

Supplementary Information

Time-dependent growth of zinc hydroxide nanostrands and their crystal structure

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Experimental Details:

Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aminoethanol ($\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$, AE), and Evans Blue were purchased from Kanto Chemical and used without further purification. Ultrapure water of 18.2 MΩ produced by a Millipore Direct-Q system was used throughout the experiments. Zinc hydroxide nanostrands were prepared by mixing an aqueous solution of aminoethanol into a zinc nitrate solution using a magnetic stirrer. In an optimized synthetic procedure, 5 mL of a 4 mM zinc nitrate solution was mixed with 5 mL of a 2.4 mM aminoethanol solution, and the nanostrands were filtered off after an aging time of 30 min. The results of other conditions are described in Table S1.

TEM images and electron diffraction patterns were obtained on a JEOL-1010 transmission electron microscope at an acceleration voltage of 100 kV. HR-TEM and dark field STEM images were obtained by using a JEOL-JEM2100F electron microscope at 200 kV. The specimens were made by floating a carbon-coated copper microgrid for 1 min on a droplet of the sample solution placed on a glass plate. The microgrid was then wiped from the rim with clean filter paper and dried in air. In TEM measurements, zinc hydroxide nanostrands gradually decomposed with increasing exposure time to the electron beam of 200 kV. Field-emission SEM observations were conducted on a Hitachi S-4800 scanning electron microscope at an acceleration voltage of 10 kV. The specimens were prepared by filtering the sample solution on a polycarbonate membrane filter by suction filtration. The polycarbonate membrane filter (Nuclepore, pore size: 0.2 μm) is a product of Whatman. To prevent the specimen from electric charge up, an about 2-nm thick platinum layer was deposited by using a Hitachi E-1030 ion sputter. UV-vis spectra were obtained by using a Shimazu UV-3150 spectrometer. Atomic coordinates (x, y, z) used for the crystallographic calculation were (0.000, 0.000, 0.500) for Zn, (0.333, 0.666, 0.200) for O₁, and (0.666, 0.333, 0.800) for O₂.

Table S1. Nanomorphologies of zinc hydroxide at different experimental conditions.

| sample | concentration (mM) | | AE / Zn | pH | morphology |
|--------|-----------------------------------|-----|---------|------|---|
| | Zn(NO ₃) ₂ | AE | | | |
| Z1 | 4.0 | 0.4 | 0.1 | 6.39 | short fibres (Fig. S1b) |
| Z2 | 4.0 | 0.8 | 0.2 | 6.52 | short fibres (Fig. 2A) |
| Z3 | 4.0 | 2.4 | 0.6 | 6.60 | nanostrands (Fig. 1 and Fig. 2D) |
| Z4 | 4.0 | 3.2 | 0.8 | 6.65 | nanoparticles (Fig. 2C) |
| Z5 | 6.0 | 0.2 | 0.033 | 6.48 | nanoparticles |
| Z6 | 6.0 | 0.4 | 0.067 | 6.58 | nanoparticles |
| Z7 | 6.0 | 0.8 | 0.13 | 6.68 | short fibres |
| Z8 | 6.0 | 1.2 | 0.2 | 6.71 | short fibres |
| Z9 | 6.0 | 1.6 | 0.27 | 6.87 | sheet-like aggregates of short rods |
| Z10 | 6.0 | 2.0 | 0.33 | 6.86 | sheet-like aggregates of short rods |
| Z11 | 6.0 | 2.4 | 0.4 | 6.97 | nanostrands (Fig. S1c) |
| Z12 | 6.0 | 3.0 | 0.5 | 7.01 | short fibres |
| Z13 | 6.0 | 4.0 | 0.67 | 6.97 | nanoparticles |
| Z14 | 8.0 | 0.2 | 0.025 | 7.08 | nanoparticles |
| Z15 | 8.0 | 0.4 | 0.05 | 7.16 | nanoparticles |
| Z16 | 8.0 | 0.8 | 0.1 | 7.32 | nanoparticles |
| Z17 | 8.0 | 1.2 | 0.075 | 7.29 | nanoparticles |
| Z18 | 8.0 | 1.6 | 0.2 | 7.36 | nanoparticles and short fibres |
| Z19 | 8.0 | 2.0 | 0.25 | 7.38 | sheet and short fibres |
| Z20 | 8.0 | 3.0 | 0.38 | 7.33 | short rods (Fig. S1d) |
| Z21 | 8.0 | 4.0 | 0.5 | 7.53 | long fibres and sheet-like aggregates |
| Z22 | 8.0 | 6.0 | 0.75 | 7.45 | thick sheet-like aggregates |
| Z23 | 10.0 | 0.4 | 0.04 | 6.84 | nanoparticles |
| Z24 | 10.0 | 0.8 | 0.08 | 6.88 | nanoparticles |
| Z25 | 10.0 | 1.0 | 0.1 | 6.96 | nanoparticles |
| Z26 | 10.0 | 1.6 | 0.16 | 7.08 | nanoparticles |
| Z27 | 10.0 | 2.0 | 0.2 | 7.13 | nanoparticles |
| Z28 | 10.0 | 3.0 | 0.3 | 7.19 | short fibres |
| Z29 | 10.0 | 4.0 | 0.4 | 7.19 | short fibres (Fig. S1e) |
| Z30 | 10.0 | 5.0 | 0.5 | 7.21 | short fibres and sheet-like aggregates |
| Z31 | 10.0 | 6.0 | 0.6 | 7.33 | submicron agglomerates |
| Z32 | 10.0 | 8.0 | 0.8 | 7.35 | submicron agglomerates (Fig. S1f) |

