

Research Article

Investigation of Adsorption Behavior of Cu_2O Submicro-Octahedra towards Congo Red

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Perfect cuprous oxide (Cu_2O) nanocrystals with octahedron shape were successfully synthesized by a facile route without chemical additive in a short time. The products were characterized by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FESEM). The adsorption ability of the products towards congo red (CR) as the pollutant was investigated and FTIR spectroscopy was employed to identify the adsorbed species. The adsorption behavior was analyzed based on the microstructure of Cu_2O submicro-octahedra.

1. Introduction

Owing to the close correlations of the surface morphologies and size of inorganic materials with the electronic structure, bonding, surface energy, and chemical reactivity, designing and delicately controlling the shape of nanocrystals is one of the most important issues in nanoscience, chemistry, and physics [1–5]. Therefore, in the past decades, great efforts have been devoted to controllable synthesis of a variety of metal oxides with all types of shapes [6–11]. Among these metal oxides, cuprous oxide has been paid much attention because of its p-type semiconductor nature with a direct band gap of about 2.17 eV and potential application in catalysis, sensors, micro-/nanoelectronics, and solar energy conversion [12–15]. In order to tune the shape of Cu_2O , surfactants were generally used to alter the relative order of the surface energy of different crystallographic facets because of preferential adsorption of them on certain crystallographic surfaces [16–19]. However, the use of surfactants would bring a tedious procedure and lead to an environmental burden to some extent. Therefore, it is highly desirable to develop a facile template-free route to tailored synthesis of Cu_2O nanostructures with highly active facets. The facets with different crystallographic characters have distinctive surface

atomic structures, reconstructions, and atomic termination features corresponding to sharp differences that have been demonstrated in chemical reactivity and light-sensing [16, 20–23]. Zhang et al. reported that Cu_2O octahedra exhibited higher adsorption capacity towards methyl orange than Cu_2O cube and cubooctahedra because of the exposure of active “Cu” atoms with dangling bond on the {111} surfaces of Cu_2O octahedra [16]. To date, a variety of methods have been employed to prepare Cu_2O octahedra [24–28]; however, most of these methods involve surfactants or toxic reagent, and some products possess large sizes and low surface areas which is unfavorable to functionalized utilization such as adsorption.

Congo red ($\text{C}_{32}\text{H}_{22}\text{N}_6\text{O}_6\text{S}_2\text{Na}_2$, CR) is a benzidine-based anionic diazo dye and is widely used in the textiles, printing and dyeing, paper, rubber, plastics industries, and so forth. CR is toxic to animals and plants and thus its introduction to water stream is of potential health, environmental, and ecological concern [29]. Therefore, CR containing effluents have to be adequately treated before they are discharged into the environment. However, CR is difficult to biodegrade owing to its structural stability. Physicochemical or chemical treatment of such wastewater is, however, possible. Adsorption is considered an attractive option in treating

such wastewater due to its simple operation, high treatment efficiency, and economy.

Herein, we present a green and simple route to the synthesis of Cu_2O submicro-octahedra with the exposure of active “Cu” atoms with dangling bond in the absence of any surfactant in a short time. In this protocol, only CuCl_2 , NaOH , glucose, and distilled water are used, and the product possesses active {111} facets. So it is a highly ideal synthetic route to produce Cu_2O submicro-octahedra under environmentally benign conditions. Moreover, the as-prepared product exhibits good adsorption ability towards congo red, which extends the application of Cu_2O architectures.

2. Experimental Section

2.1. Synthesis of Cu_2O Octahedra. All reagents were of analytical grade and were used in their as-received state. The synthesis of target polyhedral Cu_2O nanocrystals was fulfilled in an alkaline solution using D-(+)-glucose as the reducing agent. In a typical synthesis, firstly, 0.1705 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 17 mL distilled water under constant magnetic stirring. Secondly, 3 mL of NaOH aqueous solution ($2.0 \text{ mol} \cdot \text{L}^{-1}$) was added to the above solution and blue $\text{Cu}(\text{OH})_2$ precipitates appeared immediately. Thirdly, 0.1982 g D-(+)-glucose was added to the above mixture and magnetically stirred for 2 min. Finally, the mixture was immersed into water bath at 60°C and stirred for 20 min. The precipitates turned from blue into dark yellow, then yellow, and orange in three minutes, which implied the formation of Cu_2O . After the mixture was cooled to room temperature, the precipitates were separated from the solution by centrifugation at 3000 rpm for 3 min. Then the precipitates were washed with distilled water and absolute ethanol for three times and dried in a vacuum oven at 60°C for several hours.

