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A controllable synthetic route to Cu, Cu_2O, and CuO nanotubes and nanorods†

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Reducing $Cu(OH)_4^{2-}$ with hydrazine hydrate and glucose in the presence of a structure-directing surfactant at room temperature gave Cu and Cu_2O nanotubes/nanorods, respectively, whereas facile hydrothermal treatment of $Cu(OH)_4^{2-}$ precursor resulted in CuO nanotubes/nanorods.

Since the discovery of carbon nanotubes in 1991, nanoscaled one-dimensional (1D) materials have attracted considerable attention due to their unique optical, electrical, and magnetic properties and their potential applications in nanodevices.[1] As we know, these properties of nanomaterials are highly size- and shape-dependent,[2] and therefore it is extremely important to be able to properly control the size and morphology of the nanomaterials. It has been shown that Cu, Cu_2O, and CuO are industrially important materials that can be widely used in applications such as magnetic storage media, solar energy transformation, electronics, sensors, batteries and catalysis.[3–5] In particular, among all metals, Cu is the most commonly used owing to its high electrical conductivity, which may make it a suitable interconnect for future generations of electronic nanodevices. Therefore we believe, with reason, that nanostructures of Cu, Cu_2O, and CuO will be of particular interest for the applications mentioned above. However, only a few reports have dealt with Cu, Cu_2O, and CuO nanowires/nanorods[6–8] and no studies have been reported on the synthesis of their nanotubes to date.

Recently, we have reported the synthesis of PbO_2 and Pb_3O_4 single-crystalline nanorods in the presence of a surfactant,[9] in which only one shape was obtained. In this communication, we report on the synthesis of Cu, Cu_2O, and CuO nanotubes and nanorods in the presence of a structure-directing surfactant, cetyltrimethylammonium bromide (CTAB) by varying reaction conditions and using $Cu(OH)_4^{2-}$ as an inorganic precursor. *Via* this method, not only the products but also the morphologies have been selectively controlled. Cu and Cu_2O 1D nanostructures were obtained by reducing $Cu(OH)_4^{2-}$ with hydrazine hydrate and glucose at room temperature, respectively, whereas facile hydrothermal treatment of the $Cu(OH)_4^{2-}$ precursor resulted in CuO. Hydrazine hydrate and glucose are common strong and weak reducing agents in aqueous solution, respectively. Control over the morphology of the products was achieved by surfactant assembly. Surfactant mesophases have proved to be useful and versatile "soft" templates, which may form different conformations by self-assembly and lead to the formation of different nanostructures.

In a typical synthesis, three identical sets of 100 mL of 8 mM $Cu(OH)_4^{2-}$ solutions were prepared by dissolving $CuCl_2$ (0.8 mmol) in 100 mL of 3 M NaOH. CTAB (6 mmol) was added to each set and stirred vigorously for 30 minutes at 50 °C to ensure the complete dissolution of CTAB. Then the first set of the solution was directly transferred into a 125 mL Teflon-lined stainless steel autoclave, sealed, and maintained at 120 °C for 12 h; hydrazine hydrate (1 mL) and glucose (0.8 mmol) were added to the other two sets, respectively, and the resulting mixtures were maintained at room temperature for 1 h. After all reactions were complete, the resulting products were collected, washed several times using absolute ethanol and distilled water, centrifuged, and dried under vacuum at room temperature for 12 h. Cu, Cu_2O and CuO nanotubes were obtained. The whole process, appropriate for the preparation of Cu, Cu_2O and CuO nanotubes, can be conveniently adjusted to prepare their nanorods by simply changing the concentration of $Cu(OH)_4^{2-}$ from 8 mM to 15 mM.

The composition and phase purity of the as-prepared products were examined by X-ray diffraction (XRD) (Fig. 1A). All the diffraction peaks can be indexed to a cubic phase with lattice constant a = 3.615 Å for Cu nanotubes/nanorods, a cubic phase with lattice constant a = 4.267 Å for Cu_2O nanotubes/nanorods, and a monoclinic phase with lattice constant a = 4.267 Å for CuO nanotubes/nanorods, which are in good agreement with their bulk. Due to the smaller size, the diffraction peaks of all nanotubes are broader than those of the corresponding nanorods. The calculated yield for each product is above 95% (based on Cu).

