

# Simple Template-Free Solution Route for the Controlled Synthesis of $\text{Cu}(\text{OH})_2$ and $\text{CuO}$ Nanostructures

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The controlled synthesis of  $\text{Cu}(\text{OH})_2$  nanowires and nanoribbons in a solution phase has been realized with high yield at low cost by simply dropping KOH and ammonia solutions into an aqueous solution of  $\text{CuSO}_4$  at ambient temperature. It is demonstrated that the morphology of nanostructured  $\text{Cu}(\text{OH})_2$  is significantly influenced by the feeding manner of the alkaline solutions. A rational mechanism based on coordination self-assembly and oriented attachment is proposed for the selective formation of the polycrystalline  $\text{Cu}(\text{OH})_2$  nanowires and single-crystalline  $\text{Cu}(\text{OH})_2$  nanoribbons. In the presence of a polymeric additive, poly(acrylic acid) (PAA), ordered assemblies of  $\text{Cu}(\text{OH})_2$  nanorods can be readily obtained. Furthermore, well-defined  $\text{CuO}$  nanostructures, such as  $\text{CuO}$  nanoplatelets, nanoleaflets, and nanowires, were produced by thermal dehydration of the as-prepared  $\text{Cu}(\text{OH})_2$  nanostructures in solution or in the solid state. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) were used to characterize the products.

## Introduction

One-dimensional (1D) nanostructured materials, such as nanotubes, nanorods/nanowires, and nanobelts/nanoribbons, have attracted considerable attention due to their fundamental importance and potential wide-ranging applications.<sup>1</sup> Among the various methods developed for the fabrication of 1D nanomaterials, the solution-phase chemical synthesis has been considered as the most promising route in terms of cost, throughput, and the potential for large-scale production.<sup>2</sup> Generally, the solution-phase chemical approach may be classified into the template method, which employs hard<sup>3</sup> and soft<sup>4–6</sup> templates, and the template-free method, which uses surface-capping reagents for anisotropic confinements<sup>7</sup> or directly utilizes the highly anisotropic crystal structure of solid materials without capping reagents.<sup>8</sup> Accompanying the advance in synthesis method of 1D nanostructures, there is growing interest in the morphological control of the 1D nanostructures. In particular, as a new family of 1D nanostructures, nanobelts/nanoribbons are receiving increasing attention because of their unique properties and potential applications in building functional nanodevices;<sup>9</sup> however, there are few reports concerning the wet chemical fabrication of inorganic nanobelts.<sup>10–12</sup> It remains a significant challenge to realize elaborate control of the morphology of 1D nanostructures in the absence of template in aqueous solution.

As well-known layered materials,  $\text{Cu}(\text{OH})_2$  and basic  $\text{Cu}(\text{II})$  salts with an orthorhombic structure have received much attention in recent years.<sup>12–18</sup> Since its magnetic properties are sensitive to the intercalation of molecular anions,  $\text{Cu}(\text{OH})_2$  has the potential application as sensors.<sup>13</sup> Orthorhombic  $\text{Cu}_2(\text{OH})_3\text{-Cl}$  was recently found in living organisms as the first identified copper-based biomineral, which is formed in the teeth of a carnivorous marine worm and exists as polycrystalline nanofi-

bers arranged along the outer contour of the tooth tip, leading to an extraordinary resistance to abrasion.<sup>14</sup> Recently, 1D  $\text{Cu}(\text{OH})_2$  nanomaterials have been fabricated through solution-phase chemical approaches involving coordination self-assembly. For example, polycrystalline  $\text{Cu}(\text{OH})_2$  nanoribbons were prepared in aqueous solution of ammonia using  $\text{Cu}_2\text{S}$  nanowires as precursors,<sup>12a</sup> whereas single-crystalline  $\text{Cu}(\text{OH})_2$  nanoribbon<sup>12b</sup> and nanotube<sup>16</sup> arrays were prepared by surface oxidation of copper foil in alkaline solutions. On the other hand, polycrystalline  $\text{Cu}(\text{OH})_2$  nanowires were synthesized by a simple two-step process in aqueous ammonia and NaOH solutions<sup>17</sup> or by the interaction between a copper complex and NaOH at the aqueous–organic interface.<sup>18</sup> However, it is noted that the effective adjustment of 1D  $\text{Cu}(\text{OH})_2$  nanostructures between ribbon- and wirelike morphologies in one synthesis system has not been achieved so far.

As a p-type semiconductor with a narrow band gap (1.2 eV),  $\text{CuO}$  has been widely exploited for diverse applications as heterogeneous catalysts,<sup>19</sup> gas sensors,<sup>20</sup> lithium ion electrode materials,<sup>21</sup> and field emission (FE) emitters.<sup>22</sup> Many recent efforts have been directed toward the fabrication of nanostructured  $\text{CuO}$  to enhance its performance in currently existing applications. In particular, a variety of 1D  $\text{CuO}$  nanostructures have been prepared by high-temperature approaches<sup>23</sup> and low-temperature wet chemical approaches.<sup>21,24</sup> Notably, 1D  $\text{Cu}(\text{OH})_2$  nanostructures have been frequently employed as the precursors for the fabrication of 1D  $\text{CuO}$  nanostructures.<sup>12b,18,25</sup> However, a detailed study on the transformation from  $\text{Cu}(\text{OH})_2$  to  $\text{CuO}$  nanostructures is still lacking.

In this work, wire- and ribbonlike  $\text{Cu}(\text{OH})_2$  nanostructures have been selectively prepared by a two-step, template-free, wet chemical approach just through simply changing the feeding order of two alkaline solutions. The transformation from the 1D  $\text{Cu}(\text{OH})_2$  nanostructures to a variety of novel  $\text{CuO}$  nanostructures (wires, platelets, leaflets, and flowers) has been

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realized by thermal dehydration of the as-prepared  $\text{Cu}(\text{OH})_2$  nanostructures either in solution or in the solid state.