2.2. Characterization. XRD data were collected on a D/max-2600/PC diffractometer with $\text{Cu K}\alpha$ radiation at 40 kV and 150 mA. The morphology and size of these crystals were characterized by scanning electron microscopy (SEM, HITACHI SU-70). The N_2 adsorption-desorption isotherms at 77 K were measured using a Quantachrome NOVA 2000E analyzer. Before being measured, the samples were degassed at 393 K for 12 h. Specific surface area was calculated using the Brunauer-Emmett-Teller (BET) model from the adsorption branch. UV-Vis spectra were taken on a Lambda 45 (Perkin-Elmer) spectrophotometer. Fourier transform infrared spectroscopy (FTIR, Bruker, vertex 80) was employed to characterize the residual CR on the Cu_2O octahedrons after adsorption.

2.3. Adsorption Property Measurement. Different amounts of Cu_2O octahedra (0.05 g–0.15 g) were dispersed into an aqueous solution of congo red (200 mL, 10 mg/L) and the mixed solution was magnetically stirred in the dark. 5 mL of suspension was collected at each regular interval and centrifuged to remove the adsorbent powder in order to analyze the adsorption rate of CR by monitoring dye decolorization

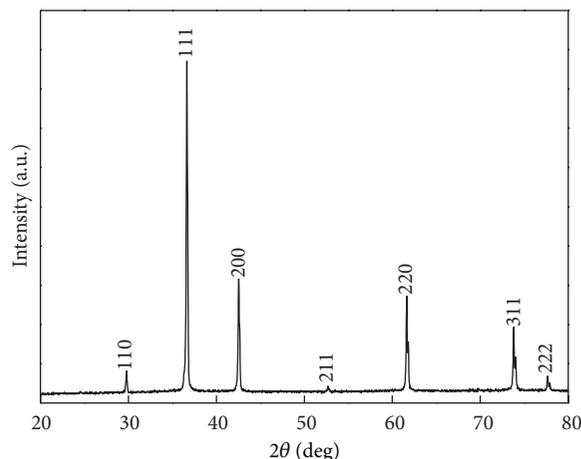


FIGURE 1: XRD pattern of the as-prepared product.

at the maximum absorption wavelength, using a Lambda 45 UV/Vis spectrophotometer.

3. Results and Discussion

Figure 1 plots the representative XRD pattern of the as-prepared sample. The sharp peaks in the pattern indicated that the samples obtained by this method were well crystallized. All patterns can be indexed as the cubic phase of cuprous oxide (JCPDS card, number 05-0667). No other characteristic peaks from impurities, such as CuO and Cu , were detected, revealing that the purity of the product was pretty high.

Figure 2 presents the typical SEM images of a Cu_2O sample prepared in the above-mentioned synthesis process when the reaction time was 20 min. It can be seen that the sample shows uniform and monodisperse octahedral morphology with edge lengths of 300~400 nm. Zhang et al. believed that the surface energy of {111} facet is higher than that of {100} facet due to the exposure of “Cu” atoms with dangling bonds and Cu_2O cubes are easily obtained in the absence of any surfactant [16]. However, in our experiment, the occurrence of Cu_2O octahedra indicated that the surface energy of {111} facet is lower than that of {100} facet. We proposed that it is glucose that plays an important role in the formation of octahedron in the absence of any surfactant. In the reaction, the glucose acts two roles: one is reductant and the other is capping agent. Glucose could be adsorbed preferentially on the surface of {111} facet and the adsorption stabilized the {111} plane, inhibiting the growth rate perpendicular to it. It resulted in the exposure of the {111} surfaces and produced high symmetry octahedra.

