Chem. Mater. **2006,** *18,* 1795−1802

Formation of Positively Charged Copper Hydroxide Nanostrands and Their Structural Characterization

Yan-Hong Luo,[†] Jianguo Huang,[†] Jian Jin,[†] Xinsheng Peng,[†] Wolfgang Schmitt,[‡] and
Izumi Ichinose*,[†]

Advanced Materials Laboratory and International Center for Young Scientists (ICYS), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Received October 13, 2005. Revised Manuscript Received February 20, 2006

Extremely narrow copper hydroxide nanostrands with a diameter of 2.5 nm were prepared by controlling the pH of an aqueous copper nitrate solution with weak bases. The nanostrands grew slowly from initially formed small particles of 2−6 nm. The growth was highly sensitive to the amount and types of weak bases. Long nanostrands were obtained in a range of pH 6.0−6.2 at a concentration of approximate 2 mM copper nitrate. The length reached several tens of micrometers after an aging time of a few days, giving an aspect ratio more than tens of thousands. Their structures were characterized by scanning electron microscopy, transmission electron microscopy (TEM), and electron diffraction. This nanostrand is composed of positively charged linear clusters, $[Cu_8(OH)_{14}(H_2O)_4]^{2+}$, as judged from the results of high-resolution TEM, UV−vis titration experiments, and crystallographic considerations. We widely investigated the nanomorphologies of copper hydroxide and related compounds by changing the synthetic conditions and then proposed a unique growth mechanism for the nanostrands of orthorhombic copper hydroxide.

Introduction

One-dimensional (1D) nanostructures, such as wires, rods, tubes, and belts, have received increasing interest from various fields of science.[1−4] In the past decade, remarkable advances have been made in the synthesis and characterization of such materials, which are expected to open the way for nano-electronics, ultrasmall optoelectronic devices, biosensors, and so forth.[5−7] Many 1D metal oxides have been synthesized through high-temperature processes such as vapor−liquid−solid growth and oxide-assisted growth.[8,9] Anisotropic growth of crystalline metal oxides has been controlled by using proper capping agents.[10] The other synthetic strategy is the use of hard templates such as porous alumina and a polycarbonate membrane, which physically confine the growing metal oxides within the 1D nanospace.[11] On the other hand, low-temperature liquid-phase techniques have an advantage in the large scale synthesis of metal oxide nanofibers. The processes are also environmentally friendly. However, liquid-phase syntheses are often prone to be phenomenological research. This is partly due to the large number of parameters that affect the nanomorphologies. Crystal growth in vacuum conditions can be analyzed by electron microscopy at the atomic scale. In contrast, crystal growth in water is usually not very clear. The real problem is the lack of basic information on the clusters or oligomers of hydrated metal ions that will be precursors of 1D metal oxides.

Recently, we discovered that micrometer-long and 2-nm-wide nanofibers of cadmium hydroxide spontaneously form by raising the pH of a dilute cadmium nitrate solution. We named these fibers inorganic nanostrands, because their size and morphology are comparable to those of rigid double-stranded DNA.[12] Interestingly, the surface of the nanostrand is extremely positively charged, similarly to a rodlike assembly of cationic surfactant molecules. This unique property was utilized for the separation of short DNA fragments and for the creation of fibrous nanocomposites with anionic dyes.[13,14] This nanostrand is thought to be made of flat positively charged hexagonal clusters of cadmium hydroxide, which are supposed to exist in water at neutral pH and which display the ability to assemble into the nanostrand. In other words, this nanostrand can be regarded as a supramolecular polymer of the hexagonal clusters. Müller and Liu et al. recently reported that some hydrophilic polyoxometalates aggregate in water to give vesicular

---

* To whom correspondence should be addressed. E-mail: ichinose.izumi@nims.go.jp. Phone: +81-29-851-3354 (ext. 8326). Fax: +81-29-852-7449.
† Advanced Materials Laboratory.
‡ International Center for Young Scientists.

(1) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Adv. Mater.* **2003**, *15*, 353.
(2) Peng, X.; Manna, L.; Yang, W.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59.
(3) Iijima, S. *Nature* **1991**, *354*, 56.
(4) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, *291*, 1947.
(5) Cui, Y.; Lieber, C. M. *Science* **2001**, *291*, 851.
(6) Duan, X.; Huang, Y.; Cui, Y.; Wang, J.; Lieber, C. M. *Nature* **2001**, *409*, 66.
(7) Cui, Y.; Wei, Q.; Park, H.; Lieber, C. M. *Science* **2001**, *293*, 1289.
(8) Wang, X.; Song, J.; Li, P.; Ryou, J. H.; Dupuis, R. D.; Summers, C. J.; Wang, Z. L. *J. Am. Chem. Soc.* **2005**, *127*, 7920.
(9) Yin, Y.; Zhang, G.; Xia, Y. *Adv. Funct. Mater.* **2002**, *12*, 293.
(10) Guo, L.; Ji, Y. L.; Xu, H. *J. Am. Chem. Soc.* **2002**, *124*, 14864.
(11) Zheng, M. J.; Zhang, L. D.; Li, G. H.; Shen, W. Z. *Chem. Phys. Lett.* **2002**, *363*, 123.
(12) Ichinose, I.; Kurashima, K.; Kunitake, T. *J. Am. Chem. Soc.* **2004**, *126*, 7162.
(13) Ichinose, I.; Huang, J.; Luo, Y. H. *Nano Lett.* **2005**, *5*, 97.
(14) Luo, Y. H.; Huang, J.; Ichinose, I. *J. Am. Chem. Soc.* **2005**, *127*, 8296.

10.1021/cm052270s CCC: $33.50

assemblies.[15,16] The polyoxometalates, negatively charged metal oxide clusters, reveal unique self-assembly properties that have never been observed for small hydrated metal ions. The cadmium hydroxide nanostrands were also assembled from the clusters. Such results suggest that charged clusters have the potential to assemble into ordered nanostructures in water and represent ideal building units and important modules for nanostructures.