### Experimental Section

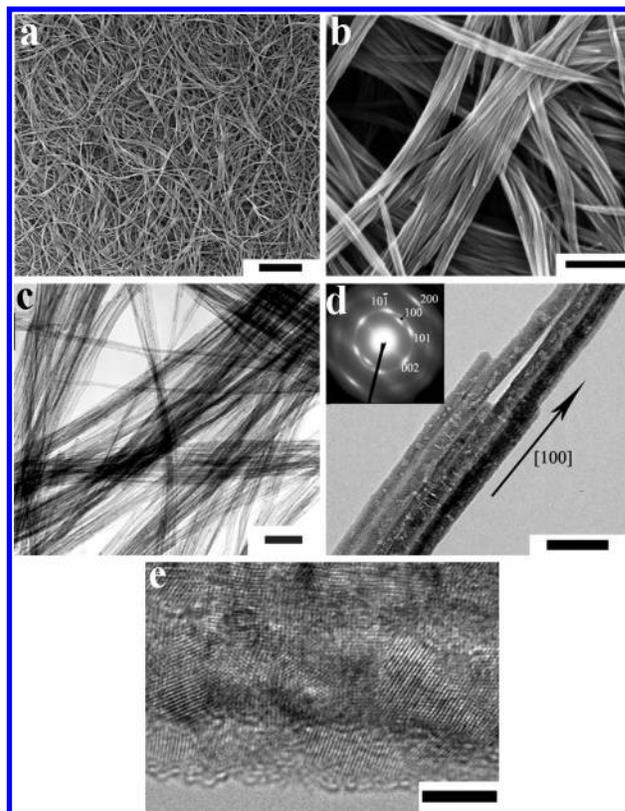
**Synthesis of  $\text{Cu}(\text{OH})_2$  Nanostructures.** Two different methods were used for the two-step synthesis of  $\text{Cu}(\text{OH})_2$  nanostructures, i.e., the  $\text{KOH}/\text{NH}_3$  route and the  $\text{NH}_3/\text{KOH}$  route. In a typical  $\text{KOH}/\text{NH}_3$  route to  $\text{Cu}(\text{OH})_2$  nanostructures, 0.8 mL of 1 M  $\text{KOH}$  solution was first dropped into 2 mL of 0.1 M  $\text{CuSO}_4$  solution under rigorous stirring at ambient temperature ( $\sim 19^\circ\text{C}$ ), which was followed by the dropping of 0.3 mL of ammonia solution (12.5 wt %,  $\sim 7.0$  M). After 3 min of further stirring, the mixed solution was kept static in a sealed vessel for 12 h (unless otherwise stated). The resultant precipitate was filtered off, washed thoroughly with deionized water, and dried in a vacuum at  $25^\circ\text{C}$  for 12 h. For the  $\text{NH}_3/\text{KOH}$  route to  $\text{Cu}(\text{OH})_2$  nanostructures, the synthesis procedure was identical to that for the  $\text{KOH}/\text{NH}_3$  route except for the feeding order of the two alkaline solutions; i.e., the  $\text{KOH}$  solution was added after the addition of the ammonia solution. Occasionally, a polymeric additive, poly(acrylic acid) (PAA, Aldrich,  $M_n = 5100$ ), was added to the solution before the addition of the alkaline solutions for the investigation of its effect on the  $\text{Cu}(\text{OH})_2$  nanostructures.

**Transformation of  $\text{Cu}(\text{OH})_2$  Nanostructures into  $\text{CuO}$  Nanostructures.** For the dehydration of  $\text{Cu}(\text{OH})_2$  nanostructures in solution, the  $\text{Cu}(\text{OH})_2$  nanostructures formed immediately after adding both alkaline solutions were heated at a given temperature (e.g.,  $30$  and  $50^\circ\text{C}$ ) for 12 h; alternatively, the as-prepared  $\text{Cu}(\text{OH})_2$  nanostructures were separated and redispersed in deionized water, followed by heat treatment at  $70^\circ\text{C}$  for a given time (e.g., 1 and 12 h). For the dehydration of  $\text{Cu}(\text{OH})_2$  nanostructures in the solid state, the as-prepared  $\text{Cu}(\text{OH})_2$  nanostructures were heated at  $120^\circ\text{C}$  for 2 h to dehydrate and subsequently at  $180^\circ\text{C}$  for another 3 h to promote crystallization.

**Characterization.** Field-emission scanning electron microscopy (FE-SEM) images were taken on a FEI STRATA DB235 microscope at an accelerating voltage of 10 kV. X-ray diffraction (XRD) was carried out on a Rigaku Dmax-2000 X-ray diffractometer equipped with  $\text{Cu K}\alpha$  radiation. Transmission electron microscopy (TEM) was performed on a JEOL JEM-200CX microscope with an accelerating voltage of 160 kV. High-resolution TEM (HRTEM) was performed on a Hitachi 9000HAR microscope. Selected samples were also investigated by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra spectrometer) with  $\text{Al K}\alpha$  monochromatized X-ray source running at 250 W and the base pressure in the analytic chamber about  $5 \times 10^{-9}$  Torr.

### Results and Discussion

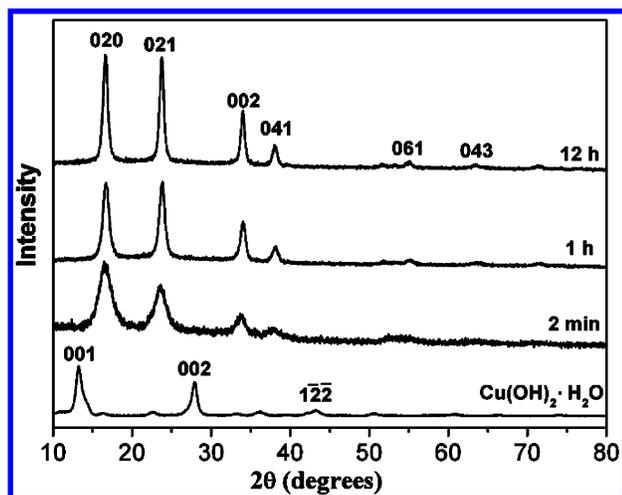
**Synthesis of  $\text{Cu}(\text{OH})_2$  Nanostructures.** The synthesis of  $\text{Cu}(\text{OH})_2$  nanostructures was simply achieved by successively dropping  $\text{KOH}$  and ammonia solutions into an aqueous solution of  $\text{CuSO}_4$  at ambient temperature ( $\sim 19^\circ\text{C}$ ). According to the feeding order of the two alkaline solutions, two different synthesis routes were adopted: the  $\text{KOH}/\text{NH}_3$  route where  $\text{KOH}$  was added first and ammonia was added subsequently, and the  $\text{NH}_3/\text{KOH}$  route where ammonia was added first followed by the addition of  $\text{KOH}$ . Figure 1 shows typical SEM and TEM images of the as-prepared  $\text{Cu}(\text{OH})_2$  nanostructures produced via the  $\text{KOH}/\text{NH}_3$  route and aged for 12 h. The product consists entirely of very long ( $\sim 20\ \mu\text{m}$ ) wirelike nanostructures (Figure 1a), and it appears that the nanowires tend to assemble into



