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Preparation of Cu_2O Hollow Nanospheres under Reflux Conditions

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Cuprous oxide hollow nanospheres were prepared by heating a solution of copper acetate and hydrazine as a reductant in 2-propanol at reflux. The size distribution of the nanospheres is mainly in the range 100–200 nm. The products were characterized by X-ray diffraction, UV/Vis diffuse reflectance spectroscopy, SEM, and TEM. The results indicated that the Cu_2O hollow nanospheres aggregated from small nanoparticles with an average size of ca. 6.6 nm. The UV/Vis diffuse reflectance spectrum indicated that the optical absorption edge of the hollow Cu_2O nanospheres is redshifted relative to their solid counterparts. The influence of the reaction conditions, such as reaction temperature, reaction time, and the amount of water, on the formation of the nanospheres as well as their morphology were studied.

Introduction

In recent years, controlled architectures and the fabrication of hollow inorganic micro- and nanostructures have attracted extensive research interests owing to their unique thermal, electrical, optical, and surface properties.[1–8] Materials with hollow interiors have potential applications in many fields, such as catalyst, adsorbent, drug delivery, photonic crystals, optical imaging, low dielectric constant materials, and acoustic insulation etc. Cuprous oxide is an important *p*-type semiconductor with a direct bandgap of 2.17 eV. Owing to its unique optical property, Cu_2O has potential applications in the catalytic oxidation of CO to CO_2,[9] photocatalytic degradation of organic pollutants, and decomposition of water into H_2 and O_2 under visible light.[10]

Various methods have been reported for the preparation of Cu_2O with various morphologies and hollow structures, such as nanowire,[11] octahedral nanocages,[12] hollow cubes, and spheres.[13–16] There have been two main preparative routes for the synthesis of the hollow structure. In the template method, raw materials or target precursors are adsorbed onto the template surface and subsequently the template is removed by calcination or dissolution with solvent.[1] Another preparative strategy concerns physical phenomena such as “Ostwald ripening”[13,14,17] and the “Kirkendall effect”.[2] Cetyltrimethylammonium (CTAB)[15] and gelatin[16] are used to prepare Cu_2O hollow nanospheres by the template-assisted method. Here, we describe a facile template-free and surfactant-free route for the formation of hollow Cu_2O nanospheres by heating a solution of copper acetate and hydrazine as the reductant in 2-propanol at reflux.

Results and Discussion

Figure 1(a) shows the SEM image of the Cu_2O nanospheres prepared by heating a solution of copper acetate and hydrazine in 2-propanol at reflux. The hollow feature of the nanospheres can be confirmed from TEM by observing that the light interior in contrast to the dark periphery as shown in the inset of Figure 1(a). The TEM image shows that the nanospheres are aggregated by small nanoparticles,

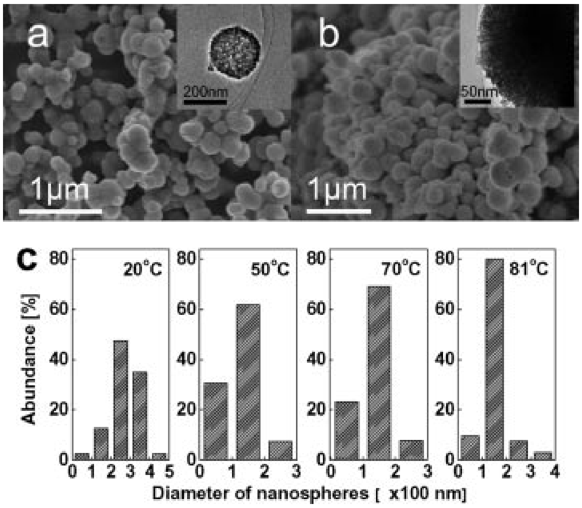

Figure 1. SEM images of Cu_2O nanospheres prepared at (a) the boiling point of 2-propanol (81 °C) and (b) at room temperature (20 °C). The insets of (a) and (b) show the TEM images of Cu_2O nanospheres. (c) The size distributions of Cu_2O nanospheres prepared at 81, 70, 50, and 20 °C.