To generalize this approach for the formation of 1D nanostructures, especially the formation of metal hydroxide nanostrands, we decided to investigate further metal hydroxides. First, we focused on divalent copper ions (Cu^{2+}). Copper hydroxide and basic copper salts are well-known layered materials. It has been long known that these materials tend to give needle-type crystals in water.[17−19] Long and narrow fibers with a width of 20−100 nm were obtained by Yang and his co-workers through the conversion of Cu_2S nanowires into $Cu(OH)_2$ in an aqueous solution of ammonia.[20] Similar crystalline nanofibers were obtainable by directly treating the surface of a copper foil with an alkaline solution.[21] Recently, aligned nanorods of $Cu(OH)_2$ were synthesized from two-dimensional $Cu_2(OH)_3NO_3$, a basic copper salt, by anion exchange using sodium hydroxide.[22] Preparation of narrow $Cu(OH)_2$ nanofibers has been reported by a few research groups.[23−25] Specifically, Song and co-workers reported that extremely narrow nanofibers of 4−5 nm in diameter were observed in their fibrous materials.[25]

Our investigations address the question of whether it is possible to obtain copper hydroxide fibers with an even smaller cross-sectional diameter, despite the fact that the proportion of the surface copper atoms quickly increases with the decrease of the diameter. Such fibers might be positively charged, as seen in the case of cadmium hydroxide nanostrands.[12] Also, the growth mechanism should be significantly affected by the surface structure. We report herein the formation of extremely narrow copper hydroxide fibers with a width of 2.5 nm. The length reached several tens of micrometers, and the aspect ratio exceeded tens of thousands. Crystallographic consideration led to the conclusion that the nanofibers are made of positively charged linear clusters of copper hydroxide.

Results and Discussion

A. Formation of Copper Hydroxide Nanostrands. Copper hydroxide is synthesized by raising the pH of a solution containing Cu^{2+} ions. Despite the simple reaction, the shapes of the crystals vary widely depending on the experimental conditions.[17,18] In the cases of copper chloride ($CuCl_2$) and copper sulfate ($CuSO_4$), the sparingly soluble basic copper salts are often formed.[18] Therefore, we chose copper nitrate ($Cu(NO_3)_2$) as a source of Cu^{2+} ions. To precisely control the pH of the solution in the neutral range, we used aminoethanol, a water-soluble weak organic base. In particular, we examined the formation of copper hydroxide in the slightly acidic and dilute solutions of copper nitrate.

The 1.6 mM aqueous solution of aminoethanol (10 mL) was quickly added into an equal volume of aqueous copper nitrate (4 mM) with vigorous stirring. The color of the mixed solution turned slightly blue as a result of the complexation of the aminoethanol. After aging for 3 days at room temperature, 5 mL of the solution was filtered by suction filtration using a porous polycarbonate membrane filter. This membrane filter was used for the sample preparation prior to the scanning electron microscopy (SEM) observation.

As a matter of fact, extremely narrow copper hydroxide nanofibers were produced in the above mixed solution. However, we did not observe any precipitates. The solution was transparent during aging. The nanofibers filtered by the membrane filter were also difficult to directly observe by SEM, because the width was close to the resolution (2−3 nm) of our instrument for the materials with low electronic conductivity. However, we could successfully visualize their structure by coating them with a thin platinum layer using a mild ion sputter. Figure 1a shows the SEM image of the nanofibers deposited on the polycarbonate membrane filter. A uniform network structure was observed in a wide area, and the length of the individual nanofibers exceeded a few micrometers. Sparser networks were obtained when the filtration volume was 0.5 mL, as shown in Figure 1b. The width of the nanofibers appeared to be 5−10 nm. However, this width includes the thickness of the platinum layer covering the individual nanofibers. From our experimental conditions, the increase should be around 4−5 nm on average. A nanofiber network was peeled from a polycarbonate membrane before platinum coating and used for transmission electron microscopy (TEM) observation. The image is shown in Figure 1c. Because of the extremely narrow structure, the electron diffraction pattern was not very clear. However, the inner strong ring and outer two weak halos were attributable to (111) and (002), (130), (151), and (221) diffractions of orthorhombic $Cu(OH)_2$.[26,27] Figure 1d shows the TEM image of copper hydroxide nanofibers on a carbon coated microgrid. To prepare the specimen, the nanofibers in the solution were directly adsorbed onto the TEM microgrid. The observed nanofibers were very long and straight. The width was estimated to be 2.5 nm. This morphology was much different from previously reported nanobelts and nanowires[20,23] and very close to that observed for cadmium hydroxide nanostrands.[12] Therefore, we decided to call them copper hydroxide nanostrands.

---

(15) Liu, T.; Diemann, E.; Li, H.; Dress, A. W. M.; Müller, A. *Nature* **2003**, *426*, 59.
(16) Liu, G.; Liu, T. *J. Am. Chem. Soc.* **2005**, *127*, 6942.
(17) Durand-Keklikian, L.; Matijeviæ, E. *Colloid Polym. Sci.* **1990**, *268*, 1151.
(18) Kratohvil, S.; Matijević, E. *J. Mater. Res.* **1991**, *6*, 766.
(19) Rodríguez-Clemente, R.; Serna, C. J.; Ocaña, M.; Matijević, E. *J. Cryst. Growth* **1994**, *143*, 277.
(20) Wen, X.; Zhang, W.; Yang, S.; Dai, Z. R.; Wang, Z. L. *Nano Lett.* **2002**, *2*, 1397.
(21) Wen, X.; Zhang, W.; Yang, S. *Langmuir* **2003**, *19*, 5898.
(22) Park, S. H.; Kim, H. J. *J. Am. Chem. Soc.* **2004**, *126*, 14368.
(23) Wang, W.; Lan, C.; Li, Y.; Hong, K.; Wang, G. *Chem. Phys. Lett.* **2002**, *366*, 220.
(24) Lu, C.; Qi, L.; Yang, J.; Zhang, D.; Wu, N.; Ma, J. *J. Phys. Chem. B* **2004**, *108*, 17825.
(25) Song, X.; Sun, S.; Zhang, W.; Yu, H.; Fan, W. *J. Phys. Chem. B* **2004**, *108*, 5200.
(26) Wang, Z. L.; Kong, X. Y.; Wen, X.; Yang, S. *J. Phys. Chem. B* **2003**, *107*, 8275.
(27) We attemped to characterize copper hydroxide nanostrands by a conventional X-ray diffraction technique. However, it was very difficut to obtain the diffraction due to the narrow width of the nanostrands.

