

Fabrication of CuO Nanoflakes at Gas-liquid Interface Via Chemical Bath Deposition with High Photocatalytic Activity

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Abstract: Fabricating materials at gas-liquid interface is a kind of novel method and has aroused a great attention. Herein, we introduce a new chemical bath deposition method to fabricate CuO nanoflakes directly at the gas-liquid interface of a solution of CuSO₄ and NH₃·H₂O. The structure and morphology are characterized by X-ray diffraction and scanning electron microscopy. The as-prepared CuO nanoflakes exhibited excellent visible light photocatalytic activity in degradation of RhB in the presence of a little amount of H₂O₂ under tungsten halogen lamp. The method is easily-manipulated, low-cost, environment friendly and promising for the fabrication of micro/nano-structured semiconductor functional materials including the photocatalyst.

1 INTRODUCTION

Copper oxide (CuO) is a typical *p*-type semiconductor with narrow band gap, excellent optical and electronic properties, mechanical stability and has been widely applied in fields of photocatalysis (Du et al., 2019), gas sensors (Hou et al., 2018), supercapacitors (Dong et al., 2016) and so on. Hydrothermal method (Andana et al., 2017), thermal oxidation of metallic Cu (Zhang et al., 2016) were used to fabricate CuO, but both of them were consist of high cost, complicated manipulations. Therefore, exploring a facile method to fabricate CuO was essential.

Surface science has played an important role in chemical research (Borders et al., 2018). Fabrication of materials at gas-liquid interface is an important branch, which has aroused a great attention because of its novelty (Hsieh et al., 2016). Generally, photochemical method (Hoshyarmanesh et al., 2016), self-assembly method (Long et al., 2017) were used to fabricate materials on gas-liquid interface. Compared with above methods, chemical bath deposition (CBD) can fabricate materials with high performance because of its homogeneity, controllability and high production (Yang et al., 2016). However, as far as we know, fabricating materials at gas-liquid interface via CBD has not been reported yet.

In this work, we develop a new chemical bath deposition method to fabricate CuO nanoflakes directly at the gas-liquid interface of a solution of CuSO₄ and NH₃·H₂O. The as-prepared CuO nanoflakes exhibited excellent visible light photocatalytic activity in degradation of RhB. The method is easily-manipulated, low-cost, environmental friendly.

2 EXPERIMENT SECTION

2.1 Materials

CuSO₄·5H₂O (AR, 99%), hydrogen peroxide (AR) and RhB (AR) were purchased from DaMao Chemical Reagent Factory (Tianjin, China). Ammonia (AR) was purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China).

2.2 Preparation of CuO Nanoflakes

The CuO nanoflakes were prepared by CBD method. A typical procedure is described as following: Firstly, 2.5 g of CuSO₄·5H₂O was dissolved in 200 mL of distilled water in a beaker. Secondly, 8 mL of 25% ammonia solution was gradually dropped into the mixed solution by a pipette and a piece of filter paper was put at the bottom of the beaker. The mixed solution was heated at 90 °C in a water bath. CuO

nanoflakes could form at the gas-liquid interface after 1 hour. The product was picked up by a glass sheet and washed by distilled water, following by drying at 60 °C for 12 hours. The dried product was finally ground into powder before storage.

2.3 Materials Characterization

The morphologies of CuO nanoflakes were investigated via scanning electron microscopy (SEM, Carl Zeiss Gemini 500). The chemical composition was characterized via X-ray powder diffraction (XRD, BRUKER D8 ADVANCE D/max2200, with Cu-K α radiation) in which the diffraction peaks and the indices of crystallographic plane were characterized by MDI Jade 6.5. The UV-Vis diffuse reflectance spectra (DRS) of all samples were measured with Shimadzu UV-2700 spectrophotometer.

2.4 Measurement of Photocatalytic Activity

Firstly, 0.025 g of as-prepared CuO nanoflakes catalyst was added in 100 mL of RhB aqueous solution in a beaker and the solution was ultrasonic treated until the catalyst was dispersed and 4 mL of 3% H₂O₂ was added. The mixture was sequentially stirred for 30 minutes in dark in order to achieve absorption equilibrium. Secondly, two 150 W commercial tungsten halogen lamps with 420 nm cut-off filter were employed as visible light source and a condenser pipe was immersed into the solution to keep the photocatalytic reactions occur at room temperature. Thirdly, 5 mL of mixed solution was taken out every 20 minutes from beaker and centrifuged at a speed of 4000 r/min for 2 minutes to remove any solids after the photocatalytic reaction started. The absorbance of the clarified liquid was measured by UV-Vis spectrophotometer (SP-752, Shanghai Spectrum, China) at a wavelength of 553 nm, which is consistent with the maximum absorption wavelength of RhB. The photodegradation rate η (%) was calculated by the following formula:

$$\eta = C_t / C_0 \times 100\%$$

where η is the photodegradation rate (%), C_0 is concentration of RhB after the absorption, and C_t is concentration of RhB at time t during photocatalytic reaction.

