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Hydrogen peroxide-assisted synthesis of novel three-dimensional octagonal-like CuO nanostructures with enhanced visible-light-driven photocatalytic activity

Xiangyu Chen [a, b], Deqing Chu [a, b, *], Limin Wang [a, c, **], Wenhui Hu [b], Huifang Yang [b], Jingjing Sun [c], Shaopeng Zhu [b], Guowei Wang [c], Jian Tao [b], Songsong Zhang [b]

[a] State Key Laboratory of Separation Membranes and Membrane Processes, Tianjin, 300387, PR China
[b] College of Environment and Chemical Engineering, Tianjin Polytechnic University, Tianjin, 300387, PR China
[c] School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin, 300387, PR China

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ABSTRACT

Novel three-dimensional octagonal-like CuO micro-/nanostructures with diameters ranging from 10 to 15 μm have been successfully prepared by hydrogen peroxide-assisted hydrothermal method and subsequent calcination. The product morphology can be changed by simply ordering the amount of hydrogen peroxide (H_2O_2). When the amounts of H_2O_2 is increased, the length of the corner portion is increased and the width is narrower. The obtained octagonal CuO nanostructures were evaluated for their ability for the degradation of hazardous organic contaminants in water under visible-light irradiation. Comparing with commercial CuO and other CuO products, the CuO octagonal nanostructures exhibit excellent performance for photocatalytic decomposition of RhB (Rhodamine B). It is well established that effective photocatalytic performance results from its unique 3D octagonal nanostructures. We believe that the present work will provide some ideas for further fabrication of other novel nanostructures and exploration of their applications.

1. Introduction

Cupric oxide is an important p-type semiconductor metal oxide, the band gap between 1.21 eV and 1.51 eV. In recent years, CuO has gained increasing attention [1] due to its potential applications, such as gas sensors [2], photocatalysts [3], lithium ion electrode materials [4], field emission emitters [5], superconductors' devices [6] etc. Most importantly, photocatalysis is a relatively important degradation of organic contaminant in aqueous solutions [7]. The properties of CuO are closely related to its micro-/nanostructures, crystal size, crystallographic forms, and morphology in particular. As a result, considerable attention has been paid to the development of micro/nano-scale inorganic materials with novel and unusual morphology. So far, a variety of CuO micro-/nano-structures with different morphologies such as nanospheres [8], nanoflowers [9], nanowires [10], nanorings [11], nanoplates [12], and nanorods [13], have been triumphantly synthesized. As far as we know, there are a few reports on the synthesis of 3D micro-/nanostructures octagonal-like CuO with the hydrogen peroxide (H_2O_2) assisted. Typically, RhB is a typical hazardous organic pollutant in the water discharged to the environment, resulting in contamination and odor of drinking water. The release of colored and toxic wastewaters in the ecosystem is a part of the non-aesthetic pollution, eutrophication and daily activities that affect aquatic life. Therefore, there is an urgent need to find a way to reduce the cost-effectiveness of organic pollutants in water. Fortunately, photocatalytic technology has proven to be an efficient pathway to degrade these organic contaminants [14–19].

In this study, we reported a simple method for large-scale synthesis of 3D octagonal-like CuO nanostructures by hydrothermal-calcination technique. Hydrogen peroxide plays an extremely important role in the shape of the product. In addition, the morphology of CuO nanostructures can be changed by simply

* Corresponding author. State Key Laboratory of Separation membranes and Membrane Processes, Tianjin, 300387, PR China.
** Corresponding author. State Key Laboratory of Separation membranes and Membrane Processes, Tianjin, 300387, PR China.
E-mail addresses: dqingchu@163.com (D. Chu), wanglimin@tjpu.edu.cn (L. Wang).

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adjusting the amount of H_2O_2. When discussing potential applications, the octagonal-like CuO prepared exhibits excellent photocatalytic activity for RhB aqueous solution under the visible light illumination due to its special octagonal structures. Meanwhile, the octagonal-like CuO photocatalysts shows good stability and reusability of visible light degradation of RhB.

2. Experiment

In a typical synthetic method, 2 mmol of copper acetate and 0.2 mmol of sodium dodecyl sulfate (SDS) were first added to 20 mL mixed solvent (the volume ratio of ethylene glycol to deionized water R = 2:3) for 15 min with a vigorous stirring at room temperature to form the homogeneous solution A. Then, 2 mmol of urea was added to 20 mL of the above mixed solvent and stirring was continued for 15 min to form Solution B. After that, 0.5 mL of hydrogen peroxide was added dropwise into the solution A for continuous stirring 10 min. Next, the solution B was quickly poured into the mixed solution while stirring was continued for 10 min. The solution was then placed in a 50 mL Teflon-lined stainless steel autoclave. After sealing, the autoclave was held at 160 °C for 6 h. Then cooled to room temperature. The mixture was centrifuged, washed with absolute ethanol and distilled water for several times, and dried under vacuum at 60 °C for 6 h. In order to prepare the octagonal-like CuO nanostructures, the resulting precipitate was calcined at 750 °C for 2 h. The product is called OC-3. When the amount of H_2O_2 was 0.1 mL, 0.3 mL and 0.8 mL, the CuO samples were labeled as OC-1, OC-2 and OC-4, respectively.

The photocatalytic tests were carried out by adding 100 mg of the CuO sample to 100 mL of an RhB aqueous solution at a concentration of 10 mgL^{-1}. The suspension was stirred in the dark conditions for 30 min to obtain adsorption equilibrium. Then, the suspension was irradiated with a 300 W Xe lamp as a light source. Cut-off filters were used in these experiments. The concentration of RhB was then measured by UV–vis spectrophotometer. The rate of degradation of the contaminant is reported as $(C_0\text{-}C)/C_0$, where C_0 is the concentration prior to irradiation and C is the concentration of any sampling time.