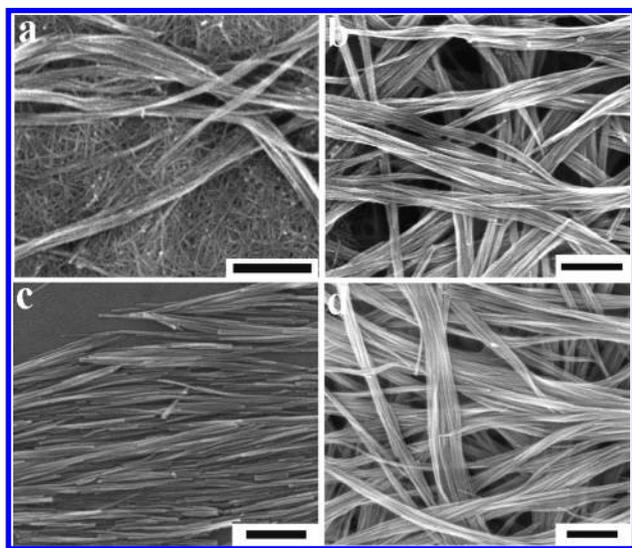
**Figure 1.** SEM (a, b), TEM (c, d), and HRTEM (e) images of  $\text{Cu}(\text{OH})_2$  nanowires prepared via the  $\text{KOH}/\text{NH}_3$  route aged for 12 h. Inset shows ED pattern of the bundled nanowires. Scale bars: (a)  $5\ \mu\text{m}$ ; (b)  $500\ \text{nm}$ ; (c)  $100\ \text{nm}$ ; (d)  $50\ \text{nm}$ ; (e)  $5\ \text{nm}$ .

nanowire bundles up to several hundreds of nanometers in diameters (Figure 1b). The TEM images (Figure 1c,d) suggest that the 1D nanostructures exhibit relatively uniform width ( $\sim 10\ \text{nm}$ ), which is consistent with a cylindrical wirelike morphology rather than a ribbonlike morphology. The HRTEM image (Figure 1e) suggests that the nanowires are polycrystalline nanowires consisting of orthorhombic  $\text{Cu}(\text{OH})_2$  nanocrystallites. However, the electron diffraction (ED) pattern corresponding to a bundle of nanowires shows some diffusive, yet strong, reflections, agreeing well with the orthorhombic structure of  $\text{Cu}(\text{OH})_2$ , which suggests that orientations of the crystallites are not random but coordinated with the  $[100]$  direction being the preferential growth direction of the polycrystalline nanowires or the growth direction on average. The XRD pattern of the nanowires aged for 12 h is presented in Figure 2, which shows sharp diffraction peaks attributed to the orthorhombic  $\text{Cu}(\text{OH})_2$ , implying the formation of pure  $\text{Cu}(\text{OH})_2$  nanowires. It is noted that only  $(0kl)$  reflections are clearly observed, which is in good agreement with the  $\text{Cu}(\text{OH})_2$  nanowires with preferential orientation along the  $[100]$  direction. The polycrystalline  $\text{Cu}(\text{OH})_2$  nanowires with preferential orientation could form through an oriented attachment mechanism,<sup>26</sup> which is reminiscent of the polycrystalline,  $[100]$ -oriented  $\text{Cu}(\text{OH})_2$  nanoribbons obtained in aqueous solution by using  $\text{Cu}_2\text{S}$  nanowires as precursors.<sup>12a</sup>

To understand the growth process of the  $\text{Cu}(\text{OH})_2$  nanowires in solution, we investigated the effect of aging time on the product. It was observed that the solution precipitated immediately after the addition of the  $\text{KOH}$  solution. As shown in Figure 2, the XRD pattern of the obtained precipitates suggests the precipitates consist of triclinic  $\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$  crystals (JCPDS 42-0746). The XRD patterns of the products obtained at different aging time after the addition of the ammonia solution

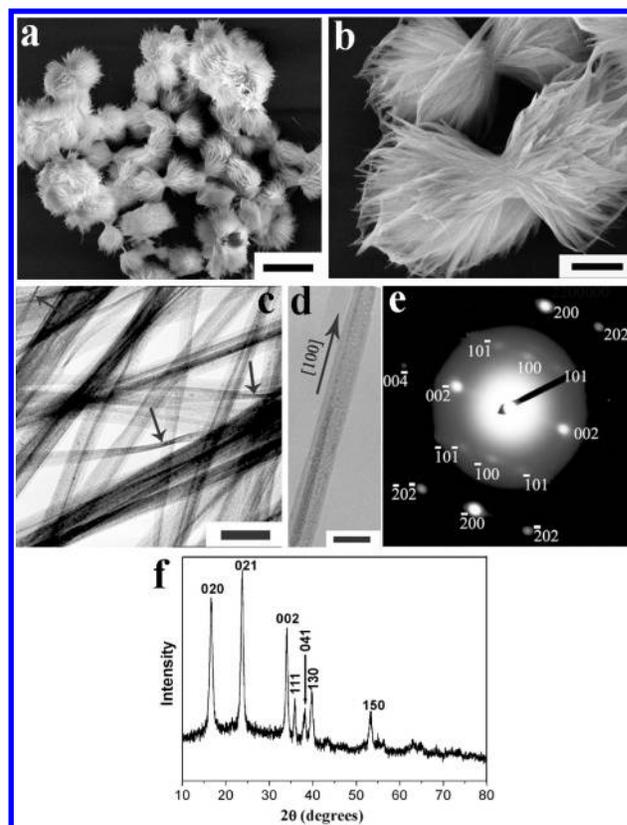


**Figure 2.** XRD patterns of  $\text{Cu}(\text{OH})_2$  nanowires prepared via the  $\text{KOH}/\text{NH}_3$  route aged for different periods. XRD pattern of  $\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$  precipitates obtained before adding ammonia is also displayed.



