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Synthesis of cuprous oxide with morphological evolution from truncated octahedral to spherical structures and their size and shape-dependent photocatalytic activities

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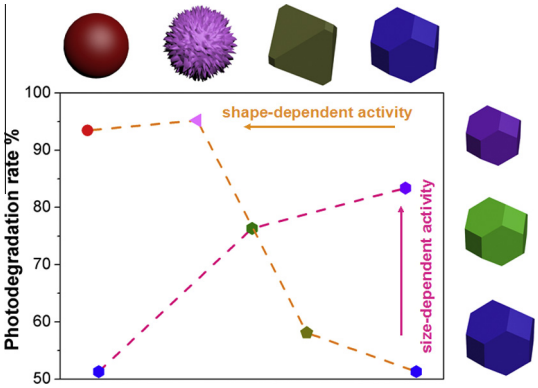
GRAPHICAL ABSTRACT

Cu_2O truncated octahedrons with different sizes, spiny spheres and spheres have been fabricated by varying the addition rates of aqueous mixture of polyvinyl pyrrolidone (PVP) and ascorbic acid (AA). The size and shape-dependent photocatalytic activities were also investigated.



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ABSTRACT

In this study, a facile room-temperature solution-chemical route has been developed to synthesize Cu_2O crystals with various sizes and morphologies. Adjustment of feeding speed of the aqueous mixture of polyvinyl pyrrolidone (PVP) and ascorbic acid (AA) enables the Cu_2O crystal morphology and size evolution. It is also interesting to find that, simple alteration of the feeding speed of AA aqueous solution enables the size of Cu_2O crystals evolved, while the morphology of Cu_2O crystals keep unchanged. These Cu_2O crystals samples were used as photocatalysts for the decomposition of methyl orange (MO) under visible light irradiation. The results show that Cu_2O spiny spheres with hierarchical structure exhibited superior photocatalytic activity compared with truncated octahedrons and spheres. In addition, the photocatalytic activity of truncated octahedral Cu_2O can be greatly improved by decreasing the size of Cu_2O particles. The work demonstrated a novel strategy for the shape and size-controlled synthesis of Cu_2O crystals with superior photocatalytic activities.

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1. Introduction

Due to the structure–morphology–property relationship of the nano- or micro-materials, engineering the shape of materials to desirable morphology has long been positively pursued [1]. In recent years, to enhance the materials' properties such as photocatalytic activity, gas sensing, lithium ion battery, supercapacitor and thermoelectricity, lots of the art of morphology controlled chemical synthesis methods have been developed. Particularly, controllable synthesis of semiconductors has attracted significant interest for both fundamental research and technical applications, because of their strong morphology- or size-dependent properties and excellent properties such as photocatalytic activity [2]. Several classical models for shape control have been studied including thermodynamic theory, selective-adsorption model, effective-monomer model, oriented-attachment model and molecular template theory [3], and there are a lot of corresponding synthesis methods were reported [4–9].

Cuprous oxide (Cu_2O), a typical p-type semiconductor with a band gap of 2.17 eV, has drawn considerable attention in the field of solar energy conversion, electrode materials, sensors and catalysis [10–17]. In recent years, because the physical and chemical characteristics of the nano- or micro-materials strongly depend on their size and shape, many efforts have been endeavored to develop effective strategies to synthesize Cu_2O crystals with different morphologies and sizes, such as cubes, spheres, octahedra, and rhombic dodecahedra [18–24]. For instance, Xu et al. [18] reported a facile room-temperature surfactant-free solution-chemical route for the synthesis of Cu_2O nanocrystals with shape evolution from nanocubes, octahedrons, spheres, plates to polyhedrons by varying the reaction atmosphere and reducing agent. Huang et al. [19] prepared a series of Cu_2O nanostructure with systematic shape evolution from cubic to rhombic dodecahedral by varying the amount of $NH_2OH{\cdot}HCl$ which added into the reaction system. Li et al. [20] found that flower-like Cu_2O architectures can be obtained in the presence of ionic liquid ($[BMIM]BF_4$) with the assistance of microwave irradiation. Despite of these progresses, it is still desirable and quite challenging to develop a facile method for the controllable synthesis of Cu_2O crystals as well as for the study of their shape- or size-dependent photocatalytic performance.