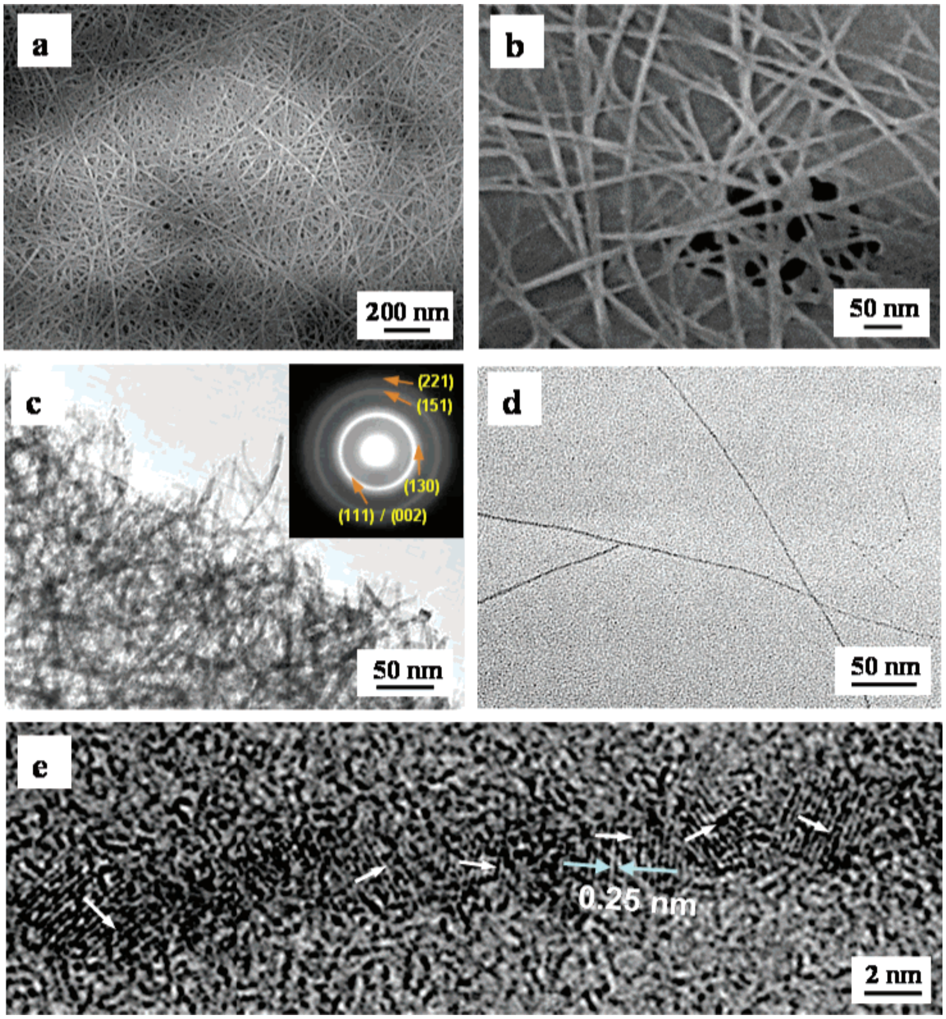


Figure 1. SEM (a, b), TEM (c, d), and HR-TEM (e) images of copper hydroxide nanostrands. The electron diffraction pattern is shown in the inset of part c. SEM images were obtained after Pt coating. All these nanostrands formed in aqueous solutions of copper nitrate.

A high-resolution TEM (HR-TEM) image of a copper hydroxide nanostrand is shown in Figure 1e. We could clearly observe the spacing of 0.250 nm, corresponding to the (111) planes of orthorhombic $Cu(OH)_2$.[28] The crystal lattice was not continuous along the nanostrand and appeared to change periodically, as indicated with arrows. This nanostrand was first deemed to have an axial chirality. However, as described later, the crystallographic consideration revealed that it was difficult for the copper hydroxide nanostrand to have such short pitch axial chirality. One of the possible explanations for the discontinuous lattice is that the crystalline nanostrand was broken when it was adsorbed on the glassy carbon surface of the TEM microgrid.

Subsequently, we investigated the effect of aging time on the morphology of the copper hydroxide. Figure 2a shows a SEM image of nanostructures produced 5 min after mixing copper nitrate and aminoethanol solutions. Observed were many short nanostrands, in other words, nanorods of 100 nm or so. The inset shows a TEM image at this aging time. The width of the nanorods was estimated to be 3−4 nm, which was slightly larger than that of the long nanostrands shown in Figure 1. The surface appeared to be very rough. In addition to these nanorods, we observed plenty of small particles in a range of 2−6 nm in diameter. The length of the nanorods increased up to 300−500 nm after aging 20 min and reached 1 μm after 1 h (Figure 2b,c). Nanoparticles observed at the initial stage disappeared after 1 day of aging. Then, extremely long and uniform copper hydroxide nanostrands were observed, as seen in Figure 2d. The nanostrands continued to grow at least for a few days and existed stably even after 1 month without giving any precipitates. We have reported that cadmium hydroxide nanostrands with a width of 1.9 nm grew within 10 min.[14] The growth of copper hydroxide nanostrands is fairly slow. Although the chemical compositions of initially formed nanoparticles and nanorods are still unclear, they must be thermodynamically unstable and are converted into long nanostrands. That is to say, the copper hydroxide nanostrand is a stable equilibrium structure in the aqueous solution.