By simply adjusting the concentrations of $Cu(OH)_4^{2-}$($C_{Cu(OH)_4^{2-}}$) in reaction solution, different 1D nanostructures of Cu, Cu_2O, and CuO can be obtained. When $c_{Cu(OH)_4^{2-}} \leq 8$ mM, the products consisted mainly of Cu, Cu_2O and CuO nanotubes, respectively. The low magnification transmission electron microscope (TEM) images of the synthesized products (Fig. 1B, 1D and 1F) show needle-like structures. The high magnification TEM images (Fig. 1C, 1E and 1G) taken of the respective

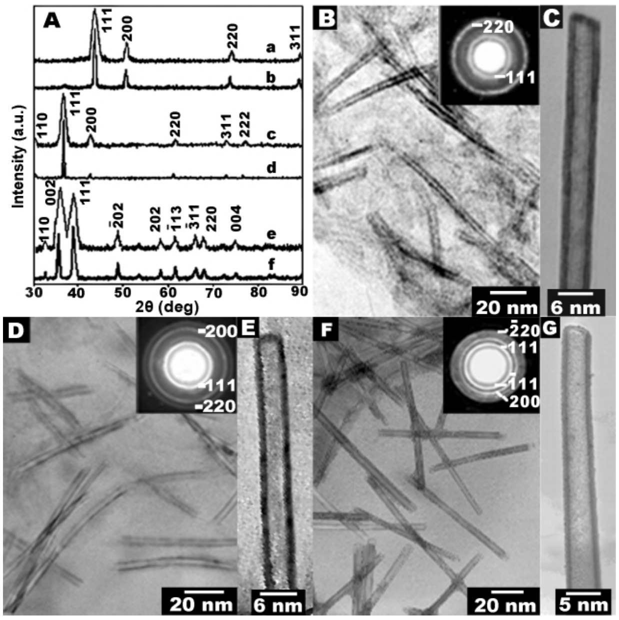

Fig. 1 (A) XRD patterns of (a) Cu nanotubes, (b) Cu nanorods, (c) Cu_2O nanotubes, (d) Cu_2O nanorods, (e) CuO nanotubes, and (f) CuO nanorods. TEM images of Cu (B), Cu_2O (D), and CuO (F) nanotubes, insets are SAED patterns of respective nanotubes, respectively. High magnification TEM images of a single Cu (C), Cu_2O (E) and CuO (G) nanotube.

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† Electronic supplementary information (ESI) available: EDS patterns of nanotubes and SEM images of nanorods. See http://www.rsc.org/suppdata/cc/b3/b304505f/

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typical needle-like structures reveal that the shell and core have a distinct boundary and no material is present in the core. Therefore, the needle-like structure is possibly a tube but with a closed end, and the darker region may correspond to the wall of the tube. The nanotubes have outer diameters of 5–8 nm, inner diameters of 3–5 nm, and lengths up to hundreds of nanometres. The intense rings resulting from selected-area electron diffraction (SAED) (insets in Fig. 1B, 1D and 1F), indexed to the XRD of the bulk materials by the method of comparative *d*-spacing, all show the polycrystalline nature of nanotubes. Energy dispersive spectroscopies (EDX) (Fig. S1, ESI†) further confirm the elemental composition of the respective products in expected stoichiometric proportions.

When $c_{\mathrm{Cu(OH)_4}^{2-}}$ was in the range 8–15 mM, we found the coexistence of tubes and rods in the products. Moreover, the higher the concentration of the $Cu(OH)_4^{2-}$ was, fewer tubes and more rods were present. When $C_{\mathrm{Cu(OH)_4}^{2-}}$ ≥15 mM, large quantities of Cu, Cu_2O, and CuO nanorods were obtained and no tubes were observed. The typical SEM images (Fig. S2, ESI†) and TEM images (Fig. 2a, 2d and 2g) both show that the samples display a rod-like shape and the nanorods are rather straight. The diameter is in the range of 10–35 nm, 10–50 nm and 50–120 nm, and the length is in the range of 0.5–1 μm, 0.5–1 μm and 1–5 μm, respectively. The SAED patterns (insets in Fig. 2c, 2f and 2i) taken of the respective nanorods (Fig. 2b, 2e and 2h) reveal that all the products exhibit a single-crystal structure. The high-resolution TEM (HRTEM) images (Fig. 2c, 2f and 2i) of the respective nanorods show the clearly resolved interplanar distances d_{111} = 2.09 Å, d_{111} = 2.47 Å, and $d_{\bar{1}11}$ = 2.53 Å; [111], [111], and [111] directions are all parallel to the long axis of the rods, suggesting the nanorods growing along the [111], [111], and [111] directions, respectively.

