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Large-scale and green synthesis of octahedral flower-like cupric oxide nanocrystals with enhanced photochemical properties

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ABSTRACT

In this work, a large-scale and green method is reported for the facile synthesis of octahedral flower-like CuO nanocrystals via a coordination-deposition route by using Fehling regents. Not any harmful organic chemicals were used during the reaction period. The obtained hierarchical nanostructure can be rationally tailored by varying the concentration of tartrate ions and reaction time. The typical flower-like CuO nanocrystals in the range of 200–250 nm are consisted of numerous small crystalline whiskers, which present a porous surface with a specific surface area of 32.12 m^2/g and a narrow band gap of 1.5 eV. Importantly, the flower-like CuO nanocrystals show an enhanced photocatalytic activity toward decomposing Rhodamine B (RhB) molecules. The degradation rate is about 87.9% in 40 min under visible light irradiation, which is about 2.5 times for the commercial CuO powers (35.2%). Moreover, the uniform flower-like monolayered CuO film exhibits an excellent photoelectrochemical (PEC) performance with a maximum photocurrent density of 58.8 $\mu A/cm^2$, which is nearly five times higher than the commercial CuO film. This novel synthesis approach provides a large-scale and green protocol for synthesizing hierarchical metal oxide nanocrystals that are useful for photocatalysis, PEC water splitting and photovoltaic device.

1. Introduction

Hierarchical micro/nanostructured metal oxide nanocrystals have attracted much attention because of their unique structure-dependent physical and chemical properties that make them promising materials in a wide range of applications, such as dye-sensitized solar cells [1], gas sensors [2], water splitting [3], photocatalysis [4], Lithium-ion battery [5], and optoelectronics [6]. Flower-like hierarchical metal oxide nanocrystals specially stimulate great interest due to their charming morphology and potential applications [7]. However, the synthesis of such morphological materials often involves multiple complicated procedures, harsh reaction conditions, and especially the very little amount of productions. Therefore, developing facile and green aqueous-chemical routes for the large-scale synthesis of high-quality flower-like metal oxide nanocrystals have attracted more and more research interest.

As a p-type semiconductor with a narrow band gap (1.2–1.5 eV), CuO has received considerable interest because of its inexpensiveness, high stability, and nontoxicity. It has been widely used in many fields including catalysis, gas sensors, and electrochemistry [8–10]. The hierarchical micro/nanostructured CuO nanocrystals with different shapes such as nanowires [11], nanoribbons [12], urchins [13], cotton [14], flowers [15], honeycomb [16], hollow [17], and core–shell structures [18] have been designed and synthesized by solution-based methods, vapor-phase routes, thermal decomposition processes, hydrothermal methods, and natural oxidation processes, etc. Typically, Liu and Zeng [12] reported the self-organization of CuO hierarchical microspheres with a puffy appearance. Liu et al. prepared the porous CuO hollow architectures based on a non-equilibrium interdiffusion process [19]. Zhu et al. synthesized hierarchically porous CuO architectures via a facile hydrothermal route [20]. Xia and co-workers described a vapor-phase approach for the synthesis of hierarchically uniform CuO nanowire array on various copper substrates [11]. Although great progresses have been achieved in the preparation of hierarchical CuO nanocrystals, it remains a great challenge to develop a facile and green method for the large-scale synthesis of uniform CuO nanocrystals with hierarchical micro/nanostructures.

In this study, we report a facile method for the large-scale synthesis of hierarchical octahedral flower-like CuO nanocrystals via a coordination-deposition technique using Fehling agents, which are often used to synthesis of Cu_2O nanocrystals [21,22]. However, Fehling regents have not been reported in previous literatures for the synthesis of uniform flower-like CuO nanocrystals up to

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now. The source materials used in the synthesis are common inorganic salts without involving complex molecular precursors, and harmful organic chemicals. Importantly, such hierarchical nanostructures can be obtained in a volume range from 40 mL to 2.5 L just by tailored reaction time. Tartrate ions in the Fehling regent play important roles for controlling the morphology of CuO nanocrystal. Moreover, the as-prepared novel nanocrystals exhibit an enhanced photocatalytic activity toward degradation of RhB molecules. Also we used an oil–water interfacial self-assembly method for the first time to assemble the uniform mono- and multilayer flower-like CuO film as the photo-anode. And the uniform CuO film presents obviously enlarged photoelectric property compared to the deposited CuO film. This work might provide a facile, green and large-scale protocol for the synthesis of other uniform metal oxides with hierarchical superstructure.

2. Experimental

2.1. Large-scale and green synthesis of octahedral flower-like CuO nanocrystals

All agents were of analytical grade and used without further purification. The precursor Fehling solutions were first prepared in two separate containers. Fehling A: 500 mg copper (II) sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$; Sinoreagent) was dissolved in 1 L of H_2O to form a 2 mM aqueous solution. Fehling B: 560 mg NaOH (Sinoreagent) and 3.68 g potassium sodium tartrate (Sinoreagent) were sequentially putted into 1 L of water to obtain a clear solution (14 mM and 16 mM, respectively). Then 20 mL Fehling A was mixed with 20 mL Fehling B to form a light-blue solution under magnetic stirring in a glass vial, which was then sealed and heated at 95 °C in an electric oven for 120 min. The color of the mixed solution gradually changed to dark-brown, indicating the reaction occurred at that condition. For enlarging synthesis of the product, different volumes of Fehling' solutions were performed at that temperature for a wide time range. Detailed experimental parameters were shown in Table S1. The product was collected by centrifugation at 8000 rpm for 10 min after reaction, and then washed with ethanol and distilled water for six times to get rid of the impurities. The obtained product was then dried at 60 °C in air for overnight. 190 mg dried product was isolated for a growth solution of 2.5 L total volume with an average yield of 95%. At last, the products were annealed at 400 °C for 2 h in the furnace for improving its crystallization.