B. Surface Charge and Crystal Growth. Copper hydroxide nanostrands strongly adsorbed negatively charged dye molecules, Evans Blue, and gave weakly gelled precipitates. When the amount of nanostrands was very much lower than that of dye molecules, the gelled precipitates were not always formed. However, their electrostatic composites

---

(28) HR-TEM images were quickly taken to prevent damages caused by the electron beam. It is known that $Cu(OH)_2$ is readily transformed to CuO by the focused electron beam (see ref 26).

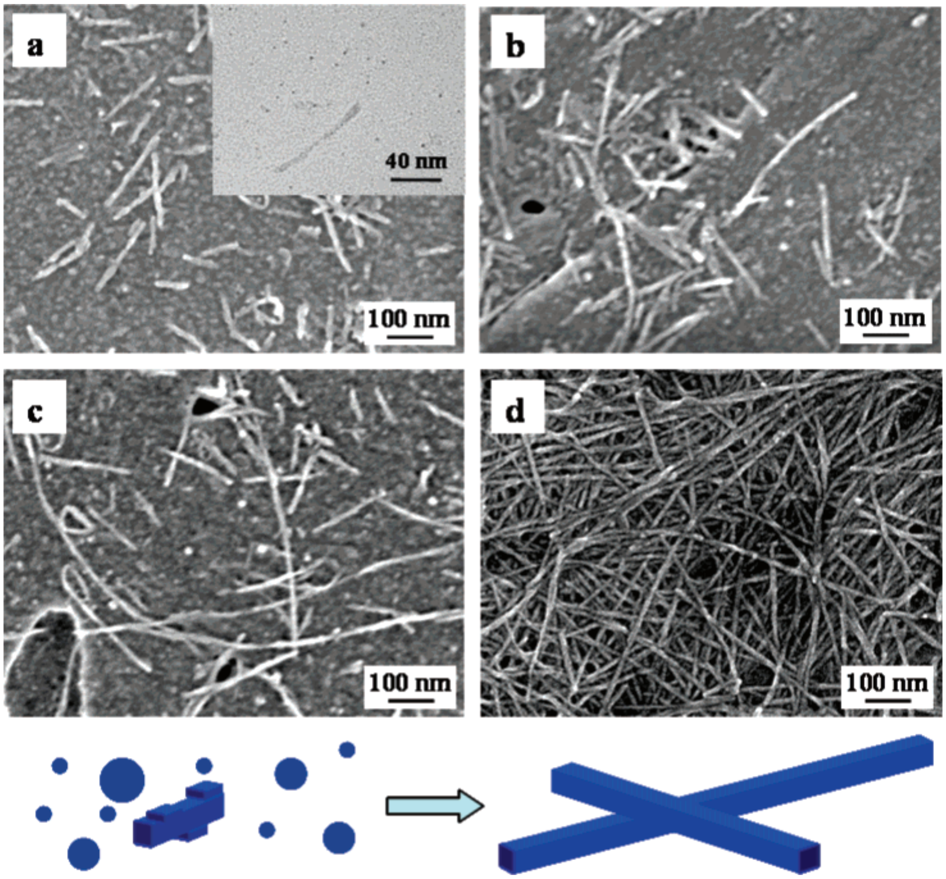
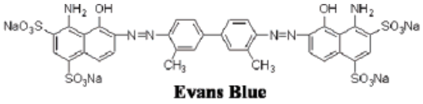


Figure 2. Time-dependent morphological changes of copper hydroxide. SEM images were obtained at aging times of 5 min (a), 20 min (b), 1 h (c), and 1 day (d). All the specimens were prepared on polycarbonate membranes with pores of 0.1 μm in diameter. Inset in part a is a TEM image obtained after 5 min of aging. The scheme at the bottom illustrates the morphological change with aging time.



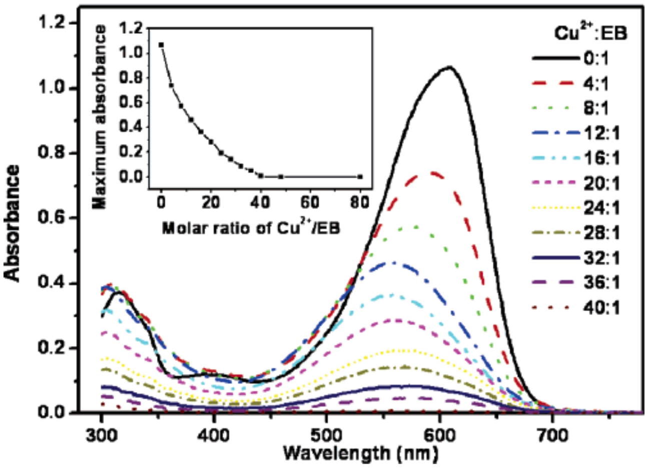


Figure 3. UV−vis absorption changes of Evans Blue solutions after filtering the electrostatic composites with copper hydroxide nanostrands. The inset shows the changes in maximum absorbance.

were readily filtered from the solution. To evaluate the trapping ability, we monitored UV−vis absorption changes of Evans Blue solutions after filtering with a polycarbonate membrane filter. The results are shown in Figure 3. The concentration of Evans Blue was fixed at 0.025 mM, and that of the nanostrands was regularly increased.

The absorption peak at 608 nm, which was attributed to Evans Blue, was decreased with the increase of copper hydroxide nanostrands. At the same time, the peak-top position blue-shifted to near 560 nm. In Figure 3, the nanostrand concentration is represented as the molar ratio of copper ions against Evans Blue molecules (Cu^{2+}:EB). As seen in the inset, all of the dye molecules were filtered off when the molar ratio was 40 or more. Now we have to discuss the percentage of copper ions that were converted into the nanostrands. The aqueous solution of copper hydroxide nanostrands was prepared by mixing 1.6 mM aminoethanol into an equal volume of 4 mM copper nitrate and aging it for 3 days. The amount of aminoethanol was only two-fifths that of the copper ions. Therefore, if all the aminoethanol added was used for the formation of copper hydroxide, about 20% of the copper ions should be converted to the nanostrands. This presumption was almost true at least in our experimental conditions. When the nanostrand was filtered from the solution using a polycarbonate membrane filter, the concentration of copper ions in the filtrate was decreased 18.7% from the original solution, as confirmed by inductively coupled plasma measurements.

