

Unidirectionally Aligned Copper Hydroxide Crystalline Nanorods from Two-Dimensional Copper Hydroxy Nitrate

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Developing a method for the controlled synthesis of nanostructures at mesoscopic levels is one of the most challenging issues presently faced by materials scientists.¹ The requirement for dimensional control is especially true of one-dimensional (1D) structures (e.g., nanotube, nanorod, and nanowire), for which the control of nucleation and growth seems to be particularly difficult. Many methods have been used to control the size and morphology of the nanomaterials, such as vapor–liquid–solid (VLS) growth,² laser-assisted catalytic growth,³ and templating method.⁴ The most important problem in these fields is the development of a method that can synthesize reasonable quantities of product while maintaining dimensional monodispersity. Further to these aims, it would be advantageous to prepare these nanorods in crystal form and with preferred crystallographic orientations.

Over the past few years, numerous works have investigated the morphology of basic copper(II) salts and $\text{Cu}(\text{OH})_2$. These materials possess a well-known layered structure and have proven to be promising candidates for the fabrication of 1D nanostructures.^{5–11} In detail, $\text{Cu}(\text{OH})_2$ colloid particles have been conventionally synthesized in copper(II) solutions, and the relationship between the morphologies of homogeneously precipitated $\text{Cu}(\text{OH})_2$ and the solution compositions was systematically investigated by Matijević and co-workers.⁸ Polycrystalline $\text{Cu}(\text{OH})_2$ nanowires and nanoribbons were synthesized by exploiting a two-step wet chemical process⁹ and by coordination self-assembly in solution using Cu_2S nanowires as precursors,¹⁰ respectively. Finally, other $\text{Cu}(\text{OH})_2$ and CuO nanoribbons were also successfully synthesized on a copper surface in a controlled fashion.¹¹ However, despite their excellent approaches on the synthesizing route, no monodispersive nanostructures could be obtained in a controlled fashion. To accomplish this purpose, we pay attention to layered materials, which are necessary for the formation of 1D structure. Accordingly, as starting material we adopt copper hydroxide nitrate ($\text{Cu}_2(\text{OH})_3\text{NO}_3$), the crystal structure¹² of which is similar to that of $\text{Mg}(\text{OH})_2$ (brucite), where one-fourth of the OH^- groups are substituted by nitrate ligands in an ordered way. In this communication, we report a novel and facile method for providing unidirectionally aligned $\text{Cu}(\text{OH})_2$ nanorods from 2D $\text{Cu}_2(\text{OH})_3\text{NO}_3$ by anion exchange reaction using NaOH solution without any membrane or template. Similar approaches to fabricate 1D structure using NaOH can be found in the literature.¹³

The $\text{Cu}(\text{OH})_2$ nanorods are prepared from direct reaction of $\text{Cu}_2(\text{OH})_3\text{NO}_3$ with aqueous NaOH solution at room temperature. The starting material was synthesized according to standard literature procedures.¹⁴ In a typical synthesis, 2.5 g of starting material was dispersed in distilled water and added to aqueous NaOH solution (2 M). The mixture was stirred in an air-free round flask for 48 h at room temperature. The faint-blue powder was then filtered, washed with distilled water and ethanol, and dried in a vacuum at 35 °C.

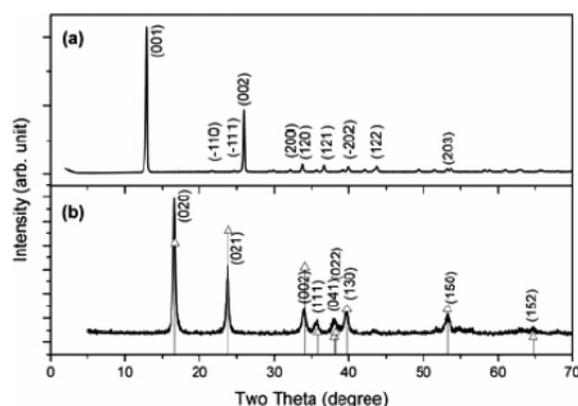


Figure 1. XRD patterns of (a) $\text{Cu}_2(\text{OH})_3\text{NO}_3$ (starting material) and (b) as-prepared $\text{Cu}(\text{OH})_2$ (direct reaction).

Figure 1 compares X-ray diffraction patterns of the as-prepared product and parent material. The starting $\text{Cu}_2(\text{OH})_3\text{NO}_3$ possesses a lamellar structure as is evident from XRD patterns shown in Figure 1a. They can be indexed on the monoclinic structure with lattice constants $a = 5.5983$, $b = 6.0848$, and $c = 6.9303$ Å, $\beta = 94.747^\circ$. The copper hydroxide nanorods were prepared starting from bulk $\text{Cu}_2(\text{OH})_3\text{NO}_3$ by direct reaction with aqueous NaOH solution. An XRD pattern of the obtained $\text{Cu}(\text{OH})_2$ product is shown in Figure 1b. All of the reflections of Figure 1b could be indexed to the $\text{Cu}(\text{OH})_2$ phase with the orthorhombic structure with calculated lattice constants $a = 2.9817$, $b = 10.622$, and $c = 5.3224$ Å (JCPDS 13-420).¹⁵ No impurity could be detected in the XRD analysis; therefore, pure $\text{Cu}(\text{OH})_2$ must have been obtained. The XRD analysis obviously indicates that the starting bulk $\text{Cu}_2(\text{OH})_3\text{NO}_3$ was transferred into $\text{Cu}(\text{OH})_2$ by direct reaction. This transformation is also confirmed by FTIR spectra (Figure S-1, Supporting Information). In addition, the intensities of (111), (130), and (020) of Figure 1b are significantly enhanced compared to the powder XRD pattern, indicating that the crystalline $\text{Cu}(\text{OH})_2$ is oriented in a particular crystallographic direction.