**Figure 3.** SEM images of  $\text{Cu}(\text{OH})_2$  nanowires prepared via the  $\text{KOH}/\text{NH}_3$  route aged for 2 min (a) and 1 h (b), and the  $\text{Cu}(\text{OH})_2$  nanowires obtained via the  $\text{KOH}/\text{NH}_3$  route aged for 1 h (c) and 12 h (d) and sonicated for 10 min. Scale bars: 500 nm.

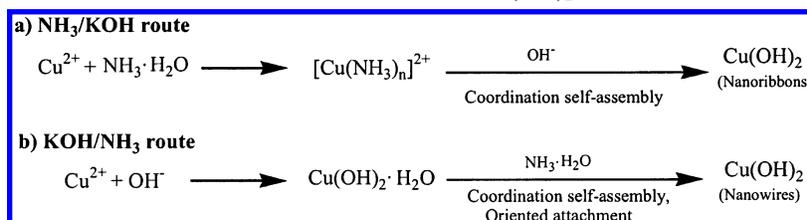
are also shown in Figure 2. After 2 min of aging, the product shows the XRD pattern corresponding to pure orthorhombic  $\text{Cu}(\text{OH})_2$ , indicating a quick transformation from  $\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$  to  $\text{Cu}(\text{OH})_2$  accompanying the addition of ammonia. The relatively broader diffraction peaks suggests the smaller crystallite size for the nanowires formed at the early stage. The typical SEM image of the sample is presented in Figure 3a, which shows that a large number of separated nanowires  $\sim 10$  nm in diameter coexisted with some bundles of nanowires (larger than 50 nm in bundle diameter). At an aging time of 1 h, the diffraction peaks were considerably narrowed, suggesting an increase in the crystallite size. Meanwhile, all the individual nanowires were assembled into bundles (Figure 3b), which is very similar to the product obtained after 12 h of aging (Figure 1a,b). However, simple ultrasonic treatment using a normal ultrasonic bath revealed a considerable difference in the toughness between the nanowires aged for 1 and 12 h. Upon 10 min of sonication, most of the long nanowires aged for 1 h were broken into short nanorods around 200–500 nm in length (Figure 3c). In contrast, the long nanowires aged for 12 h were not broken at all upon 10 min of sonication and the original



**Figure 4.** SEM (a, b) and TEM (c, d) images and ED (e) and XRD (f) patterns of  $\text{Cu}(\text{OH})_2$  nanoribbons prepared via the  $\text{NH}_3/\text{KOH}$  route. The ED pattern shown in plate e corresponds to the single nanoribbon shown in plate d. Scale bars: (a) 5  $\mu\text{m}$ ; (b) 1  $\mu\text{m}$ ; (c) 200 nm; (d) 100 nm.

morphology was almost completely reserved (Figure 3d). This result suggests that the nanowires aged for 1 h were still not well-crystallized and continued to develop into the well-crystallized nanowires probably through the Ostwald ripening process, which has been believed to assist the 1D growth process by oriented attachment.<sup>26c</sup> It is worth noting that oriented arrays of polycrystalline  $\text{Cu}_2(\text{OH})_3\text{Cl}$  nanofibers play a key role in enhancing hardness and stiffness of the teeth of a marine worm.<sup>14</sup> Therefore, the current room-temperature solution synthesis of bundles of polycrystalline  $\text{Cu}(\text{OH})_2$  nanowires, which has a similar orthorhombic structure, would have relevant biological implications.

When the feeding order of the two alkaline solutions was altered, a significant change in the morphology of the produced 1D  $\text{Cu}(\text{OH})_2$  nanostructures occurred. Figure 4 presents typical SEM and TEM images of the as-prepared  $\text{Cu}(\text{OH})_2$  nanostructures produced via the  $\text{NH}_3/\text{KOH}$  route along with their ED and XRD patterns. The SEM images (Figure 4a,b) suggest that the product consists of well-defined sheaves of nanoribbons about 5  $\mu\text{m}$  in length, and the TEM image (Figure 4c) shows thinning in the smooth bend and wring sections indicated by the arrows, which is characteristic of ribbonlike nanostructures. The nanoribbons are typically 30–100 nm in width and several nanometers in thickness. An enlarged TEM image showing a single nanoribbon is presented in Figure 4d with its related ED pattern shown in Figure 4e, which clearly shows spots associated with the  $[010]$  zone axis of the orthorhombic  $\text{Cu}(\text{OH})_2$ , indicating that the nanoribbon is a single-crystal grown along the  $[100]$  direction and enclosed with the  $(010)$  and the  $(001)$  as the top and side planes, respectively. The related X-ray diffraction pattern (Figure 4f) suggests the nanoribbons consist

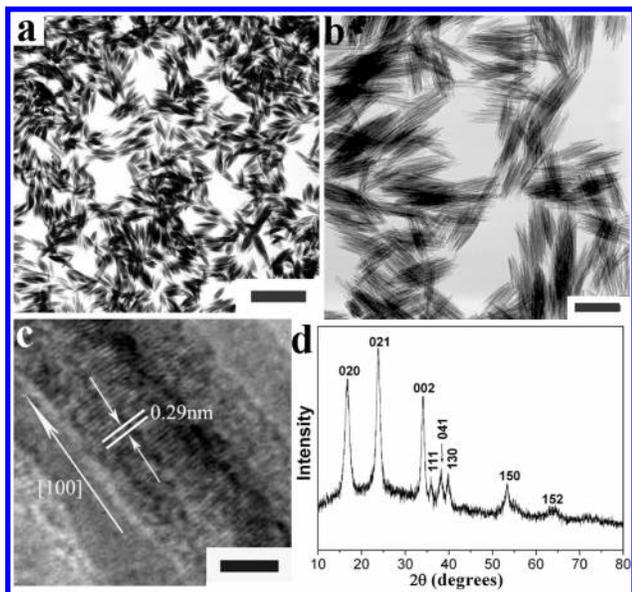
SCHEME 1: Schematic Illustration of the Growth Process of 1D Cu(OH)<sub>2</sub> Nanostructures in Solution