Evans Blue was completely removed by a 40-fold concentration of copper ions. This fact indicates that eight copper atoms in the nanostrands (20% of total copper ions) can trap one dye molecule. This also means that at least one-eighth of the copper atoms in the nanostrand need to be positively charged. In case two of the four sulfonic groups of Evans

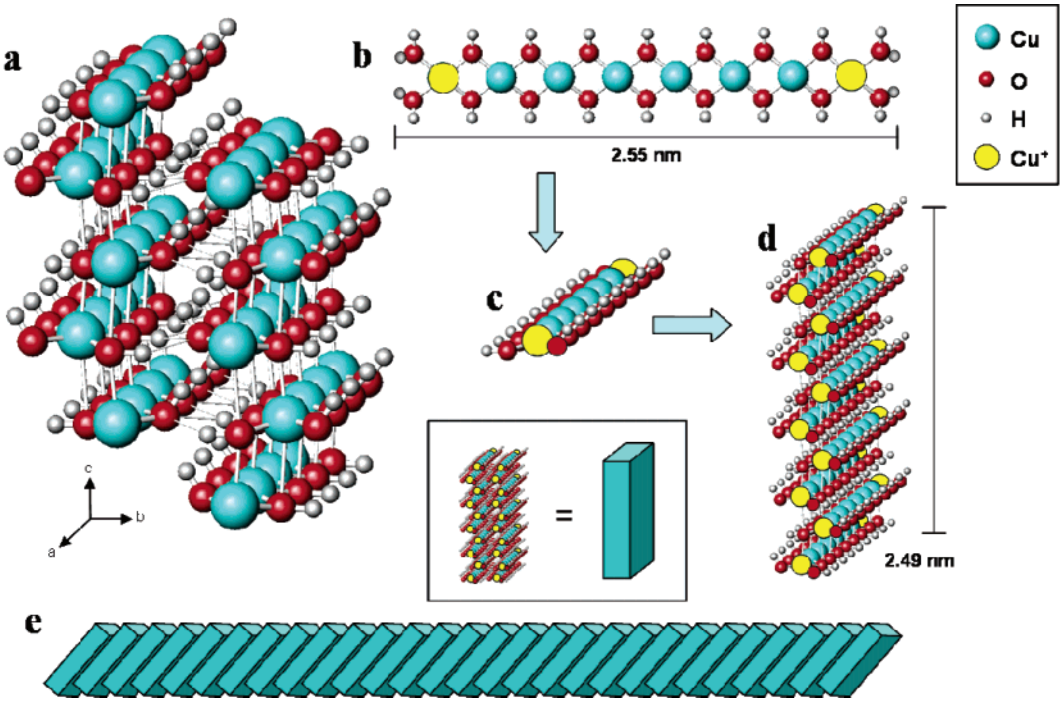


Figure 4. Crystal structure of orthorhombic copper hydroxide (a), structure of copper hydroxide octamer (b and c), square sheet made of 10 copper hydroxide octamers (d), and the most plausible structure for copper hydroxide nanostrand (e). Copper, oxygen, and hydrogen atoms are colored blue, red, and gray, respectively. Atoms colored yellow are positively charged copper atoms.

Blue electrostatically interact with copper hydroxide nanostrands, a quarter of the copper atoms need to be charged. Furthermore, when all the sulfonic groups interact with the nanostrand, half of the copper atoms need to be charged. We presume that the ratio of positively charged copper atoms in the nanostrand was in the range of 1/8 to 1/4, because 80% of the copper ions did not form nanostrands and they induced a blue shift of the absorption peak of Evans Blue. The latter should be explained by the dimer formation of Evans Blue. We believe that four sulfonated groups of the dimer are electrically neutralized by two copper ions. As a result, the negative charges of Evans Blue decrease by half. In this case, a quarter of the copper atoms in the nanostrand need to be positively charged.

We observed that the nanostrands had a width of 2.5 nm. The nanostrands are so narrow that the surface might be apt to be charged positively. The spacing of 0.250 nm was attributed to (111) planes of orthorhombic $Cu(OH)_2$. Therefore, the growth direction of the nanostrand seemed to be in the [111] direction. These features should be explainable with a reasonable structural model. The clue is in the crystal structure of copper hydroxide. Figure 4 shows the structure calculated by using the ATOMS, V6.1.2, crystal structure analysis software. Copper, oxygen, and hydrogen atoms are colored blue, red, and gray, respectively. To emphasize the copper atoms, their diameter is drawn 1.6 times larger than that of the oxygen atoms. The space group of $Cu(OH)_2$ is $Cmc2_1$ (No. 36), and the lattice parameters are $a = 2.9471$, $b = 10.593$, and $c = 5.2564$.[29] As seen in Figure 4a, copper hydroxide is made of linear coordination polymers, in which each copper atom is bridged to two copper atoms through four hydroxyl groups. In other words, square planar complexes of copper bridged with hydroxide groups are infinitely extended parallel to the a axis. These coordination polymers are weakly bonded to each other through axial coordination of hydroxyl groups that are in part of the upper and lower coordination polymers. The distance between the copper and axially coordinated oxygen atoms is 0.236 or 0.291 nm. These lengths are much longer than the distance between the copper and oxygen atoms in the linear coordination polymer (0.195 or 0.197 nm), because of the strong Jahn−Teller effect of the divalent copper ion. These two-dimensional coordination networks spread in the $a-c$ plane and then interact with each other via multiple hydrogen bonding in the [010] direction. As is clear from the length of b vector ($b = 10.593$), the unit cell of copper hydroxide contains two layers of the above-mentioned coordination network.

