Research Article

Template-Free Synthesis of Porous Cu_2O Nanospheres at Room Temperature and Investigation on Their Adsorption Property

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Porous cuprous oxide (Cu_2O) nanospheres composed of small nanoparticles with diameters at 10~20 nm were successfully synthesized without surfactant at room temperature within 5 min. The products were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), N_2 adsorption-desorption, and Fourier transform infrared (FT-IR) spectrum. The adsorption ability of the as-prepared products towards methyl orange (MO) as the pollutant was investigated and FT-IR spectrum was employed to identify the adsorbed species. In addition, the reusability of the as-prepared products was studied as well.

1. Introduction

As a p-type semiconductor material, cuprous oxide (Cu_2O) has been paid much attention owing to its fundamental significance and widespread potential applications in solar cells, gas sensors, Li-ion battery, and catalysis [1–5]. Cu_2O usually grows into large microcrystals which possess low specific surface area [6], resulting in the limitation of the application of Cu_2O . Generally, the intrinsic properties of an inorganic nanomaterial could be tuned by controlling its size and microstructure to some extent [7–13]. Therefore, it is necessary to explore easy method to synthesize cuprous oxide with relatively large surface area. Recently, porous nanostructures have received more and more attention because they are exceptionally useful in sensor [14], catalysis [15], and dye-sensitized solar cells [16] due to their high surface area, tunable pore size, and adjustable framework [17]. So far, several methods have been reported to prepare porous Cu_2O nanostructures [18–21]; however, the structure control of the Cu_2O nanocrystals in these reports often relies on organic capping agent to direct the growth of porous structure, thus leading to an environmental burden. In addition, most of these methods involve either elevated temperature or complex process in the preparation of porous Cu_2O

nanostructures. Therefore, it is highly desirable to develop a facile template-free route at room temperature to synthesize porous Cu_2O nanostructures.

Herein, we present a green and convenient approach for the synthesis of porous Cu_2O nanospheres assembled from nanoparticles without surfactant at room temperature. In this protocol, only $\text{Cu}(\text{CH}_3\text{COO})_2$, NaOH, ascorbic acid, and distilled water were used and the product possesses a relative large specific surface area. So it is a highly ideal synthetic route to produce porous Cu_2O nanomaterials under environmentally benign conditions. Moreover, the as-prepared products exhibit a good adsorption ability towards methyl orange (MO) as the pollutant.

2. Experimental Details

2.1. Synthesis of Porous Cu_2O Nanospheres. All of the chemical reagents were of analytical grade and used without further purification. In a typical procedure, 1 mmol $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ was firstly dissolved in 20 mL of NaOH aqueous solution (0.1 mol L^{-1}) under constant magnetical stirring. And blue $\text{Cu}(\text{OH})_2$ precipitates appeared immediately. Then 1 mmol ascorbic acid was added and the solution was magnetically

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

stirred for 5 min at ambient conditions. During the process, the color of the reaction mixture turned from blue into dark yellow, then yellow, and orange, which implied the formation of Cu_2O . At last, the precipitates were separated from the solution by centrifugation at 4000 rpm for 5 min. Then the precipitates were washed with distilled water and absolute ethanol sufficiently and dried in vacuum for several hours.

2.2. Characterization. The crystal structure and phase composition of the sample were characterized using X-ray powder diffraction (XRD, Rigaku D/max-2600/PC, $\text{CuK}\alpha$ radiation, $\lambda = 1.54056 \text{ \AA}$, 40 kV, 150 mA). The morphology of the products was examined by a field emission scanning electron microscope (FESEM, HITACHI S-4800 electron microscope) operated at 15.0 kV. High resolution transmission electron microscopy (HRTEM) images were recorded on JEOL JEM-2100 microscope. The N_2 adsorption-desorption isotherms at 77 K were measured using a Quantachrome NOVA 2000E analyzer. Before measuring, the samples were degassed at 393 K for 12 h. Surface areas and pore size distributions were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) models, respectively. UV-Vis spectra were taken on a Lambda 45 spectrophotometer. Fourier transform infrared spectroscopy (FT-IR, Bruker, vertex 80) was employed to characterize the residual MO on the porous Cu_2O nanospheres after adsorption.

2.3. Adsorption Property Measurement. Different amounts of porous Cu_2O nanospheres (0.02 g–0.12 g) were dispersed into an aqueous solution of methyl orange (MO, 200 mL, 30 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 MO by monitoring dye decolorization at the maximum absorption wavelength, using a UV/Vis spectrometer.

The separated porous Cu_2O nanospheres were washed with distilled water and absolute ethanol, respectively, for

three times to remove the residual organic species as thoroughly as possible and reused for the next run.

3. Results and Discussion

The phase and purity of the products were firstly investigated by XRD. Figure 1 shows a typical XRD pattern of the sample. All of the reflection peaks in this pattern can be readily indexed to a pure cubic phase of Cu_2O (JCPDS no. 05-0667). Relatively, wide diffraction peaks imply that the size of the particles is small.