2.2. Interfacial assembly of ultrathin CuO nanoflower

The ordered flower-like monolayer was prepared by an interfacial assembly technique described in the previous report [23]. The freshly prepared flower-like CuO nanocrystals were redispersed in 10 mL distilled water to form a homogeneous solution at room temperature (4 mM). After that, a mixture of 7 mL of N,N-dimethylformamide (DMF) and 26 mL of $CHCl_3$ were added into the glass mortar. Then, 5 mL of cupric oxide dispersed solution was added into the mixtures drop by drop with syringe above 5 mm of the liquid surface under magnetic stirring at 60 rpm. After 3 min, a dense, uniform and transparent CuO monolayer was formed at the oil/water interface. The ultrathin film was then transformed onto the cleaned FTO conductive glass (1 × 1.5 cm, washed in acetone, ethanol and chloroform under ultrasonic for 30 min and dried with nitrogen gas flow) by the horizontal dipping technique. The uniform CuO monolayer was dried at 60 °C in electric oven for 3 min. For deposition of multilayer uniform CuO nanoflower film, the dried CuO film on FTO glass was used as substrate for transforming the next monolayer from the oil/water interface. The operation process was repeated several times until obtaining the desired numbers.

2.3. Photoelectrochemical measurements

The photoelectrochemical tests were performed on an electrochemical workstation (CHI 760D) with the synthesized flower-like CuO nanoparticles as the working electrode, saturated Ag/AgCl as the reference electrode, and platinum foil (1 × 2 cm) as the counter electrode to study the photoelectric behaviors of the samples with a scan rate of 50 mV/s. A 0.1 M Na_2SO_4 aqueous solution was used as the electrolyte (pH = 6.0). Prior to each measurement, the electrolyte was purged with N_2 gas continuously for 30 min to remove the oxygen in the electrolyte. A 300 W xenon lamp (Newport) coupled with an AM 1.5 G filter was used as the standard light source throughout the tests, and the illumination intensity of the light on the surface of electrodes was about 100 mW/cm^2. Amperometric *I–t* photoresponse was evaluated under chopped light irradiation (light on or off cycles: 20 s) at an applied potential of 0.3 V vs. RHE. The stability was operated at an applied potential of 0.3 V vs. RHE with the light continuous illumination for 30 min.

2.4. Photocatalytic activity of the octahedral flower-like cupric oxide nanocrystals

The photodegradation experiments were performed on a photochemical reactive instrument (BiLang, BL-GHX-V) coupled with a 300 W Xenon lamp as light source and the quartz tube for reaction solution. The distance between the lamp and the quartz tube is about 8 cm. In a typical photodegradation experiment, 100 mg flower-like CuO nanocrystals were first dispersed in 30 mL of 1.0×10^{-5} mol/L aqueous Rhodamine B (RhB) solution. The entire solution was transferred into a quartz tube with a diameter of about 2.5 cm and capped at the top. Before illumination, the mixed solution was constantly stirred for 30 min in the dark for the molecules to adsorb onto the catalyst surfaces. UV-vis spectrophotometer (Shimadzu, UV-3600) was used to monitor the changes of the reaction every 5 min of irradiation for up to 40 min by removing the cap to withdraw the solution.

3. Characterization

X-ray powder diffraction patterns were recorded by using a Philips X' Pert Pro Super diffractometer with Cu Ka radiation (λ = 15.4178 nm). X-ray photoelectron spectroscopy (XPS) was performed on a VGESCALAB MKII X-ray photoelectron spectrometer with Mg_{Ka} (1253.6 eV) as the excitation source. TEM images were obtained with a Hitachi Model H-800 instrument with a tungsten filament and an accelerating voltage of 200 kV. HRTEM images, electron diffraction patterns, and energy-dispersive X-ray (EDX) analyses were recorded on a JEOL-2010 transmission electron microscope at an acceleration voltage of 200 kV. FESEM images were recorded on a JEOL JSM-6700F scanning electron microscope.

4. Results and discussion

Fig. 1 shows the typical SEM and TEM images of the as-prepared CuO samples obtained by reaction of Fehling A with Fehling B at 95 °C for 120 min. From the SEM images in Fig. 1a and b, it can be seen that the product presents a uniform morphology and a narrow size distribution on large-scale. The octahedral flowers are consisted of numerous small crystalline whiskers, resulting in a rough surface. The size is in the range of 200–250 nm with an average diameter of 220 nm. The detailed structure of the as-obtained sample was further investigated by TEM as shown in Fig. 1c and d. As can be observed, the crystalline whiskers are projected from a central zone with an ordered arrangement, suggesting that this novel hierarchical structure is not simply a result of physical contact but