We realized that only two ends of the linear coordination polymer could be positively charged. When the terminal copper atom is coordinated with two water molecules, it is possible to bear a positive charge. From the width of copper hydroxide nanostrand (2.5 nm), we assume that a copper hydroxide octamer with a length of 2.55 nm, $[Cu_8(OH)_{14}(H_2O)_4]^{2+}$, is the structural unit of the nanostrand. This structure was also consistent with the fact that a quarter of the copper atoms should be positively charged (Figure 4b). These positively charged linear clusters further assemble into a square planar sheet with a height of 2.49 nm, as shown in Figure 4c,d. Supposing a crystal structure of orthorhombic copper hydroxide, two layers of the square planar sheet have to be a unit of the nanostrands. As explained earlier, the copper hydroxide nanostrand grew in the [111] direction. In such a case, the above square prism units need to be piled after shifting one unit cell in both the direction of [100] and

---

(29) Oswald, H. R.; Reller, A.; Schmalle, H. W.; Dubler, E. *Acta Crystallogr., Sect. C* **1990**, *46*, 2279.

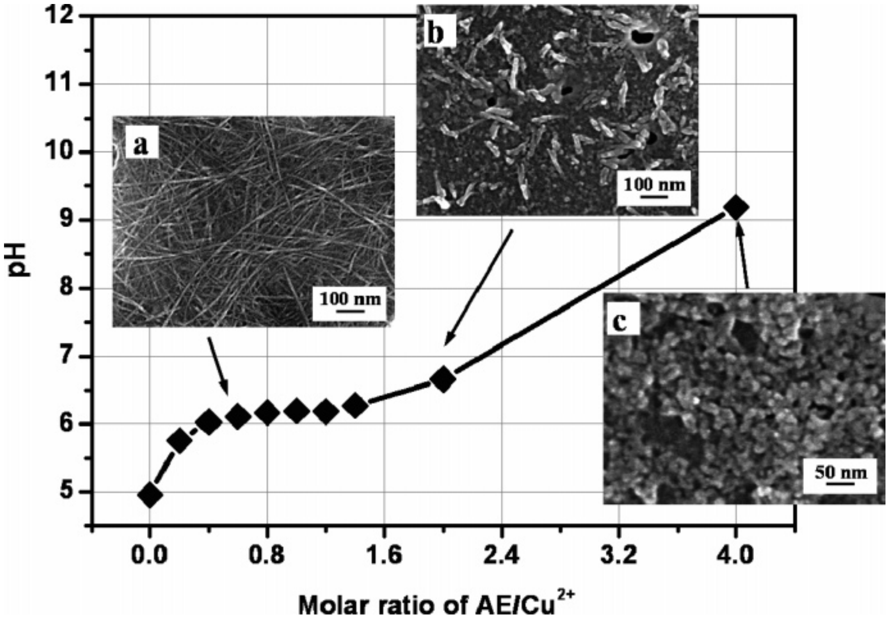


Figure 5. pH titration of copper nitrate with aminoethanol. The concentration of copper nitrate was fixed to be 2 mM. Three SEM images were obtained at the molar ratios indicated by the arrows. Aging times were 1 day for part a and 1 h for parts b and c. At any pH below 9.2, no precipitate was observed at least 1 h after adding aminoethanol. AE denotes aminoethanol.

the direction of [001]. The final proposed structure is illustrated in Figure 4e. It has been reported that copper hydroxide nanowires and nanoribbons grew in the [100] direction.[21,24] However, the growth in such a direction seemed to be prevented for copper hydroxide nanostrands because of the positively charged terminal copper atoms. Therefore, the nanostrand needs to grow in the other direction crystallographically allowed. The [111] direction must be one of the suitable directions for lowering the electrostatic repulsion within the nanostrand.

C. Nanomorphologies of Copper Hydroxide. The morphology of the copper hydroxide nanostrands is caused by the positively charged crystal planes. This assumption was supported by the fact that the nanostrands formed only in weak acidic solution. Figure 5 shows a pH titration of copper nitrate with aminoethanol. The concentration of aminoethanol is described as the molar ratio to Cu^{2+} ions. The aqueous solution of copper nitrate (2 mM) gave pH 4.9, which increased to 6.03 when the molar ratio (aminoethanol/Cu^{2+}) was 0.4. The pH value slowly increased until the molar ratio became 1.4 (pH 6.27) and then increased again with a greater gradient. The typical buffer action near pH 6.0−6.3 indicates that copper hydroxide grows as much as aminoethanol added in the solution. We investigated the nanomorphologies at the molar ratios of 0.6, 1.0, 1.5, 2.0, and 4.0 by SEM. Some images are shown in Figure 5. Long and narrow copper hydroxide nanostrands were only observed at a molar ratio of 0.6 (Figure 5a). When the molar ratio is increased to 1.0 and 1.5, rodlike structures and nanoparticles became the major morphologies. Formation of the former structure indicates that the anisotropic crystal growth of the nanostrands gradually turns to a quasi-anisotropic one. At these molar ratios, the nanostrand may not be a stable equilibrium structure. At a molar ratio of 2.0, nanoparticles and very short rods were observed (Figure 5b). Only irregular shaped particles of about 10 nm in diameter appeared at a molar ratio of 4.0 (Figure 5c).

The length of the nanostrands formed at the molar ratio of 0.6 was several hundred nanometers after aging for 1 h. The length reached several tens of micrometers after a few days of aging. That is to say, the aspect ratio of long nanostrands exceeded tens of thousands. We conclude that extremely long and narrow nanostrands are an equilibrium structure in the weak acidic solution and the structure is stabilized by the abundant surface positive charges.