In this study, we have demonstrated a facile solution-chemistry method to synthesize Cu_2O crystals with various morphologies and sizes. Cu_2O truncated octahedrons with different sizes, spiny spheres and spheres have been fabricated by simply varying the addition rates of aqueous mixture of polyvinyl pyrrolidone (PVP) and ascorbic acid (AA). It is interesting found that, simple alteration of the feeding sequence of the PVP and AA generated Cu_2O truncated octahedrons with different sizes. The as-prepared Cu_2O crystals have been employed as efficient photocatalysts in the degradation of methyl orange (MO) under visible light irradiation. The Cu_2O spiny spheres with hierarchical structure exhibited superior photocatalytic activity compared with the other Cu_2O crystals, demonstrating the importance of the shape- or size-control of the semiconductor photocatalyst.

2. Experimental section

2.1. Synthesis of Cu_2O crystals

All chemical regents used in this experiment were of analytical grade and used as received without further purification after purchase from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used throughout this study and all experiments were conducted at room temperature.

In a typical procedure, under constant stirring, 40 mL of 1 M NaOH was adding in a dropwise manner into 40 mL of 0.15 M $CuCl_2$ solution, and then blue $Cu(OH)_2$ precipitate were immediately produced. After stirring for 15 min, 1.408 g of ascorbic acid (AA) and 2 g of polyvinylpyrrolidone (PVP) mixed aqueous solution (60 mL) were dropped into it under constant strong stirring, at different adding rate of about 0.3, 0.9, 1.5, 1.8, 3 and 4 mL/min, respectively. The resulting mixture was stirring for 30 min, and then the precipitates were collected through centrifugation and washed three times with deionized water and absolute ethanol, respectively. The final samples were dried in vacuum at 45 °C for 8 h. The final products, which were fabricated by adding PVP and AA mixed solution into $Cu(OH)_2$ suspension with different adding rate of about 0.3, 0.9, 1.5, 1.8, 3 and 4 mL/min, were labeled as S-0.3, S-0.9, S-1.5, S-1.8, S-3 and S-4, respectively. To investigate the influence of addition sequence on the size and morphology of Cu_2O crystals, the contrast experiment was also conducted. In the contrast experiment, PVP was first added into $Cu(OH)_2$ slurry and then AA aqueous solution was added into the mixture of PVP and $Cu(OH)_2$ slurry at a rate of about 0.3 and 3 mL/min, while the other experimental conditions are kept the same. The as-obtained samples were labeled as C-0.3 and C-3, respectively.

2.2. Characterization

The phase purity and crystal structure of the prepared samples were examined by X-ray diffraction (XRD) recorded on a D8 Advance X-ray diffraction (Bruker axscompany, Germany) with a Cu anode as the X-ray source, employing a scanning rate of $0.02^\circ\ s^{-1}$ in the 2θ range from 10° to 80°. Scanning electron micrograph (SEM) images were obtained using a field emission SEM (FESEM) instrument (Hitachi S-4800 II, Japan). Transmission electron microscopy (TEM) was done on a JEOL-JEM-2010 (JEOL, Japan) operating at 200 kV. UV–vis diffuse reflectance spectra (DRS) was recorded on a Shimadzu UV-2401 spectrophotometer equipped with spherical diffuse reflectance accessory.

2.3. Evaluation of photocatalytic performance under visible light

The photocatalytic activity of the as-prepared Cu_2O samples for the degradation of MO was evaluated under visible light irradiation ($\lambda > 420$ nm). A 300 W xenon lamp was used as a light source with a 420 nm cutoff filter to provide visible light illumination. All experiments were conducted at room temperature in air. In each experiment, 50 mg of Cu_2O powder was added into 50 mL of MO solution (15 mg/L^{-1}). Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min in order to reach an adsorption–desorption equilibrium of MO on the Cu_2O surface and then exposed to visible-light irradiation. 4 mL of the suspensions were collected and centrifuged (8000 rpm, 10 min) to remove the Cu_2O particles. Then the catalyst-free MO solution was detected using a UV–vis spectrophotometer.

3. Results and discussion

3.1. Structure and morphology

Fig. 1 shows the XRD patterns of the as-obtained Cu_2O crystals, where all the recorded peaks can be indexed to the cubic phase Cu_2O (JCPDS card No. 05-0667) with no impurity such as cupric oxide or metallic copper. The strong and narrow diffraction peaks show that all the obtained products are highly crystalline. The results indicate that highly crystalline Cu_2O can be fabricated by the present synthetic condition.