To demonstrate the potential application of the as-prepared Cu_2O octahedra, we investigated the adsorption ability of Cu_2O octahedra with congo red (CR, shown in Figure 3) as the pollutant. The experiments were carried out by dispersing different amounts of Cu_2O octahedra in the solution of CR in the dark for various durations under constant stirring. After centrifugation, the UV-Vis absorption

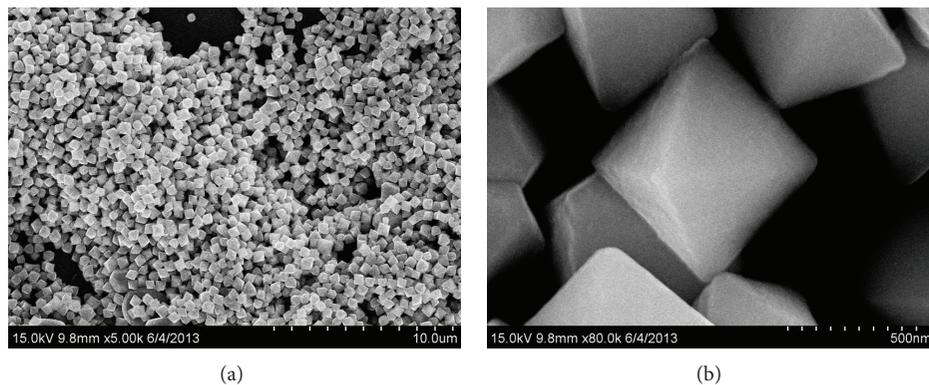


FIGURE 2: SEM images of the sample with different magnifications: (a) low magnification image and (b) high magnification image.

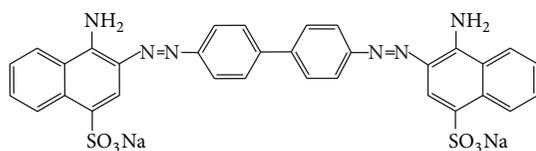


FIGURE 3: Structure of CR (molecular formula: $C_{32}H_{22}N_6O_6S_2Na_2$).

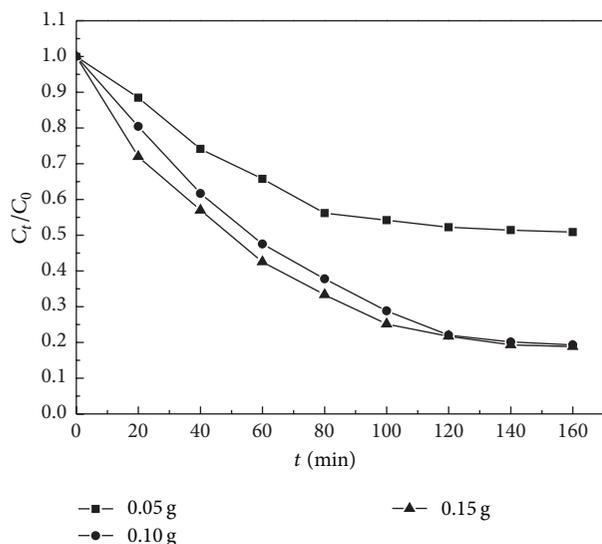


FIGURE 4: Adsorption curves of the aqueous solution of congo red (10 mg L^{-1} , 200 mL) in the presence of Cu_2O octahedra (0.05 g – 0.15 g) at different intervals, where C_t denotes the concentrations of CR changing following adsorption time and C_0 denotes the initial concentration of CR.

of the supernatant was measured and the characteristic absorption of CR at about 496 nm was selected to monitor the adsorption behavior. As illustrated in Figure 4, the same trend can be seen that the concentration of the CR progressively decreases following the adsorption time within 160 min and inclines to be constant beyond 160 min when the dosage of Cu_2O octahedra was in the range 0.05 – 0.15 g . Obviously, the adsorption capacity of the octahedra is saturated at about

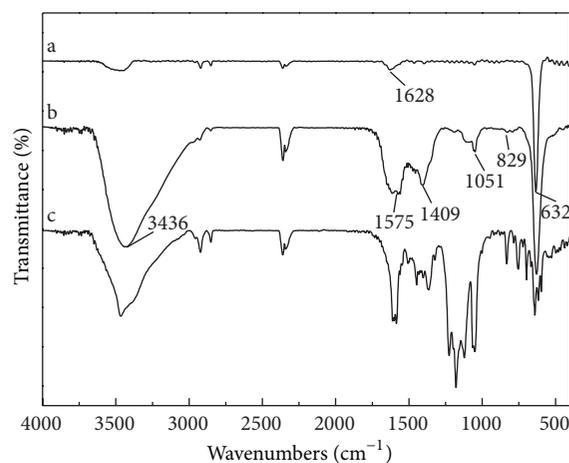


FIGURE 5: The FTIR spectra of (a) Cu_2O octahedra, (b) Cu_2O octahedra after the CR adsorption, and (c) the pure CR.