We also investigated the effect of the concentration of copper nitrate, the effect of the different types of bases, and the effect of the counteranions of copper salts. First, we fixed the molar ratio of aminoethanol to copper nitrate to be 0.4 and examined morphological changes with the concentration of copper nitrate. When the concentration was low, copper hydroxide nanostrands grew slowly. The length of the nanostrands formed from 0.5 mM copper nitrate solution was in a range of 20−300 nm. In sharp contrast, blue-green precipitates of $Cu_2(OH)_3NO_3$ were quickly produced from the solution of 8 mM copper nitrate.[19,30] Figure 6a shows a SEM image of the thin hexagonal crystals. When the concentration of copper nitrate was 4 mM, the nanostrands of a few micrometers were produced at the beginning. However, we confirmed that hexagonal crystals of $Cu_2(OH)_3NO_3$ were produced after aging for several hours. Concentration of nitrate ions (NO_3^-) should be lower than 8 mM, because this anion is prone to be incorporated in a crystalline basic salt.

When aminoethanol was replaced with ammonia and iminodiethanol, typical copper hydroxide nanostrands were obtained. Figure 6b shows a SEM image of the nanostrands prepared by using ammonia. The individual nanostrands appeared to be more flexible as compared to those obtained with aminoethanol. In the case of iminodiethanol, the growth rate was slower than the other two bases. It took about three

---

(30) Henrist, C.; Traina, K.; Hubert, C.; Toussaint, G.; Rulmont, A.; Cloots, R. *J. Cryst. Growth* **2003**, *254*, 176.

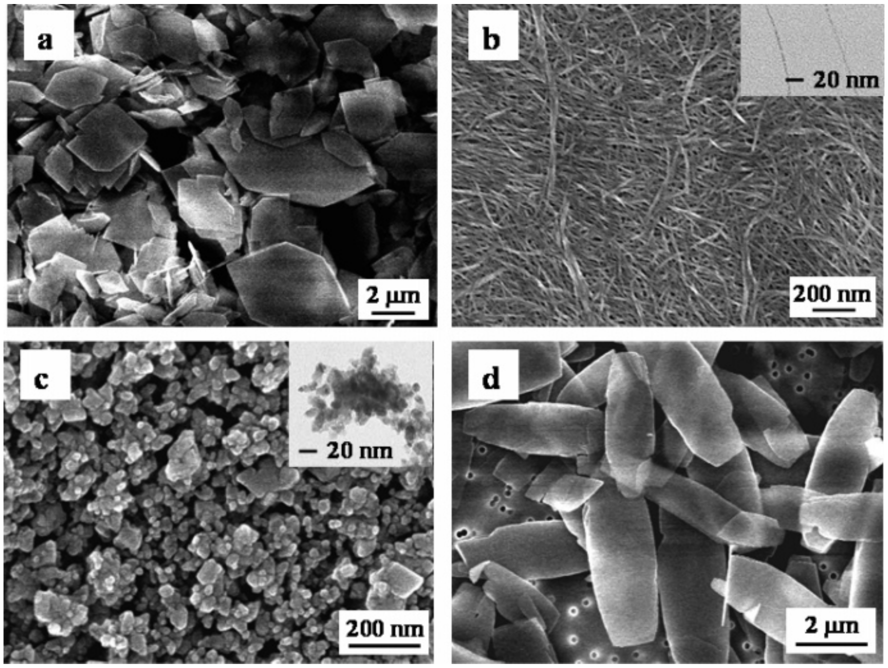


Figure 6. SEM images of hexagonal crystals of $Cu_2(OH)_3NO_3$ (a), copper hydroxide nanostrands (b), particles of copper hydroxide chloride (c), and $Cu_4(OH)_6SO_4 \cdot H_2O$ (d). Specimens were prepared from the mixed solutions containing 8 mM $Cu(NO_3)_2$ and 3.2 mM aminoethanol (a), 2 mM $Cu(NO_3)_2$ and 0.8 mM ammonia (b), 2 mM $CuCl_2$ and 0.8 mM aminoethanol (c), and 2 mM $CuSO_4$ and 0.8 mM aminoethanol (d). Aging times were 1 h for parts a, c, and d and 1 day for part b. Insets in parts b and c show the corresponding TEM images.

Table 1. Experimental Conditions and Morphologies of Copper Hydroxide and Related Compounds

system	copper salt	copper salt concn (mM)	base	base concn (mM)	morphology	corresponding images
1	$Cu(NO_3)_2$	2	AE[a]	0.8	nanostrand	Figures 1a−e and 2a−d
2	$Cu(NO_3)_2$	2	AE[a]	1.2	nanostrand	Figure 5a
3	$Cu(NO_3)_2$	2	AE[a]	2	rod and particle	none[e]
4	$Cu(NO_3)_2$	2	AE[a]	3	rod and particle	none[e]
5	$Cu(NO_3)_2$	2	AE[a]	4	particle and short rod	Figure 5b
6	$Cu(NO_3)_2$	2	AE[a]	8	irregular particle	Figure 5c
7	$Cu(NO_3)_2$	0.5	AE[a]	0.2	short nanostrand	none[e]
8	$Cu(NO_3)_2$	4	AE[a]	1.6	nanostrand	none[e]
9	$Cu(NO_3)_2$	8	AE[a]	3.2	hexagonal crystal[c]	Figure 6a
10	$Cu(NO_3)_2$	2	NH_3	0.8	nanostrand	Figure 6b
11	$Cu(NO_3)_2$	2	IM[b]	0.8	nanostrand	none[e]
12	$Cu(NO_3)_2$	2	NaOH	0.8	particle	none[e]
13	$CuCl_2$	2	AE[a]	0.8	irregular particle	Figure 6c
14	$CuSO_4$	2	AE[a]	0.8	crystalline plate[d]	Figure 6d

[a] AE = 2-aminoethanol. [b] IM = 2,2′-iminodiethanol. [c] $Cu_2(OH)_3NO_3$. [d] $Cu_4(OH)_6SO_4 \cdot H_2O$. [e] Unshown images are available in Supporting Information.

