Novel Way to Synthesize CuO Nanocrystals with Various Morphologies

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A novel and facile method for the synthesis of CuO nanocrystals with various morphologies is reported. The synthesis involves the convenient hydrothermal decomposition process of the $Cu(COOH)_2$ in the mixture of dimethyl sulfoxide (DMSO) and H_2O. The spherical, rodlike, and leaflike CuO nanocrystals are prepared by varying the concentration of water. The capacitance of CuO products was determined by cyclic voltammetry.

In recent years, synthesis and fabrication of one-dimensional (1-D) nanostructured materials, such as nanowires, nanorods, nanowhiskers, and nanofibers, have received much researsh interest, owing to their importance in basic scientific research and potential applications.[1–4] Various methods have been used to prepare 1-D objects, such as emulsion or polymetric system,[5] arc discharge,[6] laser ablation,[7] vapor transport,[8] and so on.[9,10]

Cupric oxide (CuO) has been extensively studied because of its close connection to high-T_c superconductors, and has attracted increasingly interests for both fundamental and practical reasons. It has been proved an industrially important material that can be widely used in applications such as gas sensor, magnetic storage media, electronics, solar-energy transformation, semiconductors, and catalysis.[11–15] Recently, many efforts have been made to synthesize 1-D nanotructured cupric oxide. For example, Chen et al.[16] prepared CuO shuttle-like nanocrystals via a hydrothermal decomposition route. Guan et al.[17] reported that CuO superfine fibers could be made via an electrospinning technique. Jiang et al.[18] synthesized CuO nanowires by heating copper substrates in air.

In this letter, we report the preparation of cupric oxide nanocrystals with various morphologies via a simple and convenient hydrothermal decomposition route. The synthetic procedure was as follows. In a Teflon-lined autoclave of 90-mL capacity, 0.5 g of $Cu(COOH)_2$ was dissolved in a series of mixture of anhydrous dimethyl sulfoxide (DMSO) and distilled water (total volume 70 mL). The volume ratios of DMSO to water were 50:3; 10:1; 5:1; 5:2, and 1:1, respectively. The autoclave was maintained at 110 °C for 3 h and then cooled to room temperature naturally. According to the ideal gas law, the pressure values in autoclaves were estimated to be ≈29.5 to 112.5 MPa. The obtained black precipitates were collected and washed with distilled water and absolute ethanol several times. The final products were dried in vacuum at 60 °C for 6 h.

Figure 1 shows the XRD patterns of the as-prepared samples under different reaction conditions. 2θ values of the major peaks located in the range of 30° to 70° correspond to the characteristic diffractions of monoclinic CuO (JCPDS 41-0254), verifying that the CuO products are phase-pure. As the content of distilled water increases, the diffraction peaks become sharper and stronger. This result indicates that the crystallinity of CuO is greatly improved by increasing the content of distilled water.

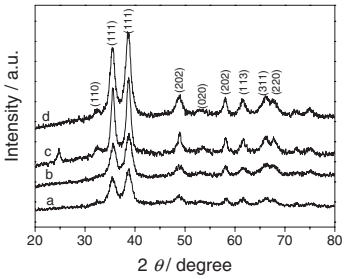

Figure 1. X-ray diffraction patterns of the samples prepared at different volume ratios of DMSO to water: (a) 50:3; (b) 5:1; (c) 5:2; (d) 1:1.

The TEM photographs of the different samples are shown in Figure 2. The spherical nanocrystals of CuO with an average diameter of 7 nm were prepared when the volume ratio of DMSO to water was 50:3, as shown in Figure 2a. The morphology of CuO nanocrystals changes with the increase of water in the reaction system. In Figure 2b, it is found that the spherical and rodlike nanocrystals coexist, and the rodlike nanocrystals with 5 nm in width and 15 nm in length almost reach 50%. When the ratio of DMSO to water is 5:1, the spherical CuO nanocrystals disappear completely. The sample completely consists of weakly aggregated rodlike nanocrystals. The width and length increase to 7 and 30 nm, respectively (Figure 2c).

As shown in Figure 2d, another interesting phenomenon is found that as the volume ratio of DMSO to water is varied from 50:3 to 5:2, the rodlike nanocrystals change to a partially aggre-