3 RESULTS AND DISCUSSION

3.1 Composition and Morphology Characteristic

Figure 1A shows the XRD pattern of CuO formed at the gas-liquid interface. Diffraction peaks at 35.5°, 38.7° and $2\theta=58.0^\circ$ correspond to the (002), (111) and (202) planes of tenorite CuO (JCPDS card No. 48-1548) (Ahmadi and Siadati, 2018). The high intensity of the peaks reveals that the CuO has high crystallinity. No other diffraction peaks were observed in the XRD pattern, meaning that the as-fabricated sample had high purity. Figure 1B shows the morphology of the as-fabricated CuO nanoflakes. It could be clearly observed that the sample was composed of uniform and rhombus nanoflakes, which was corresponding to its tenorite crystal system mentioned above and their average thickness was 20 nm.

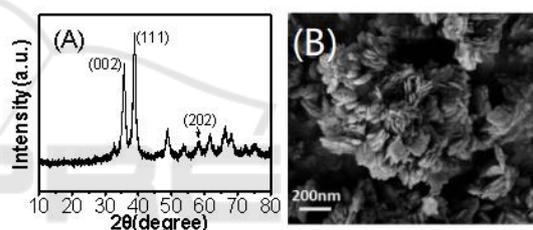
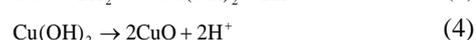
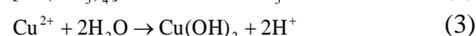
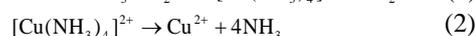
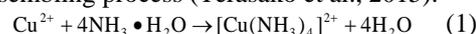


Figure 1: XRD spectrum (A) and SEM image (B) of CuO nanoflakes.

3.2 Growth Mechanism

Briefly, when ammonia was added into the CuSO₄ solution, it could combine Cu²⁺ ions by coordination action to gradually produce [Cu(NH₃)₄]²⁺ ions (Eq. 1). During the subsequent CBD process, the ions would gradually transformed into CuO (Eqs. 2-4). The gas-liquid interface acts as a special nucleation site which induces the formation of CuO nanoflakes by a self-assembling process (Terasako et al., 2015).



3.3 Photocatalytic Activity

To analyze the photocatalytic activity of CuO nanoflakes (CuO flake), the degradation reactions of RhB after the addition of CuO nanoflakes commercial CuO powder (C-CuO), P25 with H₂O₂

and pure H₂O₂ without catalyst were observed and the degradation rate of RhB were calculated and compared. Before the reaction, the catalysts were added into RhB aqueous solution and the solution was ultrasonic treated until the catalyst was well dispersed. The mixture was then kept in dark for 30 minutes to build an absorption-desorption equilibrium. The result indicated that the sample nearly had no discernible adsorption for the RhB aqueous solution. The results of degradation rate of RhB in 90 minutes were shown in Figure 2A. The RhB aqueous solution with CuO flake catalyst and 3% H₂O₂ added had obtained excellent photodegradation rate and the corresponding value could reach 85.9%, while the solutions with C-CuO and P25 had degradation rate of 65.9% and 59.3%, respectively. Furthermore, concentration of RhB aqueous solution was almost constant when pure H₂O₂ was added, which reveals that pure H₂O₂ had poor activity. The curve of apparent reaction rate (ARR) constant of CuO nanoflakes, C-CuO, P25 with H₂O₂ and pure H₂O₂ added in RhB aqueous solution and the corresponding ARR constant were calculated and plotted in Figure 2B. It could be obviously observed that the curve of ARR constant followed the pseudo-first-order kinetics. The corresponding equation was suggested as followings: $\ln(C_0/C_t) = kt$ (Sudrajat et al., 2018), where k represents the apparent reaction rate (ARR) constant. The corresponding ARR constant of catalyst was 0.0218 min⁻¹ for CuO nanoflakes, 0.0119 min⁻¹ for C-CuO, 0.0100 min⁻¹ for P25, and 0.0001 min⁻¹ for pure H₂O₂.

