much larger than that in the presence of the commercial CuO as catalyst despite that fact that the commercial catalyst has the largest BET surface. This demonstrates that our CuO nanocatalysts exhibit better catalytic activity than the commercial one. It has been demonstrated that the catalytic performance of nanocatalysts is closely associated with their morphology. Because they possess more edges, corners and faces, those shape-anisotropic nanocatalysts can provide more active sites for catalytic reactions. Therefore, the polyhedral CuO nanostructures in our case are supposed to have more active sites for the decomposition of H_2O_2 into free radicals, which will result in relatively high degradation rates of RhB. On the other hand, it is observed that the BET surface of the as-prepared CuO samples decreases when the calcination temperature of samples increases. This is understandable because the particle sizes of polyhedral CuO nanoparticles increase as increasing the calcination temperature of samples, as observed in the TEM images. It is noted that the normalized rate constant is the largest when the CuO nanostructures calcined at 550℃ act as catalyst. This implies that CuO nanostructures calcined at 550℃ exhibit the highest intrinsic catalytic activity among the three CuO samples. As shown in Fig. 2, the shape of CuO nanostructures calcined at 550℃ is more regular than those of the other two samples. It is possible that regular CuO nanostructures possess more active crystal surface for the RhB degradation. The detailed role of the morphology of the as-prepared CuO sample on RhB degradation is interesting but is not well understood, and further investigation is still necessary.

To investigate the effect of temperature on catalytic performance of CuO, in this study, degradation of RhB at 25℃, 35℃, 45℃ and 55℃ is carried out. Like previous report[7], the curves in Fig. 4 indicate that the degradation

Table 1 Specific surface areas of different CuO nanomaterials, rate constants and surface area normalized rate constants in the oxidation of RhB when these CuO nanomaterials used as catalysts

Sample	Commercial CuO	CuO (450℃)	CuO (550℃)	CuO (650℃)
Rate contant/min^{-1}	0.0039	0.0240	0.0176	0.0113
Specific surface area/(m^2•g^{-1})	10.658	4.336	2.589	1.943
Surface area normalized rate constant/(min^{-1}•m^{-2})	0.018	0.277	0.340	0.291

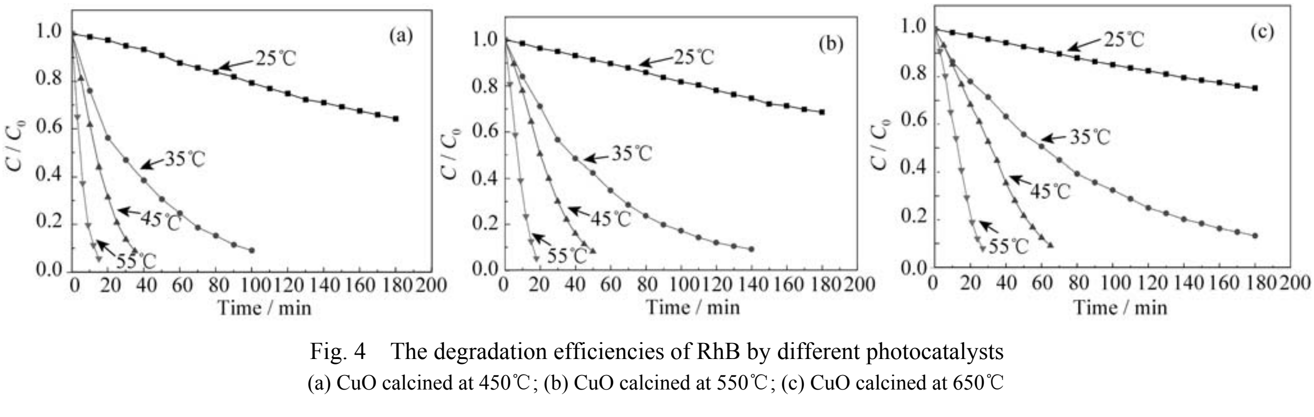

Fig. 4 The degradation efficiencies of RhB by different photocatalysts

(a) CuO calcined at 450℃; (b) CuO calcined at 550℃; (c) CuO calcined at 650℃

rate will rise with increasing reaction temperature. It takes about 20 min to 30 min to degrade RhB completely at 55℃ and the degradation rate is much higher than the other three temperatures. This should be attribute to the fact that the conversion of H_2O_2 into •OH is accelerated at higher temperature[1].

3 Conclusion

In conclusion, polyhedral CuO nanoparticles were successfully synthesized through a facile molten salt method and exhibited much higher catalytic activities on RhB degradation than the commercial CuO nanoparticles. In this study, the factors affecting the catalytic performance were investigated. It was found that grain size, crystallinity, specific surface area, polyhedral structure and temperature in degradation process played key roles in determining catalytic activity.

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熔盐法制备纳米多面体结构氧化铜及其催化性能研究

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摘 要: 在不添加任何表面活性剂及模板剂的情况下用熔盐法制备出纳米氧化铜颗粒, 用扫描电子显微镜观察发现制备的纳米氧化铜呈现多面体结构, 且氧化铜晶粒大小可通过控制合成过程的煅烧温度来控制, 煅烧温度越高则晶粒越大。在 H_2O_2 作用下进行了纳米多面体结构氧化铜催化降解罗丹明 B 的研究。研究结果表明: 与商用纳米氧化铜相比, 该实验制备的纳米氧化铜尽管具有更低的比表面积, 但是其催化性能得到显著的提升。这可能是因为纳米多面体氧化铜的高结晶度及特定指数晶面的暴露所构成的协同作用大幅度提高了其催化性能。

关 键 词: 氧化铜; 多面体; 催化剂; 纳米材料

中图分类号: X703 **文献标识码:** A