of pure orthorhombic Cu(OH)<sub>2</sub> and the presence of reflections other than the (0*kl*) reflections can be rationalized by considering that the nanoribbons are not well-aligned parallel to the substrate as they aggregate into sheaflike assemblies. The obtained [100]-oriented Cu(OH)<sub>2</sub> nanoribbons are reminiscent of the single-crystalline Cu(OH)<sub>2</sub> nanoribbons prepared by surface oxidation of copper foil in ammonia solutions where Cu(OH)<sub>2</sub> nanoribbons were grown almost vertically on the copper surface to form nanoribbon arrays.<sup>12b</sup> To the best of our knowledge, this is the first realization of selective synthesis of Cu(OH)<sub>2</sub> nanowires and nanoribbons in an aqueous solution system through simple alteration of the feeding order of two alkaline solutions. It is noteworthy that for the current NH<sub>3</sub>/KOH route to the Cu(OH)<sub>2</sub> nanoribbons, a considerable excess of ammonia with respect to CuSO<sub>4</sub> (e.g., [NH<sub>3</sub>]/[CuSO<sub>4</sub>] ~ 10) was required; otherwise, Cu(OH)<sub>2</sub> nanowires may be formed. For example, it was reported that only Cu(OH)<sub>2</sub> nanowires were obtained at a relatively low ammonia concentration ([NH<sub>3</sub>]/[CuSO<sub>4</sub>] ~ 1) when a similar NH<sub>3</sub>/NaOH route was employed.<sup>17</sup>

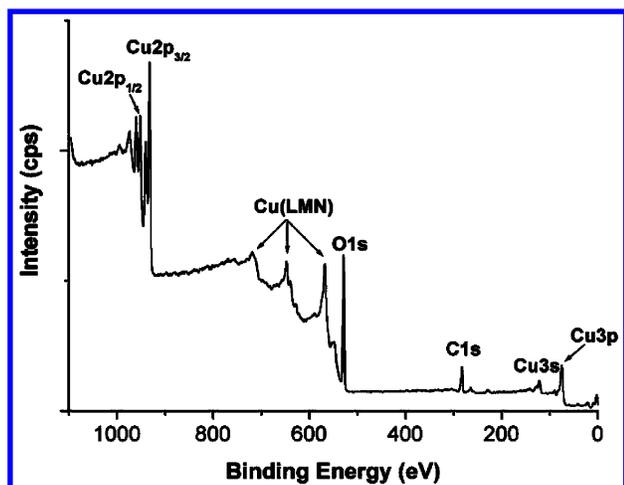
The exact mechanism for the selective formation of Cu(OH)<sub>2</sub> nanowires and nanoribbons remains to be investigated in more detail. As is well-known, the orthorhombic Cu(OH)<sub>2</sub> with a layered structure parallel to (010) consists of olated >Cu(OH)<sub>2</sub>Cu< chains oriented along [100] and characterized by the square-planar coordination of the Cu<sup>2+</sup> ions by OH<sup>-</sup> ions with strong σ<sub>yz</sub>-γ<sub>2</sub> bonds. According to the Bravais–Donnay–Harker law, the growth of Cu(OH)<sub>2</sub> along [100] is much faster than along other directions and the [010] direction is the lowest growth direction, leading to a tendency to form a ribbonlike structure.<sup>12,16</sup> Based on the recently discussed coordination self-assembly mechanism for the formation of Cu(OH)<sub>2</sub> nanoribbons, a tentative mechanism (Scheme 1) involving coordination self-assembly and oriented attachment was proposed for the formation of the current 1D Cu(OH)<sub>2</sub> nanostructures. For the NH<sub>3</sub>/KOH route to Cu(OH)<sub>2</sub> nanostructures, a homogeneous [Cu(NH<sub>3</sub>)<sub>n</sub>]<sup>2+</sup> solution was formed during the first step. Upon adding the KOH solution, OH<sup>-</sup> replaced NH<sub>3</sub> in the [Cu(NH<sub>3</sub>)<sub>n</sub>]<sup>2+</sup> complex to form square-planar [Cu(OH)<sub>4</sub>]<sup>2-</sup> units and a coordination self-assembly of the >Cu(OH)<sub>2</sub>Cu< chains occurred quickly, resulting in the formation of single-crystalline Cu(OH)<sub>2</sub> nanoribbons. The nucleation of Cu(OH)<sub>2</sub> could start from localized regions with relatively high [Cu(NH<sub>3</sub>)<sub>n</sub>]<sup>2+</sup> concentrations. Once the nuclei were formed, the growth of Cu(OH)<sub>2</sub> nanoribbons started on it, leading to the formation of sheaves of nanoribbons. The complex of [Cu(NH<sub>3</sub>)<sub>n</sub>]<sup>2+</sup> may act as a molecular transporter that transports Cu<sup>2+</sup> to the growing nanoribbon tips with OH<sup>-</sup> ligands attached; moreover, NH<sub>3</sub> may probably adsorb on the (010) surface to further slow the growth along the [010] direction, favoring the formation of the ribbonlike structure. When the feeding order of the NH<sub>3</sub> and KOH solutions was altered, i.e., the KOH/NH<sub>3</sub> route was employed, Cu(OH)<sub>2</sub>·H<sub>2</sub>O precipitated during the first step. Upon adding the ammonia solution, the Cu(OH)<sub>2</sub>·H<sub>2</sub>O precipitate was converted to Cu(OH)<sub>2</sub> crystals, probably through a solid–liquid–solid (SLS) process where the complex [Cu(NH<sub>3</sub>)<sub>n</sub>]<sup>2+</sup>

may also play an important role as a transporter. Although there was still a tendency to form Cu(OH)<sub>2</sub> nanoribbons by coordination self-assembly, during the SLS process, the [Cu(NH<sub>3</sub>)<sub>n</sub>]<sup>2+</sup> concentration in the solution could be relatively lower, which did not favor the formation of nuclei for the Cu(OH)<sub>2</sub> nanoribbons. Therefore, individual Cu(OH)<sub>2</sub> nanoparticles rather than long Cu(OH)<sub>2</sub> nanoribbons were formed at the beginning. Then Cu(OH)<sub>2</sub> nanowires grew preferentially along the [100] direction by the oriented attachment of the primary nanoparticles, which was coupled with coordination self-assembly, resulting in polycrystalline Cu(OH)<sub>2</sub> nanowires. The individual nanowires were further attached side by side to assemble into bundles on further aging, accompanying an Ostwald ripening process leading to larger crystallite sizes and tougher nanowires. The obtained nanowire bundle structures are reminiscent of the bundles of BaSO<sub>4</sub>/BaCrO<sub>4</sub> nanofibers obtained in the presence of polymeric additives;<sup>7d,e</sup> however, the current nanowire bundles were produced in polymer-free processes, and the driving force could partly come from the lateral capillary forces. On the other hand, the nanobelt bundles obtained via the NH<sub>3</sub>/KOH route may be formed due to the growth from the central nucleation points, which is somewhat similar to the bundles of BaSO<sub>4</sub>/BaCrO<sub>4</sub> nanofibers formed by growth from individual nucleation points under the direction of polymers.<sup>7d,e</sup>