weeks to grow more than several hundred nanometers. We have not succeeded in the synthesis of developed copper hydroxide nanostrands by using sodium hydroxide. In this case, nanoparticles of less than 10 nm were often produced, giving a light blue colloidal solution. It is clear that ammonia or organic amines are essential for the growth of copper hydroxide nanostrands. Probably, one of their important roles is to stabilize the positively charged linear clusters such as copper hydroxide octamers (Figure 4b) through the coordination to the two copper atoms at the ends. Ammonia and amines are also necessary to block the crystal growth of copper hydroxide, especially in the [100] direction, by adsorbing on the crystal surfaces.[19]

The effect of counteranions was also very significant. Copper chloride ($CuCl_2$) gave a light blue stable colloidal suspension immediately after mixing with aminoethanol. This colloid was made of irregular nanoparticles of about 10 nm and their aggregates, as seen in Figure 6c. Copper sulfate ($CuSO_4$) rapidly produced blue-green precipitates of the basic salt ($Cu_4(OH)_6SO_4 \cdot H_2O$). The SEM image showed the typical morphology (Figure 6d).[18,19] Probably, at the initial stage of the crystal growth, these anions electrostatically interact with the positively charged clusters of copper hydroxide and decrease the net positive charges. As a result, they are incorporated into their basic salts.

Conclusions

The experimental conditions and nanomorphologies observed in this study are summarized in Table 1. Copper hydroxide nanostrands were obtainable only from copper nitrate solution with an approximate concentration of 2 mM. Ammonia or amine bases were indispensable. Specifically, the nanostrands slowly grew only in the weak acidic solution. In the typical preparative condition, the concentration of bases was only one-fifth of that required for stoichiometric formation of copper hydroxide. In other words, 80% of copper atoms probably exist as hydrated ions in water. There should be equilibrium between the hydrated copper ions and copper hydroxide nanostrands.

The copper hydroxide nanostrand is a stable equilibrium structure in water, and the nanostrands are easily isolated by filtering with a membrane filter. To the best of our knowledge, this nanostrand is the narrowest copper hydroxide with the highest aspect ratio. Furthermore, the extremely small cross section enables this nanostrand to have enormous positive charges. This feature is a distinctive characteristic of metal hydroxide nanostrands which have never been observed in other 1D structures. We should emphasize again that the nanostrands are produced under conditions very far from the mixing ratio for stoichiometric formation of copper hydroxide.

In this paper, we proposed a formation mechanism of copper hydroxide nanostrands, in which positively charged linear clusters of copper hydroxide, $[Cu_8(OH)_{14}(H_2O)_4]^{2+}$, were produced at the beginning of the olation process. These clusters assemble into the square planar sheets and, finally, give long and narrow copper hydroxide nanostrands. Strong hydrogen-bonding interactions between the square clusters must be a driving force for the nanostrand growth. The octamer we propose might merely be the tip of the iceberg. In other words, at the beginning of the olation process of other metal ions, there should be various clusters with a unique molecular structure. Such clusters must be important building blocks of novel inorganic materials and inorganic supermolecules. Nanostructures created by incomplete olation should be widely investigated in the next decade.

Materials and Methods

Copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$), copper chloride ($CuCl_2 \cdot 2H_2O$), copper sulfate ($CuSO_4 \cdot 5H_2O$), 1 N ammonia, 2-aminoethanol (NH_2-CH_2CH_2OH), 2,2′-iminodiethanol ($NH(CH_2CH_2OH)_2$), and Evans Blue were purchased from Kanto Chemical and used without further purification. The polycarbonate membrane filter, Nuclepore, is a product of Whatman. Ultrapure water of 18.2 MΩ produced by a Millipore direct-Q system was used throughout the experiments. Copper hydroxide nanostrands were synthesized by quickly mixing a base solution into a copper−salt solution using a magnetic stirrer and by aging at room temperature. The nanostrand prepared from 2 mM copper nitrate and 0.8 mM aminoethanol was stable at room temperature at least for 1 month. In general, the nanostrand was unstable in the alkaline solution and gave yellow or brown precipitates.

TEM images and electron diffraction patterns were obtained by using a JEOL-1010 TEM at an accelerating voltage of 100 kV. HR-TEM images were obtained by a JEOL-JEM2000 at 200 kV. The specimens were made after the solutions were aged. A drop of the sample solution was put on a glass plate, and a carbon coated copper microgrid was floated on the droplet for 1 min. The microgrid was wiped from the rim with clean filter paper, dried in the air, and used for TEM observation. Field-emission SEM observations were conducted on a Hitachi S-4800 microscope at an accelerating voltage of 25 kV. The specimens were prepared on a polycarbonate membrane filter. The sample solution was filtered with the polycarbonate membrane by suction filtration, and the membrane filter was dried in the air. The pore size used was 0.2 μm, except for the cases in Figure 2 (0.1 μm). To prevent the specimen from electric charge up, a platinum layer, about 2-nm-thick, was deposited by using a Hitachi E-1030 ion sputterer. The electron diffraction pattern was obtained as follows: First, 1 mL of nanostrand solution was filtered with a polycarbonate membrane, and the membrane filter was dispersed in 1 mL of chloroform. After the polycarbonate membranes dissolved in chloroform, the suspension was centrifuged, rinsed two times with 1 mL of chloroform, and re-dispersed in a small volume of ethanol. The specimen for electron diffraction experiments was prepared using this solution.

Atomic coordinates (x, y, z) used for the crystallographic calculation were (1/2, 0.6820, 1/4) for Cu, (0, 0.5583, 0.2534) for O1, (0, 0.7994, 0.1967) for O2, (0, 0.5058, 0.4118) for H1, and (0, 0.9001, 0.1914) for H2. UV−vis absorption spectra were obtained by using a Shimadzu UV-3150 spectrophotometer. The pH was monitored by using an IQ240 pH meter.

Supporting Information Available: Unshown SEM images listed in Table 1; pH titration curves of copper sulfate and copper chloride with aminoethanol; and pH titration curves of copper nitrate with ammonia and sodium hydroxide (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM052270S