Recently, Gou *et al.*[10] reported the synthesis of Cu_2O nanocubes, with CTAB as the directing agent too. But the growth mechanisms may be different. In the synthetic procedure of Cu_2O nanocubes, the CTAB was used as a capping agent, whereas, in our synthetic system, the CTAB was used as a "soft" template. We propose a new growth model for these 1D nanomaterials including Cu_2O. CTAB has been systematically studied in the synthesis of mesostructured materials and may form spherical, cylindrical micelle, or even higher-order phases depending on the solution conditions.[11] In our system, we speculate that due to electrostatic interactions, inorganic precursor $Cu(OH)_4^{2-}$ and cationic surfactant CTAB can form different conformational inorganic–surfactant composites under different reaction conditions, which may serve as templates. The $Cu(OH)_4^{2-}$ anions present in the reaction mixture electrostatically interact with the surfactant cationic head groups, CTA^+, to form CTA^+–$Cu(OH)_4^{2-}$ ion pairs. When the concentration of $Cu(OH)_4^{2-}$ anions is lower, the number of necessary charge compensating cations decreases and thus the optimal value of the surfactant head group increases so that the system finds its minimum energy configuration by adopting the rodlike micelle structure.[12] Before the randomly oriented and loosely structured surfactant micelles surrounded by two or three monolayers of $Cu(OH)_4^{2-}$ anions form the higher phase, for example, the hexagonal mesostructure, the $Cu(OH)_4^{2-}$ has been changed into different products under different conditions such as hydrothermal conditions or addition of reducing agents. Thus, the Cu, Cu_2O and CuO nanotubes are formed. As the concentration of $Cu(OH)_4^{2-}$ increases to a higher value, the required number of charge compensating cations remarkably increases as well. So, the system favors a complete lamellar phase structure to obtain its minimum energy configuration.[12] The interlayers might serve as microreactors and are responsible for the ultimate formation of nanorods. During increasing the concentration of $Cu(OH)_4^{2-}$, the mesophase structure should be in the transition from a micellar to a lamellar phase and then leads to the coexistence of both phases in the mixture, which explains the coexistence of rods and tubes at a moderate concentration of $Cu(OH)_4^{2-}$.

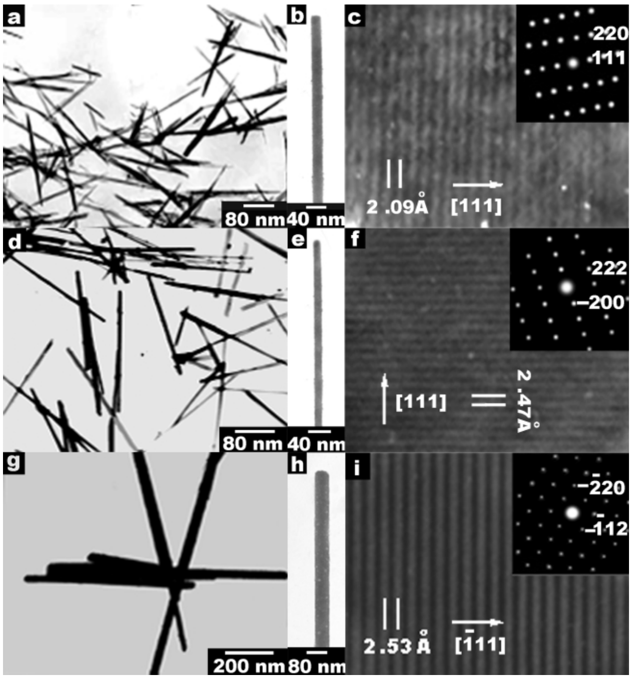

Fig. 2 TEM images of Cu (a), Cu_2O (d), and CuO (g) nanorods. Single nanorod images of Cu (b), Cu_2O (e), and CuO (h). HRTEM images of Cu (c), Cu_2O (f), and CuO (i) nanorods, and insets are SAED images of Cu, Cu_2O, and CuO nanorods, respectively.

In summary, we have selectively synthesized Cu, Cu_2O and CuO nanotubes and nanorods by using the same precursor $Cu(OH)_4^{2-}$ in the presence of CTAB under different reaction conditions. Our approaches effectively manipulate surfactant–inorganic aggregates in solutions. A lower concentration of $Cu(OH)_4^{2-}$ precursor favors tubular formation, whereas a higher concentration generally leads to rodlike formation. This simple synthesis strategy may represent a general approach for the synthesis of nanostructures of other amphoteric metal oxides, such as Al_2O_3, ZnO, SnO_2 and so forth.

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