Although the NH<sub>3</sub>/KOH route seems to be favorable for the formation of Cu(OH)<sub>2</sub> nanoribbons, such a tendency can be restrained by polymeric additives present in the solution. Poly(acrylic acid) (PAA) is a typical crystal growth inhibitor for many inorganic minerals.<sup>27</sup> When 2.5 × 10<sup>-4</sup> M PAA was present in the CuSO<sub>4</sub> solution before the addition of the two alkaline solutions, the product obtained by the NH<sub>3</sub>/KOH route consisted of relatively uniform assemblies of parallel-aligned Cu(OH)<sub>2</sub> nanorods 5–10 nm in width and ~200 nm in length (Figure 5a,b). From the HRTEM image (Figure 5c), it is observed that the nanorod is a single-crystal grown along the [100] direction, the fastest growth direction of the orthorhombic Cu(OH)<sub>2</sub>. The amorphous area can be observed on both sides of the nanorod, implying the adsorption of the polymer molecules on the nanorod. The corresponding XRD pattern (Figure 5d) is indicative of orthorhombic Cu(OH)<sub>2</sub>, confirming the formation of Cu(OH)<sub>2</sub> nanorod assemblies. The XPS result (Figure 6) shows typical Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> peaks with the measured binding energy of 934.5 and 954.2 eV, respectively, as well as their concomitant shake-up lines at 942.4 and 962.4 eV, which is indicative of the paramagnetic chemical state of Cu<sup>2+</sup>;<sup>28</sup> moreover, the well-resolved C 1s peak is observed at 284.8 eV, confirming the presence of PAA within the assemblies, i.e., the formation of PAA/Cu(OH)<sub>2</sub> hybrid nanomaterials. It is therefore reasonable to believe that the adsorption of PAA modifies the growth rate for special crystal planes to some extent. Especially, it could restrain the preferential growth along the [001] direction with respect to the [010] direction, resulting in the formation of Cu(OH)<sub>2</sub> nanorods rather than nanoribbons. The presence of adsorbed PAA molecules may also be contributed to the parallel attachment of the short



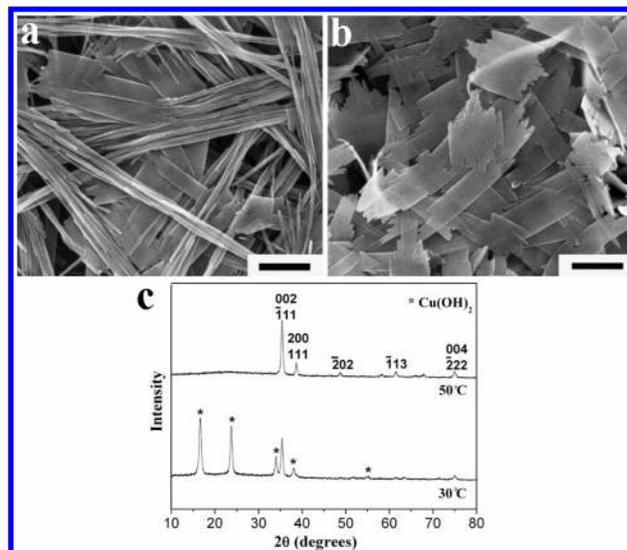
**Figure 5.** TEM (a, b) and HRTEM (c) images and the XRD pattern (d) of  $\text{Cu}(\text{OH})_2$  nanorod assemblies prepared via the  $\text{NH}_3/\text{KOH}$  route in the presence of PAA. Scale bars: (a)  $1 \mu\text{m}$ ; (b)  $200 \text{ nm}$ ; (c)  $3 \text{ nm}$ .



**Figure 6.** X-ray photoelectron spectrum of  $\text{Cu}(\text{OH})_2$  nanorod assemblies prepared via the  $\text{NH}_3/\text{KOH}$  route in the presence of PAA.

nanorods, which leads to the formation of the novel assemblies of  $\text{Cu}(\text{OH})_2$  nanorods. Such  $\text{Cu}(\text{OH})_2$ -based organic–inorganic hybrids with ordered nanostructures would find potential application as ferromagnets.<sup>29</sup> It is worth mentioning that the  $\text{Cu}(\text{OH})_2$  product obtained by the  $\text{KOH}/\text{NH}_3$  route in the presence of PAA still exhibited bundles of nanowires, suggesting that PAA would be favorable for the formation of cylindrical 1D nanostructures.

**Synthesis of CuO Nanostructures.** It is well-known that orthorhombic  $\text{Cu}(\text{OH})_2$  can be easily transformed to monoclinic CuO upon heat treatment. The thermal dehydration of the obtained 1D  $\text{Cu}(\text{OH})_2$  nanostructures in the solution phase and in the solid state was investigated but special effort was devoted to the transformation in solution as the transformation of  $\text{Cu}(\text{OH})_2$  nanoribbons to CuO nanoribbons/nanowires in solid state has been well-documented.<sup>12b,25</sup> When the  $\text{Cu}(\text{OH})_2$  nanowires obtained by the  $\text{KOH}/\text{NH}_3$  route were heated in the original solution immediately after the addition of the two alkaline solutions, a complete transformation to CuO occurred at a temperature as low as  $50^\circ\text{C}$ . As shown in Figure 7a, some nanoplatelets showing irregular contours appeared in addition to the bundles of  $\text{Cu}(\text{OH})_2$  nanowires after being aged for 12 h