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and the thickness of the hollow sphere shell is estimated to be ca. 20 nm for the nanosphere with a diameter of 210 nm as shown in the inset of Figure 1(a). The size distribution of the Cu_2O nanospheres is mainly in the scale of 100–200 nm as shown in Figure 1(c).

Temperature is a crucial factor in the formation of the hollow structure. The boiling point of 2-propanol is 81.5 °C, and Cu_2O nanospheres can also be prepared at lower temperature. Although spherical morphology was observed in the products prepared at 20 °C, as shown in Figure 1(b), a longer reaction time of 90 min was necessary and only solid nanospheres were observed by TEM from the inset of Figure 1(b). The diameter of these solid nanospheres varies from 100 to 500 nm, and is mainly concentrated in the region 200–400 nm as shown in Figure 1(c). As the temperature was increased to 50 °C, the size distribution of the spheres narrowed, but still only solid nanospheres were observed. As the temperature was increased to 70 °C, hollow nanospheres were observed to coexist with the solid nanospheres. Figure 2 shows that all of the nanospheres prepared at 81 °C were hollow.

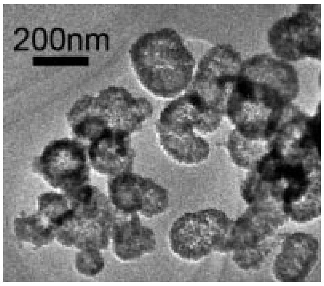

Figure 2. TEM image of Cu_2O hollow nanospheres prepared at 81 °C.

Figure 3 shows the XRD patterns of the samples prepared at 20, 50, 70, and 81 °C. All the diffraction peaks can be indexed to cubic Cu_2O (JCPDS card No. 05–0667). The average particle size of the primary particles that agglomerated into nanospheres was estimated from the line broadening of the XRD peak (111) by using the Scherrer equation ($D_{hkl} = k\lambda/\beta_{hkl}\cos\theta$). The results indicate that the average size of the primary particles decreased slightly from 9.6 to 7.9 nm, and then to 6.6 nm within the same reaction time of 10 min when the preparation temperature was increased from 50 to 70 °C, and then 81 °C.

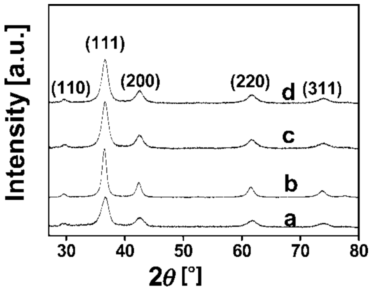

Figure 3. XRD patterns of the cubic Cu_2O samples prepared at different temperatures: (a) 20 °C, (b) 50 °C, (c) 70 °C, and (d) 81 °C.

Reaction time had an influence on the morphology of the nanospheres as well as the average size of the primary particles. Figure 4 show the SEM images of the Cu_2O hollow spheres prepared by heating for 20, 30, and 120 min at 81 °C in 2-propanol. In Figure 4(a), the Cu_2O hollow spheres that were prepared in 20 min have smooth surfaces that are similar to the products prepared after 10 min. The spherical diameter distribution is concentrated in the range 100–300 nm as shown in Figure 4(d). When the reaction time was increased to 30 min, the surfaces of the products were relatively rough as shown in Figure 4(b), and the spherical diameter distribution was then concentrated in the region from 200 to 400 nm as shown in Figure 4(d). When the reaction time was increased to 120 min, irregular spheres with large sizes and rough surfaces were observed in Figure 4(c), and many broken particles were spread around. There was no change in the size of the primary particles when the reaction time was less than 20 min. The average size of the primary particles increased from 6.6 to 9.3 nm when the reaction time was increased from 20 to 30 min, according to the XRD line broadening.