The volumes of aqueous solutions of Zn(NO₃)₂ and aminoethanol (AE) were 5 mL. All samples were aged for 30 min.

Nanomorphologies of Zinc Hydroxide:

We have reported that cadmium hydroxide nanostrands were formed by mixing aqueous solutions of cadmium nitrate and NaOH (*J. Am. Chem. Soc.* **2004**, *126*, 7162). The preparation of zinc hydroxide nanostrands was first attempted in a similar way. However, all the products obtained by using NaOH were the aggregates of small particles with diameters of 20-40 nm. Figure S1a shows the typical particles obtained from 2.4 mM NaOH and 4 mM Zn(NO₃)₂ solutions after aging for 30 min.

On the other hand, the nanomorphology of zinc hydroxide widely changed with experimental conditions when NaOH was replaced by aminoethanol (AE). Figure S1b shows an SEM image of short fibres obtained from 4 mM Zn(NO₃)₂ and 0.4 mM AE. The

short fibres often formed when the mixing ratio of AE against zinc ions was low. We also observed the formation of nanoparticles at the low mixing ratio of AE against zinc ions. Figure S1c shows zinc hydroxide nanostrands obtained from 6 mM Zn(NO₃)₂ and 2.4 mM AE. The nanostrand formation was observed only at the concentrations of 4 mM and 6 mM for Zn(NO₃)₂ and at the mixing ratios of AE of 0.4 and 0.6. Figure S1d shows short rods obtained from 8 mM Zn(NO₃)₂ and 3 mM AE. Short fibres were obtained from 10 mM Zn(NO₃)₂ and 4 mM AE (Figure S1e). When the concentrations of zinc ions and AE were high, agglomerates in submicron scale were often observed. Figure S1f shows the typical SEM image obtained from 10 mM Zn(NO₃)₂ and 8 mM AE.