The morphology of the products was observed by SEM. Figure 2(a) is a typical low magnified SEM image of the sample, showing that a large quantity of spherical particles with a narrow size distribution was achieved. The high magnified SEM image (Figure 2(b)) demonstrates that the spherical shaped particles possess an average diameter about 400 nm, and the surfaces of the spheres are rough and porous since they are constructed by aggregation of a lot of small particles with diameters 10–20 nm, as confirmed by the TEM image (Figure 2(c)). Based on the EM images with different magnifications, it is clear that pores were distributed on both the surface and the interior of the Cu_2O nanospheres that permits the rapid penetration of the adsorbates from the outside to the inside for deep adsorptions. The aggregating feature is further confirmed by HRTEM image (Figure 2(d)), in which randomly oriented lattice fringes can be found, indicating that the porous spheres are composed of nanocrystals with different growth directions. Circles in the SAED pattern (inset in Figure 2(d)) further show the polycrystalline nature of the porous Cu_2O nanospheres; that is, the crystal planes of the small Cu_2O nanoparticles are randomly oriented.

The N_2 adsorption and desorption isotherms of the porous Cu_2O nanospheres are provided in Figure 3. The specific surface area is calculated to be $26.67 \text{ m}^2 \text{ g}^{-1}$. Moreover, the corresponding pore size distribution (the inset of Figure 3) shows a peak pore diameter of 10 nm with pores up to 60 nm in size. Such porous structure provides efficient transport pathways to the interior cavities and is in favor of adsorption.

To demonstrate the potential application of the as-prepared porous Cu_2O nanospheres, we investigated its adsorption ability with methyl orange (MO) as the pollutant. The adsorption was carried out by dispersing different amount of porous Cu_2O nanospheres in the solution of MO in the dark for various durations under constant stirring. After centrifugation, the UV-Vis absorption of the supernatant was measured and the characteristic band of MO at about 464 nm was selected to monitor the adsorption behavior. As shown in Figure 4, the same trend can be seen that the concentration of the MO progressively decreases following the adsorption time within 120 min and is kept constant beyond 120 min when the amount of Cu_2O nanospheres was from 0.02 to 0.12 g. Obviously, the adsorption capacity of the porous nanospheres is saturated at about 120 min, which is much shorter than the saturation time of reported polyhedral Cu_2O on adsorption of MO under identical conditions [22]. The more the amount of the porous nanospheres is used, the

FIGURE 2: EM images with different magnifications: (a) low magnification SEM image of the sample, (b) high magnification SEM image of the sample, (c) TEM image of the sample, and (d) HRTEM image taken at the edge of porous nanospheres and the corresponding SAED pattern (inset).

FIGURE 3: The N_2 adsorption and desorption isotherms and the pore size distribution curve (inset) of the porous Cu_2O nanospheres.

larger is the adsorption rate. However, the adsorption behaviors are very similar when the used amount of the porous Cu_2O nanospheres is 0.10 g and 0.12 g, the concentration of MO lowered by about 60% after about 20 min of adsorption,

FIGURE 4: Adsorption curves of the aqueous solution of methyl orange (30 mg L^{-1} , 200 mL) in the presence of Cu_2O (0.05 g–0.12 g) at different intervals, where C_t denotes the concentrations of MO changing following adsorption time and C_0 denotes the initial concentration of MO.

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

FIGURE 6: Cycling tests of adsorption ability of the porous Cu_2O nanospheres towards MO.

and the final adsorption rate could reach about 95% when the adsorption time is 120 min. Obviously, the optimum using amount of the as-prepared adsorbent is around 0.1 g.

Since the adsorption experiments were carried out in the dark, the decolorization of the MO 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 porous Cu_2O nanospheres before adsorption exhibits two strong vibration bands. The band at 630 cm^{-1} corresponds to the Cu–O bond [23] (optically active lattice vibration in the oxide), and the peak at 1628 cm^{-1} is attributed to the –OH bending vibration, which originates from the surface-adsorbed H_2O . In comparison with the FTIR spectrum of the pure Cu_2O nanospheres, some new peaks appear after adsorption (curve (b) in Figure 5). Combined with the FTIR spectrum of pure MO (curve (c) in Figure 5), the new peaks can be assigned to the characteristic vibrations of MO. The peaks at 1446 and

1372 cm^{-1} are the signals from the methyl group. The peaks at 817 and 843 cm^{-1} result from the absorption peaks of C–H bonds of di-substituted benzene. The peaks at 697 cm^{-1} , 1029 cm^{-1} , and 1120 cm^{-1} come from the vibrations of the sulfonic group [24]. Thus, the FTIR characterization results provide solid evidence for the adsorption of MO on the porous Cu_2O nanospheres.

Cycling use as well as maintaining high adsorption ability of adsorbent is a critical issue toward long-term adsorption applications. Therefore, the stability of the as-synthesized Cu_2O adsorbent was evaluated by performing the recycle experiments for adsorbing MO under identical conditions and the results are shown in Figure 6. After five cycles, the adsorption rate does not decrease apparently, indicating that the adsorbent possesses high adsorption stability.

4. Conclusion

In summary, porous Cu_2O nanospheres composed of small nanoparticles with diameters 10–20 nm have been successfully prepared through an environmental benign method in the absence of template within 5 min at room temperature. The BET surface area of the sample is $26.67\text{ m}^2\text{ g}^{-1}$ and the average pore diameter is ca. 10 nm. The porous nanospheres exhibit good adsorption property and stability towards MO as the pollutant, and the initial adsorption rate could reach about 95% within 120 min under optimum conditions.

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