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Controllable Synthesis of CuO Nanowires and Cu_2O Crystals with Shape Evolution via γ-Irradiation

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Copper oxide nanowires and cuprous oxide crystals had been synthesized through γ-irradiating aqueous $CuCl_2$−NaOH−sodium dodecyl sulfate (SDS)−isopropyl alcohol solutions under ambient conditions. The product composition could be changed by modulating the amount of base, NaOH. The morphology of the products could be accurately controlled by altering the amounts of SDS and isopropyl alcohol. A possible formation mechanism was also proposed.

Materials in the nanoscale due to small-size and quantum confinement effects have excellent physical and chemical properties different from the corresponding bulk. Many ways, such as hydrothermal or solvothermal methods, are used for the synthesis of nanomaterials.[1,2] γ-Irradiation is a distinctive approach that was first discovered for the preparation of nanomaterials by Hiroshi Fujita in 1962.[3] In recent years, the γ-irradiation route has been well-developed in the synthesis of semiconductors and inorganic materials.[4−7]

Nanosized semiconductors such as CuO and Cu_2O have lately been intensively investigated for their particular optical and electronic properties. As one of the most popular p-type semiconductors with a narrow band gap (1.2 eV), CuO is employed as the anode for lithium-ion batteries,[8−10] catalysts,[11−13] and gas sensors.[14−16] Cu_2O, which is an important p-type semiconductor with a direct band gap (2.17 eV), has been demonstrated to be used for solar energy conversion,[17] the photochemical decomposition of water into H_2 and O_2 under visible-light irradiation.[18] The different morphology of Cu_2O nanocrystals could exhibit special properties. For example, octahedral Cu_2O nanocrystals with entirely {111} surfaces show a better performance in the photocatalytic degradation of dye molecules than those of other shapes.[19]

Previously, we have reported the preparation of cuprous oxides with a variety of morphologies such as eight-pod cubes and six-armed starlike, octahedral, spindlelike structures via γ-irradiation.[5] In this work, we further designed an environmentally convenient system to prepare CuO nanowires and octahedral and cubic Cu_2O with smaller and more uniform distributions in size. Interestingly, by delicately modulating the ratio of the copper and hydroxyl ions, we could control the synthesis of CuO nanowires and Cu_2O of octahedral or cubic structure. Moreover, it has been found that the amount of isopropyl alcohol has a significant impact on the morphology of Cu_2O crystals.

In a typical procedure for synthesizing CuO nanowires, 0.270 g of $CuCl_2 \cdot 2H_2O$ was dissolved into 30 mL of distilled water. A total of 10 mL of 0.375 M NaOH and 1.000 g of sodium dodecyl sulfate (SDS) were added in sequence. The ratios of the reaction products for the preparation of a Cu_2O cube and octahedron were slightly different. The amount of NaOH decreased to 0.3 M, while other reactants were the same. Besides, isopropyl alcohol was added as a scavenger of oxidative radicals produced during irradiation. Then, the

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Table 1. Synthesis Conditions and Morphology of the Obtained Products

sample	NaOH (mol/L)	α[a]	isopropyl alcohol (mL)	composition	morphology
1	0.093	2.35	5	CuO	nanowire
2	0.075	1.90	5	Cu_2O	octahedral
3	0.075	1.90	12	Cu_2O	truncated octahedral
4	0.075	1.90	20	Cu_2O	cubic

[a] α = molar ratio of OH^- to Cu^{2+}.

mixed solution was slowly stirred for 15 min to form a uniform blue suspension. Finally, the blue mixed solution was poured into a wide-mouth bottle and sealed. Then, the bottle was placed in the field of a 2.22×10^{15} Bq ^{60}Co γ-ray source at a dose rate of 30 Gy/min for 72 h. When irradiation was over, the precipitates were collected. The products were washed with a distilled water and ethanol solution several times and then dried in an oven at 50 °C. Table 1 shows the detailed synthesis conditions of the obtained products.