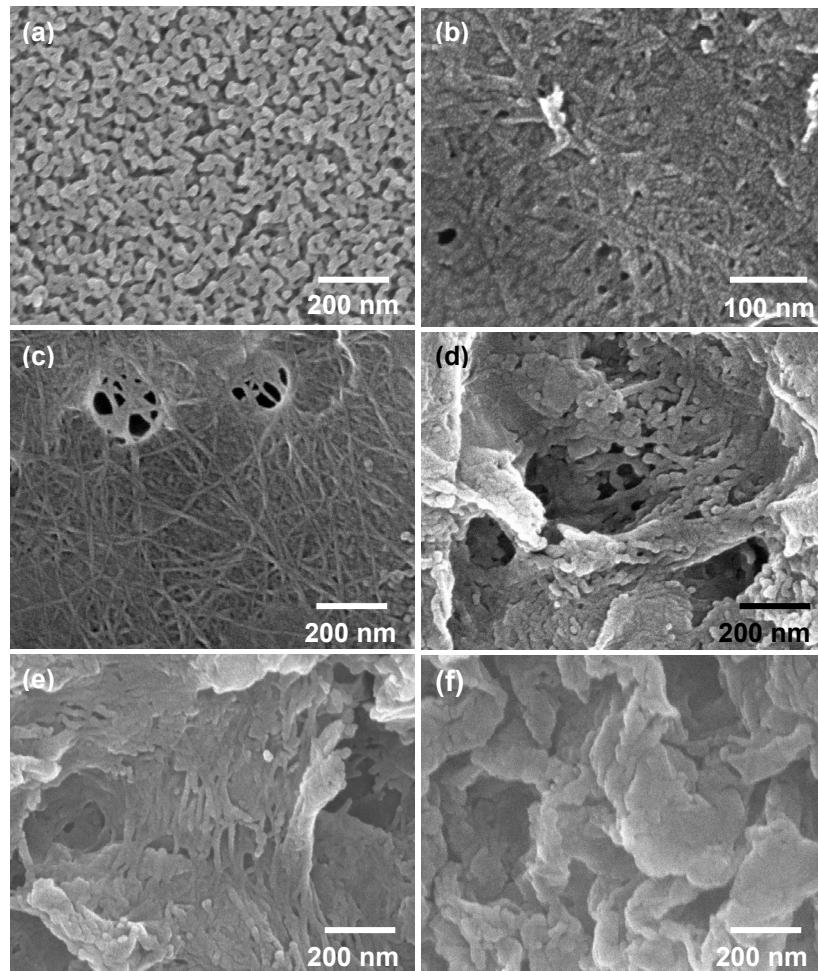


Figure S1. SEM images of nanomorphologies of zinc hydroxide. (a) Nanoparticles obtained from 4 mM Zn(NO₃)₂ and 2.4 mM NaOH, (b) short fibres obtained from 4 mM Zn(NO₃)₂ and 0.4 mM AE, (c) nanostrands obtained from 6 mM Zn(NO₃)₂ and 2.4 mM AE, (d) short rods obtained from 8 mM Zn(NO₃)₂ and 3.0 mM AE, (e) short fibres obtained from 10 mM Zn(NO₃)₂ and 4.0 mM AE, and (f) submicron agglomerates obtained from 10 mM Zn(NO₃)₂ and 8.0 mM AE. All samples were obtained after 30-min aging. The experimental conditions for (b-f) are corresponding to Z1, Z11, Z20, Z29, and Z32 in Table S1.

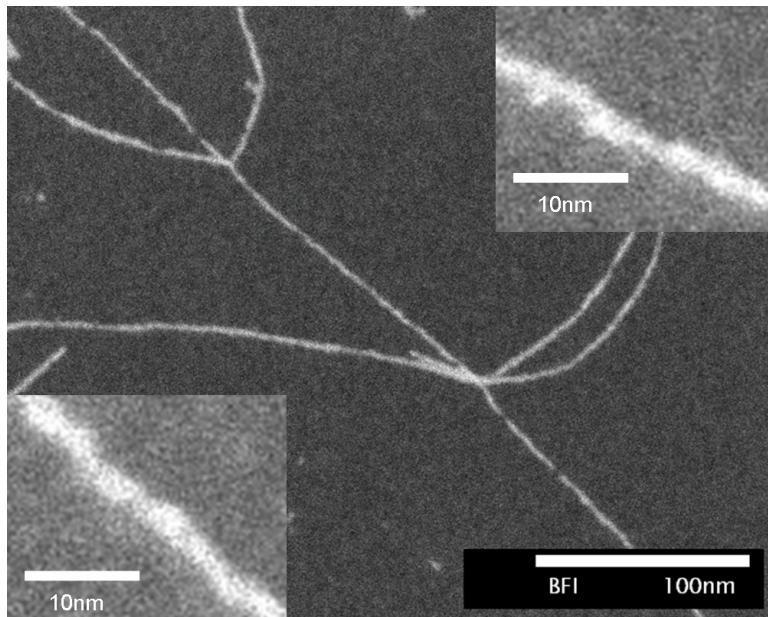


Figure S2. Dark field STEM images of the nanostrands obtained from 2.4 mM aminoethanol and 4 mM $\text{Zn}(\text{NO}_3)_2$ after 30-min aging. The insets show the high-resolution images.

Figure S2 shows dark field STEM (scanning transmission electron microscopy) images of zinc hydroxide nanostrands. As seen in the low-resolution image, we often observed the zigzag structure. The structure was also visible in the high resolution images.

Formation of Bundles:

When the nanostrands were prepared by mixing equal volume of aminoethanol (2.4 mM) and $\text{Zn}(\text{NO}_3)_2$ (4 mM), the bundle-like structures were observed after aging time of 45 min, as shown in Figure S3.

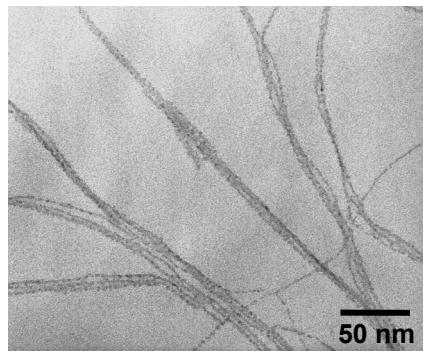


Figure S3. TEM image of the nanostrands prepared by mixing equal volume of aminoethanol (2.4 mM) and $\text{Zn}(\text{NO}_3)_2$ (4 mM), after aging time of 45 min.

EDX measurements:

The energy dispersive X-ray (EDX) spectra were obtained by using a JEOL-JEM2100F electron microscope at 200 kV. The spectrum of zinc hydroxide nanostrands is shown in Figure S4. The atomic ratio of zinc and oxygen was 32.2/67.8, as calculated from the corresponding peak areas. This value was in good agreement with the composition of zinc hydroxide (Zn(OH)_2). Copper peaks in Figure S4 are from copper microgrid.