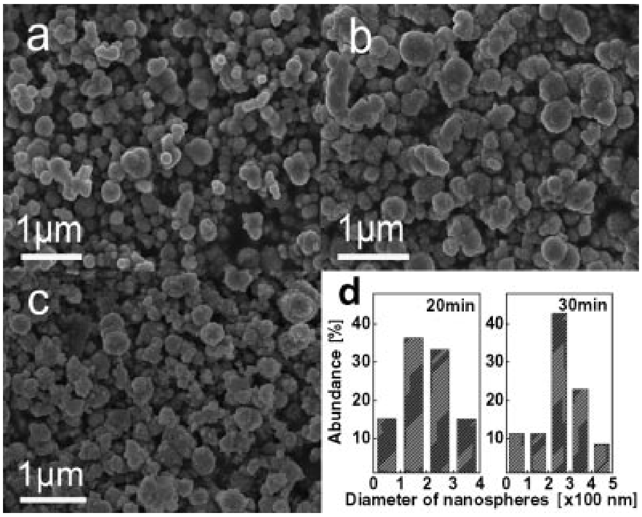

Figure 4. SEM images of hollow Cu_2O nanospheres prepared at 81 °C after (a) 20 min, (b) 30 min, and (c) 2 h. (d) The size distribution of the Cu_2O nanospheres.

There is a small amount of water that exists in the reaction system owing to the hydrazine aqueous solution. Although the products maintain their spherical morphology when additional water is introduced, the size of the nanospheres as well as the primary particles changed significantly. Figure 5(a) and (b) show the products prepared by adding 10 mL and 20 mL of water, respectively. The majority of the products are still hollow spheres as shown in the inset of Figure 5(a), but they have relatively small hollow interiors relative to the nanospheres that were prepared without additional water. As shown in Figure 5(c), the size distribution of the nanospheres prepared with an additional 10 mL of water is in the range 100–700 nm and is mainly concentrated around 300–400 nm. When 20 mL of water were added, we found that the size distribution of the nanospheres changed to 200–800 nm and was basically concentrated around 600–700 nm. This change indicates that the size of the spheres increases by adding more water. According to the XRD line broadening, the average size of the primary particles increased to ca. 15.4 nm and ca. 14.7 nm for the samples with the additional 10 mL and 20 mL of water.

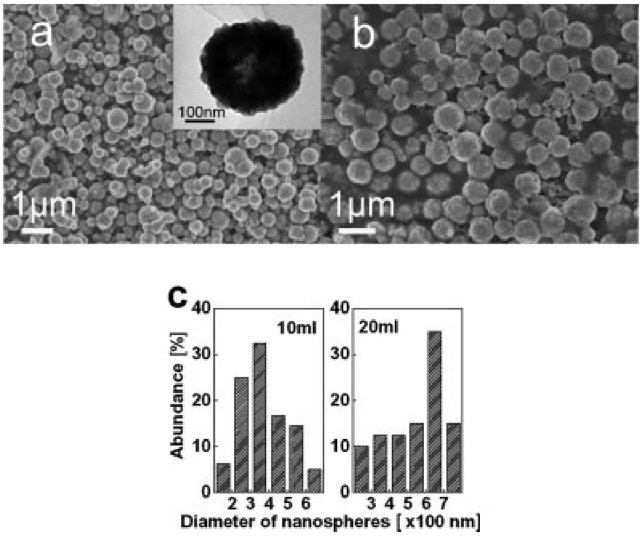

Figure 5. SEM images of hollow Cu_2O nanospheres prepared with (a) 10 mL and (b) 20 mL of additional water. The inset of (a) shows a TEM image of a hollow sphere. (c) The size distribution of Cu_2O nanospheres prepared with 10 mL and 20 mL of additional water.