The compositions of these products were determined by powder X-ray diffraction (XRD), which was performed on a Rigaku TTR-III X-ray diffractometer with Cu Kα radiation (λ = 1.541 78 Å). Figure 1a gives the XRD pattern of the as-synthesized CuO (sample 1). The XRD pattern shows the expected (110), ($\bar{1}$11), (111), and ($\bar{2}$02) reflection peaks. All of the peaks can be indexed to temorite (monoclinic) CuO (JCPDS card no. 05-661) with cell parameters a = 4.684 Å, b = 3.425 Å, and c = 5.129 Å. The XRD pattern of the as-synthesized Cu_2O (sample 2) is shown in Figure 1b. All of the peaks can be indexed to cuprite (cubic) Cu_2O (JCPDS card no. 05-667) with cell parameter a = 4.269 Å. No other characteristic peaks were observed, indicating the high purity of the as-synthesized products. As can be seen, the high intensity of the (111) diffraction peak suggests that the obtained Cu_2O crystals (sample 2) are mainly dominated by (111) facets.

The equations involved in the reaction processes are described as follows:[20]

$$H_2O \rightsquigarrow e_{aq}^-, H\cdot, \cdot OH, H_3O, H_2, H_2O_2, \text{etc} \quad (1)$$

$$CH_3CH(OH)CH_3 + \cdot OH \longrightarrow CH_3C\cdot(OH)CH_3 + H_2O \quad (2)$$

$$Cu^{2+} \xrightarrow{e_{aq}^-, CH_3C\cdot(OH)CH_3} Cu^+ \quad (3)$$

$$Cu^+ + OH^- \rightarrow CuOH \quad (4)$$

$$2CuOH \rightsquigarrow H_2O + Cu_2O\downarrow \quad (5)$$

$$Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_2 \quad (6)$$

$$Cu(OH)_2 \rightsquigarrow H_2O + CuO\downarrow \quad (7)$$

As is reported, the aqueous solution by γ-radiolysis produces many active intermediates, such as strong reductive hydrated electrons (its standard redox potential of −2.77 V) and oxidative radicals $^{\bullet}OH$ (eq 1).[21] Isopropyl alcohol is introduced to scavenge $^{\bullet}OH$,[22] and the obtained $CH_3C\cdot(OH)CH_3$ radicals also possess reducibility (−1.1 V). When a small quantity of NaOH is added into the solution, the dissociative state Cu^{2+} would be mainly reduced into Cu^+ by e_{aq}^- and $CH_3C\cdot(OH)CH_3$ radicals (eq 3), and OH^- then

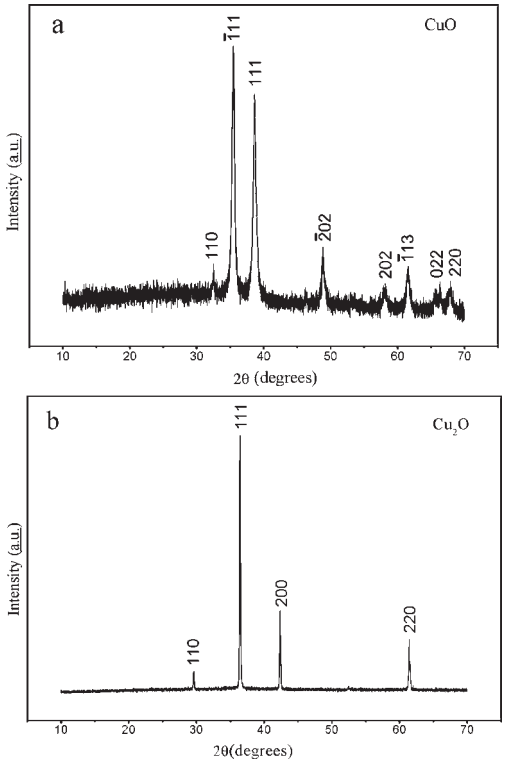
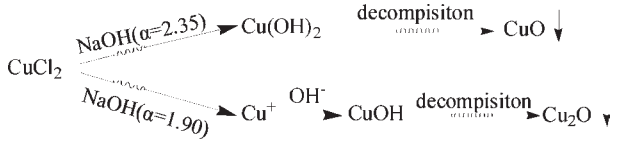


Figure 1. XRD patterns: (a) synthesized sample 1, CuO nanowires; (b) synthesized sample 2, Cu_2O octahedron.