160 min . The more the amount of the octahedra is used, the larger the adsorption rate is. However, the adsorption curves are very close to each other when the used amount of the Cu_2O octahedra is 0.10 g and 0.15 g , and the final adsorption rate could reach about 81% when the adsorption time is 160 min . Obviously, the optimum used amount of the as-prepared adsorbent is around 0.10 g .

Since the adsorption experiments were carried out in the dark, the decolorization of the CR solution must result from the adsorption of Cu_2O particles, which is further corroborated by the FTIR analysis. As shown by curve a in Figure 5, the FTIR spectrum of the Cu_2O octahedra before adsorption exhibits two strong vibration bands. The band at 632 cm^{-1} corresponds to the Cu–O bond [30] (optically active lattice vibration in the oxide), and the peak at 1628 cm^{-1} is attributed to the –OH bending vibration [31], which originates from the surface-adsorbed H_2O . In comparison with the FTIR spectrum of the pure Cu_2O octahedra, some new absorption bands appear after adsorption (curve b in Figure 5). Combined with the FTIR spectrum of pure CR (curve c in Figure 5), the new absorption bands can be

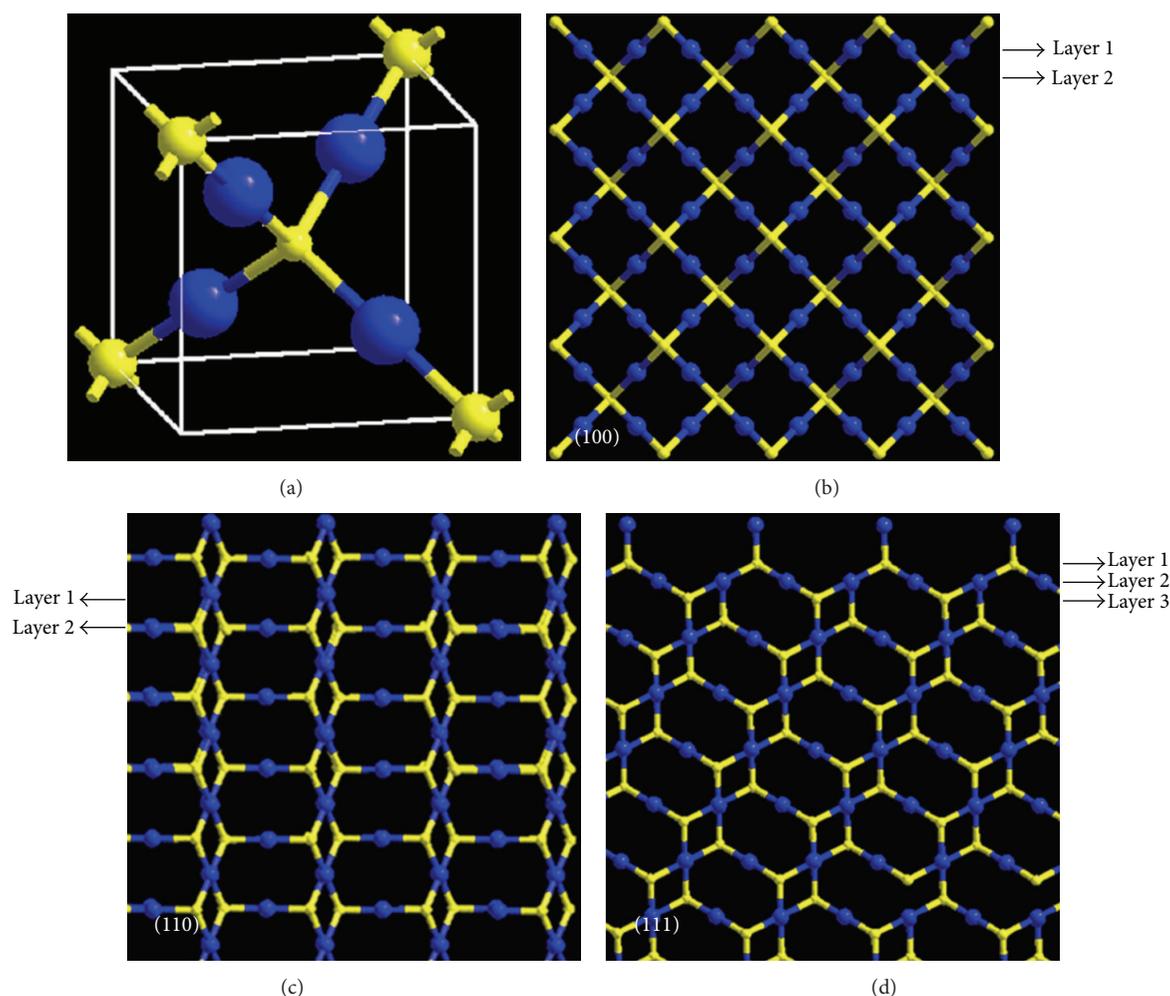


FIGURE 6: (a) The unit cell of the cuprite Cu_2O structure. The blue spheres represent copper atoms and yellow spheres indicate oxygen atoms. ((b)–(d)) The atomic arrangements in the (100), (110), and (111) planes of the Cu_2O structure, respectively.

assigned to the characteristic vibrations of CR. The absorption band at 3458 cm^{-1} (Figure 5(c)), corresponding to the stretching vibration of $-\text{N}-\text{H}$ in the structure of dye CR, shifted to lower wave number 3436 cm^{-1} after adsorption with Cu_2O octahedra (Figure 5(b)). The broadened band at 1575 cm^{-1} was assigned to $-\text{N}=\text{N}-$ stretching vibration of CR. The bands at 1409 and 829 cm^{-1} were assigned to characteristic absorption vibrations of aromatic skeletal groups. The band at 1051 cm^{-1} was attributed to $\text{S}=\text{O}$ stretching vibration [32]. Thus, the FTIR characterization results provide solid evidence for the adsorption of CR on the Cu_2O octahedra.