Figure 6 shows the UV/Vis diffuse reflectance spectrum of Cu_2O nanospheres that were prepared at 20, 50, 70, and 81 °C. The bandgaps of Cu_2O were estimated according to the absorption edge position as shown in Figure 6 by intercepting the two linearly extrapolated lines. It is observed that the optical absorption edge of the Cu_2O hollow nanospheres prepared at 81 °C occurs at about 616 nm, corresponding to a bandgap energy of 2.01 eV. The optical absorption edge of the Cu_2O solid nanospheres prepared at 20 °C is at about 600 nm, corresponding to a bandgap energy of 2.07 eV. It is worth noting that the hollow nanospheres exhibit similar features in the DRS spectra (Figure 6a and b) whereas there are significant differences with that of solid nanospheres (Figure 6c and d). Relative to the solid nanospheres, the optical absorption edge of hollow the Cu_2O nanospheres is redshifted. It is well known that the optical absorption would be altered considerably by the morphology and crystallinity of the nanospheres. The average particle size of the primary particles that were agglomerated into hollow and solid nanospheres is in the range of 6–10 nm, according to the XRD line broadening. The size distributions of hollow and solid nanospheres are all basically in the region of 100 to 400 nm. Hence, we speculate that the enhanced optical absorption of the nanospheres results from their hollow structure. The surface structure and adsorbed species on the surface have an influence on the optical absorption. The inner and outer surfaces of the hollow nanospheres may be different, which will result in a redshift.

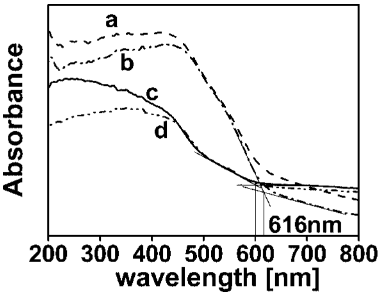

Figure 6. UV/Vis diffuse reflectance spectra of Cu_2O nanospheres prepared at different reaction temperatures: (a) 81 °C, (b) 70 °C, (c) 50 °C, and (d) 20 °C.

Conclusions

A facile template-free and surfactant-free route was developed for the preparation of hollow Cu_2O nanospheres. Cuprous oxide hollow nanospheres with diameters of ca. 100–200 nm were successfully prepared by heating a solution of $Cu(OAc)_2 \cdot H_2O$ and hydrazine as a reductant in 2-propanol at reflux. The nanospheres were aggregated from small primary particles with an average size of 6–10 nm. Temperature is a critical factor in the formation of the hollow nanospheres, and hollow spheres come into being only when the temperature is close to the boiling point of the solvent. Both the reaction time and the amount of water have an influence on the formation of the Cu_2O hollow structures as well as the morphology and the size of the primary particles. The UV/Vis diffuse reflectance spectrum indicated that the hollow structure enhanced the absorption of visible light relative to their solid counterpart.

Experimental Section

All reagents (A.R) were from the Beijing Chemical Reagent Corporation and used without further purification. In a typical synthesis procedure, $Cu(OAc)_2 \cdot H_2O$ (2.0 g) was added to 2-propanol (100 mL) in a three-necked flask whilst stirring. The solution was heated at reflux (81 °C) for 20 min. and then a hydrazine (2.5 mL, 1 $mol\,L^{-1}$) solution was added dropwise. The resulting deep green mixture was stirred for another 10 min, and a reddish brown suspension came into being. The solid product was separated from the solution by centrifugation, washed with absolute ethanol, and dried in air.

The X-ray powder diffraction (XRD) patterns of the products were collected with a Rigaku D/MAX 2500/PC X-ray diffractometer with graphite-filtered Cu-K_α radiation at 40 kV and 200 mA with a scan rate of $1°\,min^{-1}$. The morphologies were observed by SEM with a JSM-6700F electron microscope and TEM with a JSM-3010 electron microscope. UV/Vis diffuse reflectance spectra of the products were measured with a UV/Vis spectrometer Lambda 20.

Acknowledgments

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