Scheme 1. Formation Processes of CuO and Cu_2O



quickly combines with Cu^+ to form CuOH, which finally decomposes into Cu_2O (eqs 4 and 5) under γ-rays. Products are pure Cu_2O because α (the molar ratio of OH^- to Cu^{2+}; Table 1) equals 1.90. When the concentration of NaOH was increased to a certain extent (α ∼ 2.35; Table 1), $Cu(OH)_2$ precipitate formed. Then, $Cu(OH)_2$ decomposes into CuO under γ-irradiation (eqs 6 and 7), through which it was ultimately assembled into nanowires. To prove the role of γ-irradiation in the formation of CuO nanowires, parallel experiments under no γ-irradiation were carried out while keeping other conditions the same as above. In this case, no CuO nanowires were found. So, γ-irradiation is important for the formation of CuO nanowires. Scheme 1 shows the formation processes of CuO and Cu_2O.

The morphology of the as-synthesized products was observed using field-emission scanning electron microscopy (SEM; FEI Sirion 200). The SEM image in Figure 2a shows that sample 1 is composed of wires with a diameter of ∼20 nm. That CuO nanowires interlace together can be seen from the image. The length of each nanowire, which could not be precisely measured, should be greater than 5 μm. SDS also has an effect on the formation of CuO nanowires. To understand this effect, parallel experiments without SDS assistance were carried out. Only the uniform nanoleaves could be seen from the image (Supporting Information). This proves that SDS affects the growth of CuO crystals.

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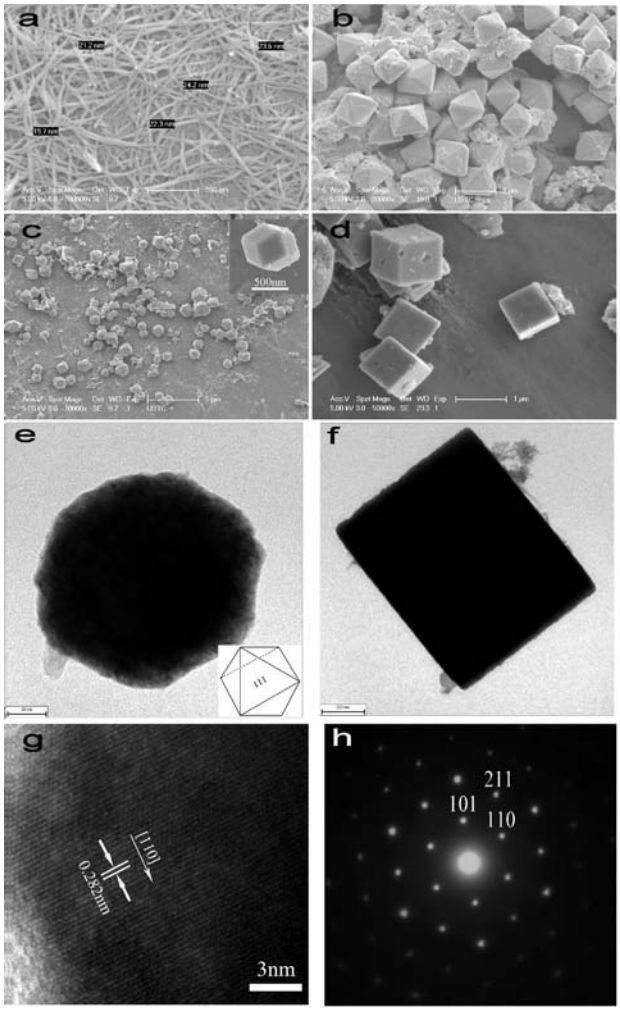

Figure 2. (a−d) SEM images of samples 1−4. (e and f) TEM images of samples 2 and 4. (g and h) HRTEM image of sample 2 and its corresponding SAED pattern.