The specific surface area of the as-prepared Cu_2O octahedra is calculated to be $3.622\text{ m}^2\text{ g}^{-1}$ by the Brunauer-Emmett-Teller (BET) model from the sorption isotherms. Obviously, the specific surface area seems too little for the relatively high adsorption capacity. We proposed that the microstructure of the Cu_2O octahedra may play an important role in the adsorption of organic pollutant. For cuprite structured Cu_2O , each “O” is surrounded by a tetrahedron of “Cu”, and each “Cu” has two “O” neighbors as illustrated by its unit cell model

(Figure 6(a)). The atomic arrangements along different crystallographic planes of Cu_2O are displayed in Figures 6(b) to 6(d). Structurally, the cuprite Cu_2O crystal can be described as layers of atoms stacking alternately and periodically. Along the [100] and [110] directions (Figures 6(b) and 6(c)), the periodicity can be defined as two layers, in principle, layer 1 and layer 2 have equal possibility as a termination layer in both of these two cases. However, since the growth took place in aqueous media, “Cu”-terminated (layer 1 in Figure 6(b) and layer 1 in Figure 6(c)) would be rather unstable due to the active interaction with the hydroxyl group. Thus, “O”-(layer 2 in Figure 6(b)) and “-O-Cu-O-Cu-”-(layer 2 in Figure 6(c)) terminated surfaces are expected for {100} and {110} planes, respectively [16]. With respect to the [111] direction, three atom layers consist of one period, where the “Cu” layer is sandwiched between two layers of “O” atoms (Figure 6(d)). However, the distance between two adjacent layers in such a period is so short that the three layers can be approximately regarded as in the same surface. Every two “Cu” atoms have a dangling bond perpendicular to the {111} planes [16]. CR is an anionic dye with two negative charges in a molecule.

The active “Cu” atoms with dangling bond in the {111} surfaces of Cu₂O octahedra tend to interact with negatively charged CR (i.e., -SO₃⁻) to compensate the local surface charge imbalance. Based on the above discussion, we proposed that the interaction between Cu₂O octahedra and CR is not simple physical adsorption.

4. Conclusions

In summary, we have successfully synthesized octahedral morphology Cu₂O nanocrystals with edge length of 300~400 nm using glucose as the reducing agent via a facile procedure, where glucose also acts as capping agent to control the growth of octahedra. The as-prepared Cu₂O submicro-octahedra exhibit good adsorption ability towards CR due to the exposure of active “Cu” atoms with dangling bond on the {111} surfaces.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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