The morphology of the as-prepared $\text{Cu}(\text{OH})_2$ products was obtained by field-emission scanning electron microscopy (FE-SEM). It is evident that starting material possesses hexagonal plate morphology, as shown in Figure 2a. However, FE-SEM images, Figure 2b–d, reveal that the $\text{Cu}(\text{OH})_2$ products consist of nanorod arrays with diameters of 10–20 nm and lengths up to several μm . It is an important feature of the present system that most of $\text{Cu}(\text{OH})_2$ nanorods are uniformly aligned in a particular crystallographic direction within hexagonal plates.

The nanorodlike structure of the products was further examined by high-resolution TEM (HRTEM) (Figure 3). Bulk quantities of nanorods were formed with relatively uniform diameters of about 10 nm. The nanorods are relatively straight and long and tightly packed, leading to giant bundle arrays of few μm (Figure 3a). Figure

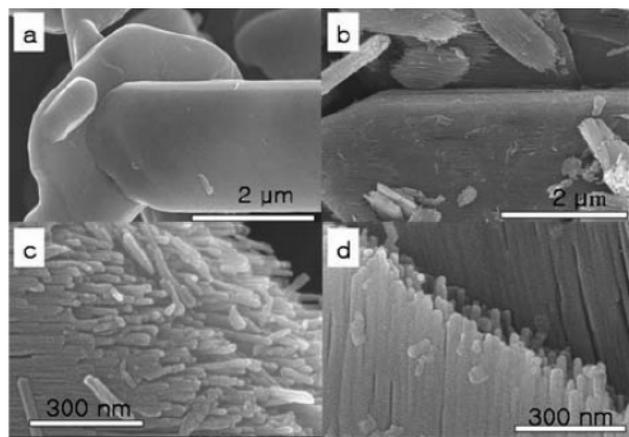


Figure 2. FESEM images of (a) $\text{Cu}_2(\text{OH})_3\text{NO}_3$, exhibiting hexagonal plates, (b) as-prepared $\text{Cu}(\text{OH})_2$, displaying unidirectionally aligned textures on a hexagonal thin plate, and (c and d) end-sides of a hexagonal plate in $\text{Cu}(\text{OH})_2$ arrays, exhibiting uniform rods in size of diameters (see magnification)

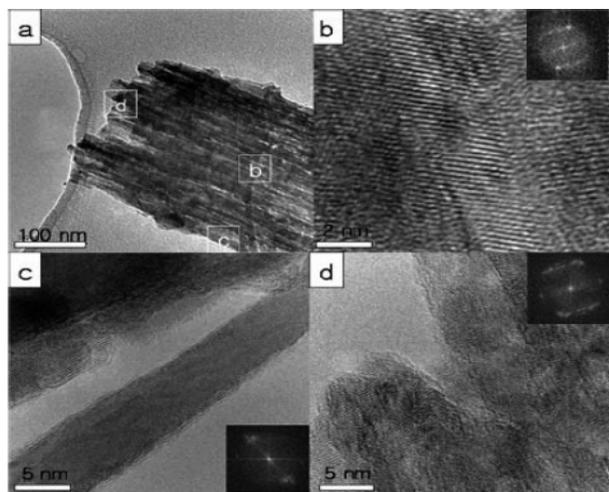


Figure 3. HRTEM images of (a) as-prepared $\text{Cu}(\text{OH})_2$, showing tightly bound nanorod arrays, leading to giant bundle, and (b–d) magnification images of selected area in giant nanorod bundle (insets: SAED shows that the crystalline rods are oriented with particular direction).

3b–d shows the magnification of selected areas of giant nanorod bundle arrays as shown in Figure 3a. Insets of Figure 3 show the selected-area electron diffraction (SAED), which revealed that $\text{Cu}(\text{OH})_2$ nanorods were single crystals.

We suggest that the material transformation from $\text{Cu}_2(\text{OH})_3\text{NO}_3$ to $\text{Cu}(\text{OH})_2$ originates from the structural feature of $\text{Cu}_2(\text{OH})_3\text{NO}_3$. $\text{Cu}_2(\text{OH})_3\text{NO}_3$ exhibits a botallackite-type structure,¹² where Cu^{2+} occupies two nonequivalent positions: $\text{Cu}(\text{I})$ is coordinated by four equatorial OH^- groups and two oxygen atoms belonging to NO_3 groups ($[4 + 2]$ -coordination), whereas $\text{Cu}(\text{II})$ is coordinated by four equatorial OH^- groups and by one OH^- and one NO_3 group in the axial directions ($[4 + 1 + 1]$ -coordination), respectively. Because the coordination polyhedra of $\text{Cu}(\text{II})$ are less distorted than those of $\text{Cu}(\text{I})$, the slight modification of the structure mainly concerns the nitrate group position, especially the positions of the nitrogen and the two terminal oxygen atoms. This reorientation takes

place in a plane almost parallel to (001).¹⁶ In the present system, replacement of the nitrate group position with a OH^- ion allows strong deformations of the octahedral cationic coordination, in special “antiferrodistortive” ordering,¹⁷ which might be realized in $\text{Cu}(\text{OH})_2$.¹⁸ It is worth noting that our strategy for the fabrication of 1D nanostructure is based on the modification of interlayer interactions (van der Waals or hydrogen bonding) in layered materials by exchange or substitution, leading to instability of intralayer interactions.

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Supporting Information Available: FTIR spectra of $\text{Cu}(\text{OH})_2$ nanorods and starting material, $\text{Cu}_2(\text{OH})_3\text{NO}_3$ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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