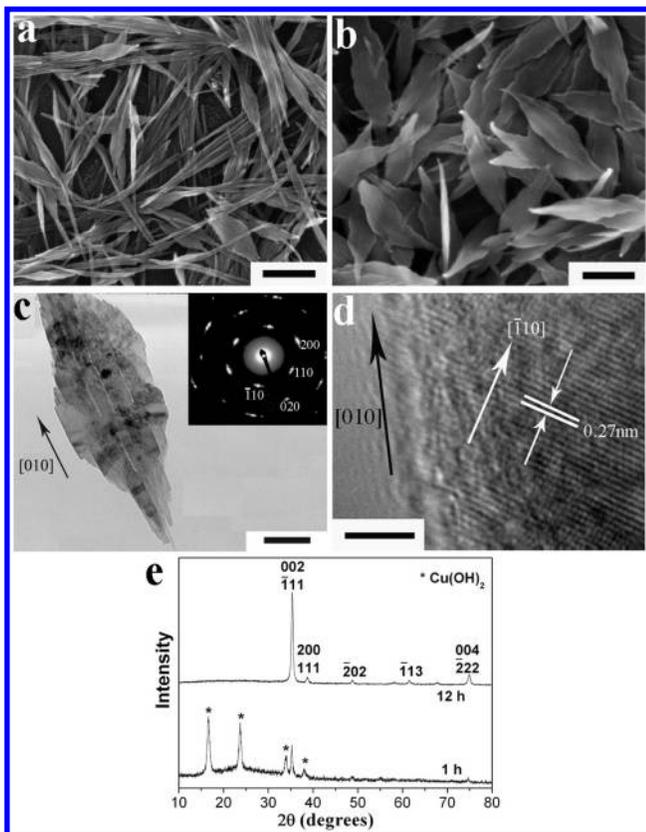


**Figure 7.** SEM images (a, b) and XRD patterns (c) of CuO nanoplatelets obtained by thermal dehydration of the  $\text{Cu}(\text{OH})_2$  nanowires prepared via the  $\text{KOH}/\text{NH}_3$  route immediately after the addition of the  $\text{KOH}$  and ammonia solutions: (a)  $30^\circ\text{C}$ ; (b)  $50^\circ\text{C}$ . Scale bars:  $500 \text{ nm}$ .

at  $30^\circ\text{C}$ . The corresponding XRD pattern (Figure 7c) shows the appearance of reflections attributed to monoclinic CuO, suggesting the part transformation of  $\text{Cu}(\text{OH})_2$  to CuO. When aged at  $50^\circ\text{C}$ , the  $\text{Cu}(\text{OH})_2$  nanowires were completely converted to the irregular CuO nanoplatelets (Figure 7b), which was confirmed by the corresponding XRD pattern (Figure 7c).

If the well-developed  $\text{Cu}(\text{OH})_2$  nanowires after 12 h of aging were separated and redispersed in water, the temperature for a complete transformation to CuO within 12 h was increased to  $\sim 70^\circ\text{C}$ . Figure 8 shows typical TEM and HRTEM images as well as the XRD pattern of the products dehydrated at  $70^\circ\text{C}$  for different times. When heated for 1 h, rhombic, leafletlike nanostrips appeared in addition to the original bundles of  $\text{Cu}(\text{OH})_2$  nanowires accompanying the appearance of the XRD peaks characteristic of monoclinic CuO; after 12 h of heating, uniform nanoleaflets  $0.7\text{--}0.8 \mu\text{m}$  in length,  $\sim 250 \text{ nm}$  in width, and  $\sim 50 \text{ nm}$  in thickness were obtained, and the corresponding XRD pattern suggests that the product consists of pure monoclinic CuO. This result suggests a gradual transformation of the  $\text{Cu}(\text{OH})_2$  nanowire bundles to the CuO nanoleaflets with heating at  $70^\circ\text{C}$ . The ED pattern of a single CuO nanoleaflet shows spots due to the [001] zone axis of monoclinic CuO, indicating that the CuO nanoleaflet is a single crystal elongated along the [010] direction with the top surface of the (001) plane, which is supported by the related HRTEM image.

It is noted that Matijević et al. have prepared polycrystalline ellipsoidal CuO colloids by a controlled double-jet precipitation technique using NaOH and  $\text{Cu}(\text{NO}_3)_2$  as the reactants, and they believed that the polycrystalline CuO ellipsoids were formed by aggregation of primary CuO nanoparticles.<sup>24a</sup> Recently, Zeng et al. have prepared hierarchical dandelion-like architectures constructed with single-crystalline rhombic CuO nanostrips as building units through a hydrothermal synthesis in alkaline ethanol solution, and they proposed that the CuO nanostrips (larger than  $600 \text{ nm}$  in breadth) were formed by oriented attachment of CuO nanoribbons (about  $10\text{--}20 \text{ nm}$  in breadth).<sup>24d</sup> It should be pointed out that during the solution synthesis of CuO, the final product composition and morphology are largely dependent on the synthesis condition, such as basicity and solvent, and the solid precursors including  $\text{Cu}(\text{OH})_2$  may exist only momentarily or may not exist at all. In the current situation,

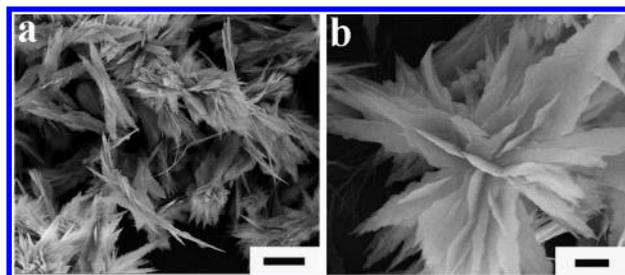


**Figure 8.** SEM (a, b), TEM (c), and HRTEM (d) images and XRD patterns (e) of CuO nanoleaflets obtained by thermal dehydration of the as-prepared Cu(OH)<sub>2</sub> nanowires in water at 70 °C for different times: (a) 1 h; (b–d) 12 h. Inset shows ED pattern of the single CuO nanoleaflet. Scale bars: (a, b) 500 nm; (c) 100 nm; (d) 3 nm.