3. Result and discussion

This experiment used a thermal decomposition method to prepare CuO by calcining a precursor [20]. Fig. 1a presents SEM images of the prepared uniform octagonal-like CuO nanostructures (OC-3). The general form of the product is showed in Fig. 1a, indicating the high yield and uniformity. The close-up observation of the enlarged SEM image showing the microstructures is displayed in Fig. 1b, which reveals that the detailed morphology of the product is a well-defined octagonal-like structure with an average diameter of 10–15 μm. The crystal phase of the CuO product was characterized by XRD, and the data is shown in Fig. 1c. The curve shows the typical XRD pattern of the as-synthesized product, which can be indexed well as the octagonal monoclinic phase of CuO (JCPDS No. 48–1548) [21]. As a result, it was concluded that no peaks for other crystal phases such as Cu_2O or $Cu(OH)_2$ were observed except for the peak of CuO. Thus, it can be shown that the formation of highly pure and highly crystalline octagonal-like CuO. The elemental composition and chemical status were analyzed by XPS. Fig. 1(d, e and f) shows XPS spectra of octagonal-like CuO nanostructures. The peaks at 934.2eV and 954.4eV in the Cu 2p region (Fig. 1e) are attributed to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. The presence of Cu 2p with strong satellite characteristics at 944.4 eV and 963.1 eV precludes the possibility of the presence of Cu_2O phase. Fig. 1f shows the O 1s spectrum. The binding energy at 530.1eV corresponding to O 1s is attributed to Cu-O. The XPS

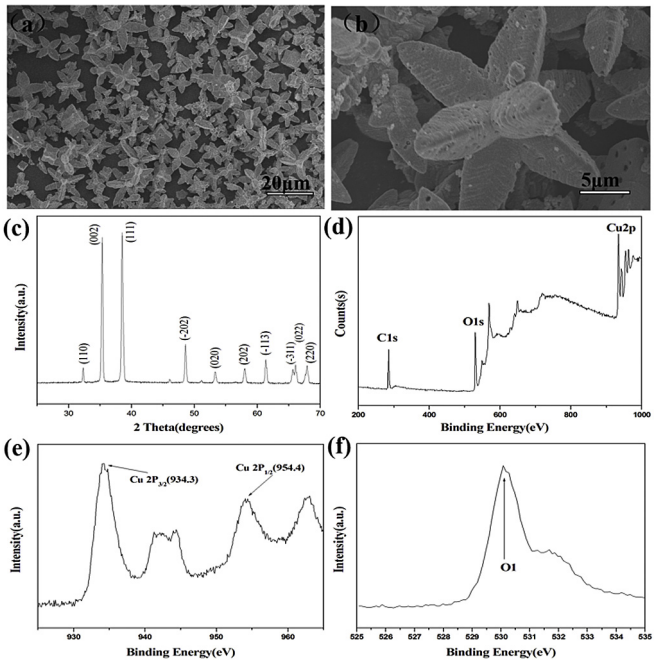

Fig. 1. (a) and (b) SEM images of the as-synthesized octagonal-like CuO (OC-3); (c) XRD pattern; (d) XPS survey spectrum; (e) XPS spectra of Cu2p region; (f) XPS spectra of O1s region.

analysis strongly suggests that there is no Cu_2O and $Cu(OH)_2$ impurity in the sample [22]. All of these species were confirmed from XRD and XPS. Hence, we concluded that octagonal-like CuO nanostructures has been successfully synthesized.

Experiments were conducted to investigate the effect of the amount of H_2O_2 in the experiment. Fig. 2(a,c and e) show the morphology evolution of octagonal-like CuO micro-/nanostructures prepared by using different amounts of H_2O_2. In the

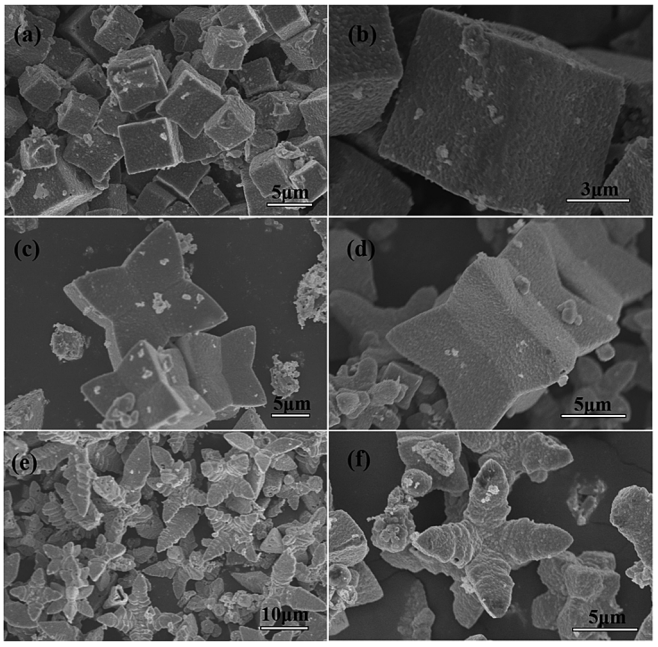

Fig. 2. The SEM images of the as-prepared CuO microstructures in different concentration of H_2O_2: (b). OC-1; (d). OC-2; (f). OC-4. ((a), (c) and (e) are precursor respectively).