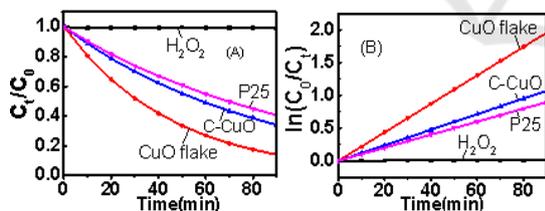


Figure 2: The photocatalytic activities of CuO nanoflakes, commercial CuO powder, P25 with H₂O₂ and pure H₂O₂ without catalyst (A) The degradation rates of RhB in 90 minutes; (B) The curve of apparent reaction rate (ARR) constant of CuO nanoflakes, C-CuO, P25 with H₂O₂ and pure H₂O₂ without catalyst.

3.4 Mechanism of Photocatalysis

The optical property of CuO nanoflakes was measured by ultraviolet-visible (UV-Vis) diffuse reflectance spectra (DRS) and the result was shown in Figure 3A. It can be observed in Figure 3A that the absorption edge of the pure CuO sample is at wavelength of about 725 nm and the corresponding

energy band gap (E_g) is ~1.71 eV. The DRS results indicate that CuO nanoflakes possessed narrow band gap, which lead to higher photocatalytic activity. In order to determine the effect of hole (h⁺), hydroxyl radical (·OH), superoxide radical (·O₂⁻), we additionally drop methanol, which was used as h⁺ scavenger and t-butanol, which was used as OH scavenger into the RhB aqueous solution, also, pure nitrogen, which was considered as ·O₂⁻ removal agent was bubbled through the RhB aqueous solution in the control photocatalytic experiments. As shown in Figure 3B, compare with the solution without any scavenger, the addition of methanol or t-butanol had almost completely prevented the degradation of RhB, while pure nitrogen was bubbled through the solution, the degradation rate of RhB was obviously decreased. Therefore, as Figure 3C indicated, holes and electrons were generated when the semiconductor was irradiated by UV light or visible light, during the reaction, the photo-generated electrons react with dissolved oxygen and thus lead to the generation of superoxide radicals, the superoxide radicals further react with photo-generated holes, H⁺, to form hydroxyl radicals. Furthermore, the hydroxyl radicals, which are conducive to the degradation of RhB, are generated by the reaction of H₂O₂ and photo-generated electrons or superoxide radicals (Wang et al., 2016, Li et al., 2018) and the reaction of photo-generated holes and H₂O (Huang et al., 2015, Ma et al., 2018, Zhang et al., 2012).

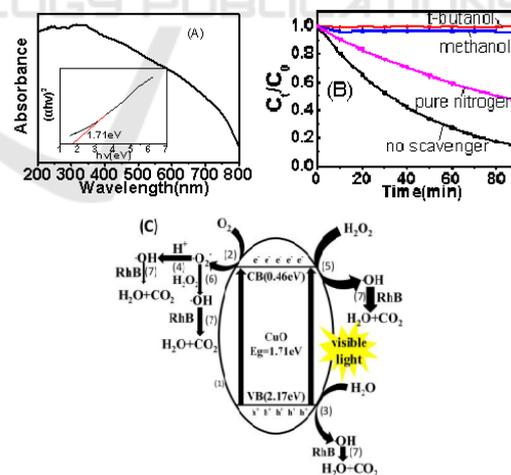


Figure 3: (A) UV-vis diffuse reflectance spectra (DRS) and band gap energy(inset) of CuO nanoflakes; (B) Photodegradation dynamics of the RhB aqueous solution in the presence of CuO nanoflakes, H₂O₂ and t-butanol, CuO nanoflakes, H₂O₂ and methanol, CuO nanoflakes, H₂O₂ and pure nitrogen, CuO nanoflakes and H₂O₂, respectively; (C) Schematic of proposed mechanism of the RhB aqueous solution degradation in the presence of CuO nanoflakes and H₂O₂.

4 CONCLUSIONS

In summary, CuO nanoflakes at gas-liquid interface was fabricated by a facile CBD method. The product was composed of uniform and rhombus nanoflakes with high crystalline. The CuO nanoflakes exhibited excellent photocatalytic activity with the addition of H₂O₂ and the corresponding photodegradation rate was 85.9%. The results indicated that fabricating materials on gas-liquid interface via chemical bath deposition was a promising method.

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