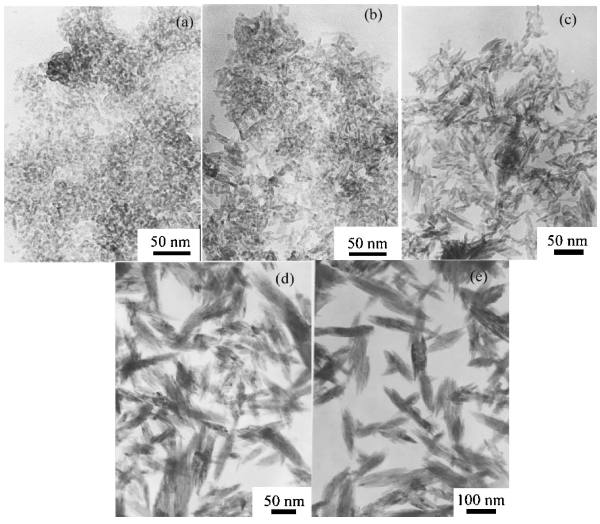

Figure 2. Representative TEM images of CuO nanocrystals synthesized at various volume ratios of DMSO and water: (a) 50:3; (b) 10:1; (c) 5:1; (d) 5:2; (e) 1:1.

gated state and take on leaflike morphology. The sizes of CuO nanocrystals in sample (e) grow twice of the nanocrystals in sample (d) and reach the width and length in the range of 40–45 nm and 150–200 nm, respectively, when the volume ratio of DMSO to water is 1:1.

Supported by the above observations, the concentration of water plays a crucial role in the formation of CuO nanocrystals. The corresponding reaction equations are listed as following:

$$D + H\text{–}O\text{–}H \rightleftarrows [D\text{–}H]^+ + OH^- \text{ (where D = DMSO)}$$

$$Cu(COOH)_2 + 2OH^- \rightarrow Cu(OH)_2 + 2COOH^-$$

$$Cu(OH)_2 \rightarrow CuO + H_2O$$

The surface tension of the DMSO–H_2O mixtures increases with water content.[19] When the water content is low, the DMSO tends to absorb the water vapor more quickly which results in abundant and small nuclei. DMSO acts as a dynamic stabilizer,[20] whose molecules can be bound to the surface of the nuclei through donating the lone electron pairs of their oxygen atom to the empty orbitals of the copper atoms, which tend to hinder the more combinations of Cu^+ and OH^-, and the steric effect of the DMSO molecules can also limit the growth of the nuclei. The experimental data show that the pH value increases slightly with the increase of water content in the mixture of water and DMSO without Cu^{2+}. So, more OH^- appears with the increase of water content. Because $Cu(OH)_2$ has layered structure and the growth rate is anisotropic,[21] They grow gradually in a 1-D direction to result in the rodlike structured CuO by dehydration process of $Cu(OH)_2$. With the increase of water content, the cementing process (e.g. oriented attachment) occurs because of the direct joining of suitable crystal planes.[22,23]

For comparison, we repeated the reaction at 90 °C for 3 h and 110 °C for 6 h for sample (c) and (d), and found the morphologies of the two samples were almost unchanged under these two conditions. These results show that the essential factor in the range of 90 to 110 °C, which determines the morphology of CuO nanocrystals in this hydrothermal reaction, is the water concentration.

Cyclic voltammograms (CVs) of electrodes prepared by pressing a mixture of various morphologies of CuO nanocrystals, acetylene black, and binder (PTFE) in a ratio of 85/10/5 are depicted in Figure 3. The electrodes were immersed in 1 M KOH, and the scan rate was 10 mV/s in the potential range of −400 to 800 mV vs Hg/Hg_2SO_4 to obtain a measurement of

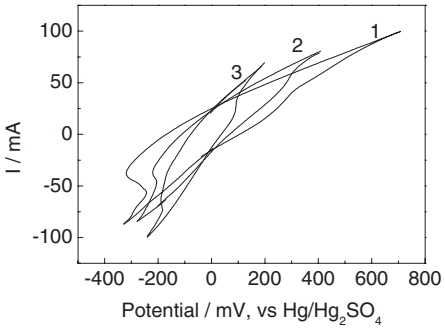

Figure 3. Cyclic voltammogram (sweep rate: 10 mV/s) of the electrodes in 1 M KOH. The electrode consists of CuO nanocrystals prepared at different volume ratio of DMSO and water: (1) 50:3; (2) 5:1; (3) 1:1.

the capacitances of the electrodes. The total capacitances from Figure 3 was calculated by $C = i/mv$, where i is the even current response, m is the mass of CuO and v is the potential sweep rate. The specific capacitances of the three electrodes were: (1) 23.8, (2) 23.1, and (3) 22.7 F/g, respectively. These results indicate that the capacitance of CuO nanocrystals increases as decreasing the particle size, and the nanostructured CuO can be used as promising electrode materials.

In summary, cupric oxide nanocrystals with different morphologies of spherical, rodlike, and leaflike shapes have been synthesized successfully via a simple and convenient hydrothermal decomposition route. The dynamic stabilizer of DMSO can limit the growth of CuO nanocrystals and the concentration of water determines the morphologies of the products. The CVs of electrodes prepared by CuO nanocrystals indicates that the nanostructured CuO can be a promising candidate for electrode materials.

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