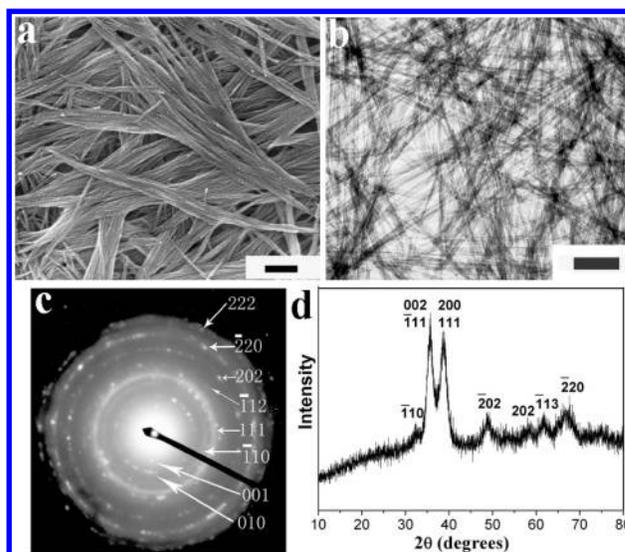
the CuO nanoleaflets may form by a reconstructive transformation from Cu(OH)<sub>2</sub> in aqueous solution involving a dissolution reaction followed by the crystallization of CuO.<sup>30</sup> It is noteworthy that at the early stage of the transformation, the intermediate state of transformation can be observed, which indicates that the CuO nanoleaflets were grown from some parts of the Cu(OH)<sub>2</sub> nanowires (Figure 8a). Moreover, when the transformation was complete, some parallel linear traces on the CuO nanoleaflets due to the sacrificial precursors of Cu(OH)<sub>2</sub> nanowire bundles can be clearly observed (Figure 8c). Therefore, it can be reasonably proposed that upon heating in water, some parts of the Cu(OH)<sub>2</sub> nanowires were preferentially dissolved and then CuO nucleated on some parts of the undissolved Cu(OH)<sub>2</sub> nanowires, which was followed by the gradual growth of CuO nanoleaflets accompanying the dissolution of the Cu(OH)<sub>2</sub> nanowires, both the bare nanowires and the nanowires encapsulated within the CuO nanoleaflets.

For comparison purpose, the thermal dehydration of the sheaves of Cu(OH)<sub>2</sub> nanoribbons, which were obtained by the NH<sub>3</sub>/KOH route, in solution was also investigated. As shown in Figure 9, unique, flowerlike aggregates consisting of CuO nanopetals were obtained after the as-prepared Cu(OH)<sub>2</sub> nanoribbons were redispersed in water and heated at 70 °C for 12 h. This result supports the mechanism of reconstructive transformation in solution involving a dissolution process followed by the CuO crystallization.

For the thermal dehydration of 1D Cu(OH)<sub>2</sub> nanostructures in the solid state, the Cu(OH)<sub>2</sub> nanowires obtained by the KOH/NH<sub>3</sub> route were selected as a representative example. After dehydration in the solid state at 120 °C for 2 h, bundles of CuO nanowires, which essentially reserved the morphology of the



**Figure 9.** SEM images of CuO nanostructures obtained by thermal dehydration of the as-prepared Cu(OH)<sub>2</sub> nanoribbons in water at 70 °C for 12 h. Scale bars: (a) 2 μm; (b) 500 nm.



**Figure 10.** SEM (a) and TEM (b) images and ED (c) and XRD (d) patterns of CuO nanowires obtained by thermal dehydration of the as-prepared Cu(OH)<sub>2</sub> nanowires in the solid state at 120 °C for 2 h. Scale bars: (a) 500 nm; (b) 200 nm.

original Cu(OH)<sub>2</sub> nanowires, were obtained (Figure 10a,b). The related ED and XRD patterns demonstrate the complete conversion of Cu(OH)<sub>2</sub> to monoclinic CuO. The relatively broad peaks shown in the XRD pattern (Figure 10d) indicates that the CuO nanowires are actually polycrystalline nanowires consisting of primary nanocrystallites. This result suggests that the morphology of the 1D Cu(OH)<sub>2</sub> nanostructures obtained by the solution route can be well-reserved upon a simple heating process in the solid state, which is consistent with the result reported for the Cu(OH)<sub>2</sub> nanoribbons obtained by the surface oxidation of Cu and solution-phase coordination self-assembly.<sup>12b</sup>

## Conclusions

In summary, a facile, template-free, low-temperature synthesis of Cu(OH)<sub>2</sub> nanowires and nanoribbons has been realized by simply dropping KOH and ammonia solutions into an aqueous CuSO<sub>4</sub> solution. According to the feeding order of the two alkaline solutions, the KOH/NH<sub>3</sub> route and the NH<sub>3</sub>/KOH route were employed to selectively fabricate polycrystalline Cu(OH)<sub>2</sub> nanowires and single-crystalline Cu(OH)<sub>2</sub> nanoribbons, respectively. It has been reasonably proposed that the Cu(OH)<sub>2</sub> nanoribbons were formed by solution-phase coordination self-assembly at a relatively high [Cu(NH<sub>3</sub>)<sub>n</sub>]<sup>2+</sup> concentration, whereas the Cu(OH)<sub>2</sub> nanowires were formed by oriented attachment coupled with coordination self-assembly through a solid–solution–solid process, where a relatively low [Cu(NH<sub>3</sub>)<sub>n</sub>]<sup>2+</sup> concentration was retained. Ordered assemblies of Cu(OH)<sub>2</sub> nanorods were readily synthesized under the direction

of a polymeric additive in the solution. Furthermore, the transformation of the 1D Cu(OH)<sub>2</sub> nanostructures to well-defined CuO nanostructures, such as nanoplatelets, nanoleaflets, and nanowires, in the solution phase and in the solid state was investigated. It has been revealed that the conversion from Cu(OH)<sub>2</sub> to CuO in solution occurred mainly through a reconstructive transformation involving a dissolution process followed by the CuO crystallization, while the thermal dehydration of 1D Cu(OH)<sub>2</sub> nanostructures in the solid state normally resulted in the morphology-reserved 1D CuO nanostructures. The obtained low-dimension copper-based nanomaterials generally promise potential applications as sensors, catalysts, ferromagnets, and lithium ion electrode materials; moreover, the 1D Cu(OH)<sub>2</sub> nanostructures may have relevant biological implications due to their similarity in structure and morphology to the Cu<sub>2</sub>(OH)<sub>3</sub>Cl nanofibers existing in living organisms as the first identified copper-based biomineral.<sup>14</sup> Finally, this simple route may provide an effective method for the morphological control of 1D nanostructures, and it is potentially extendable to other systems involving metal complexes with suitable combination of metals and ligands.

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