To evaluate the effect of isopropyl alcohol on the morphology of Cu_2O crystals, contrast experiments with only changes in the amount of isopropyl alcohol were carried out. Panels b−d of Figure 2 show the SEM images of the Cu_2O products obtained with different quantities of isopropyl alcohol. In the presence of 5 mL of isopropyl alcohol, the products were composed of uniform octahedral Cu_2O (Figure 2b), whose size distribution was from 900 to 1100 nm. When the amount of isopropyl alcohol was increased to 12 mL, the Cu_2O products showed the morphology of the truncated octahedron (Figure 2c). When increased to 20 mL, the obtained Cu_2O crystals, whose size remains the same as that of sample 2, have morphology of the cube (Figure 2d). The results demonstrated above indicate that the amount of isopropyl alcohol has a dramatic effect on the morphology of the obtained Cu_2O products. The growth of Cu_2O crystals may explain this as follows: At an early stage after irradiation, small Cu_2O seed particles are formed. These small particles then aggregate into larger particles. Isopropyl alcohol is employed as $^{\bullet}OH$ oxidative radical scavengers for the creation of a reductive system.[21] So, the higher the volume of isopropyl alcohol that is added, the faster the small particles Cu_2O grow in the γ-irradiation system. Thereby, the amount of isopropyl alcohol might influence the growth rate along the [100] direction relative to that of the [111] direction. The ratio is defined as R.[23] When R is ~0.58, perfect cubic Cu_2O crystals are produced. When R is ~1.73, octahedral crystals are prepared. When R is ~1.15, the morphology of Cu_2O is truncated octahedral, which is between cube and octahedron. In these γ-irradiation reaction systems, it is believed that the formation processes are in agreement with those in the reported case (other related results can be found in the Supporting Information).

Further morphology characterization of Cu_2O samples was performed by transmission electron microscopy (TEM; JEOL-2010) operating at 200 kV. The TEM images of samples 2 and 4 are shown in parts e and f of Figure 2, respectively. Figure 2g gives the high-resolution TEM (HRTEM) image of the obtained Cu_2O crystals. The image clearly shows the lattice fringes with interplanar spacing of 0.282 nm, which is close to the separation between the (110) lattice planes of the cubic crystal structure of Cu_2O (0.302 nm, standard in JCPDS card no. 05-667). The corresponding selected-area electron diffraction (SAED) pattern (Figure 2h) also verifies that the as-prepared products are signal crystals of cubic Cu_2O, which is in well agreement with the XRD pattern results.

In summary, CuO nanowires and Cu_2O crystals with shape evolution from cubic to octahedral structures have been successfully prepared via a simple γ-irradiation route at room temperature and under ambient pressure. As far as we know, this is the first time to report the synthesis of CuO nanowires and Cu_2O cubes by using the γ-irradiation method. It has been found that the product compositions could be changed by modulating the molar ratio of OH^- and Cu^{2+}. For Cu_2O crystals, the morphology could be accurately controlled by altering the amount of isopropyl alcohol. The formation mechanism is also proposed. Related studies surely enriched the application and theory for the γ-irradiation method.

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Supporting Information Available: SEM images of CuO nanoleaves without SDS and of Cu_2O products with 0.5 g of SDS, low-magnification SEM images of samples 1 and 3, low- and high-magnification SEM images of sample S1, TEM image of sample 2, XRD pattern of sample S1, and table of the synthesis conditions and morphology of sample S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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