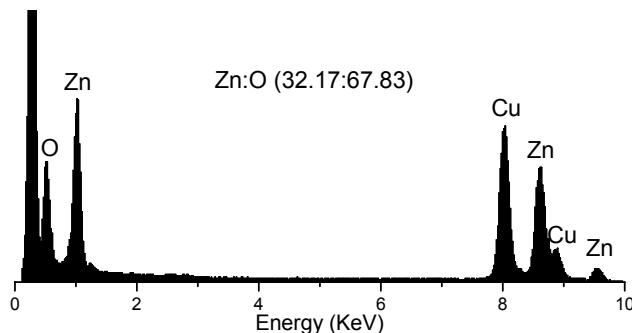


Figure S4. Energy dispersive X-ray spectrum of zinc hydroxide nanostrands.

Estimation of Positive Charges:

Zinc hydroxide nanostrands strongly adsorbed negatively charged dye molecules, Evans Blue, and formed weakly-gelled precipitates. The photograph is shown in Figure S5b. In contrast, no precipitate appeared from the solution containing hydrated zinc nitrate (Figure S5a). These results demonstrate that the dye molecules are trapped by the nanostrands. To evaluate the trapping ability, we monitored the UV-vis absorption changes of Evans Blue solutions after filtering the precipitates by using a polycarbonate membrane filter. The results are shown in Figure S5c. The concentration of Evans Blue was fixed at 1.6×10^{-5} M, and that of nanostrand was regularly increased. The absorption peak at 608 nm, which was attributed to Evans Blue, decreased with the increase of zinc hydroxide nanostrands. At the same time, the peak maximum was blue-shifted to 550 nm. The nanostrand concentration is represented as the molar ratio of zinc ions against Evans Blue molecules (Zn : EB). As seen in Figure S5c, all the dye molecules were filtered off when the molar ratio was 125 or more. For the estimation of surface positive charges of the zinc hydroxide nanostrands, we supposed that all the positive charges are electrostatically compensated by negative charges of Evans Blue. This molecule has four sulfonate groups. Therefore, four atoms of 125 zinc atoms should be positively charged. On the other hand, the nanostrands were prepared by mixing 4 mM $\text{Zn}(\text{NO}_3)_2$ and 2.4 mM aminoethanol (AE) (See Table S1, condition "Z3"). In this experimental condition, 30 % of zinc ions are converted to the nanostrands. Therefore, positively charged zinc

atoms should be four atoms in three tenths of 125 zinc atoms. From these calculations, we estimated about one tenth of zinc atoms in the nanostrand are positively charged.

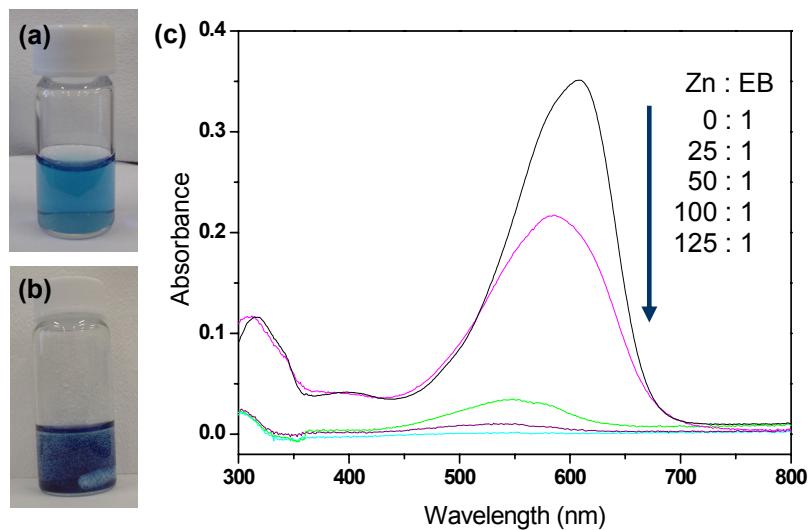


Figure S5. Photographs of Evans Blue (EB) solutions containing $\text{Zn}(\text{NO}_3)_2$ (a) and zinc hydroxide nanostrand (b) and changes in UV-vis absorption spectra (c). The solution (a) was prepared by mixing 0.16 mL of 1 mM EB solution and 10 mL of 2 mM $\text{Zn}(\text{NO}_3)_2$ solution. The solution (b) was prepared by mixing 0.16 mL of 1 mM EB solution and 10 mL of the nanostrand solution which was prepared in condition "Z3" in Table S1. UV-vis absorption spectra were obtained after filtering the precipitates of EB/nanostrand composite by using a polycarbonate membrane filter (pore size: 0.2 μm). The concentration of nanostrand was tuned by diluting the nanostrand solution with pure water, keeping the concentration of EB constant.

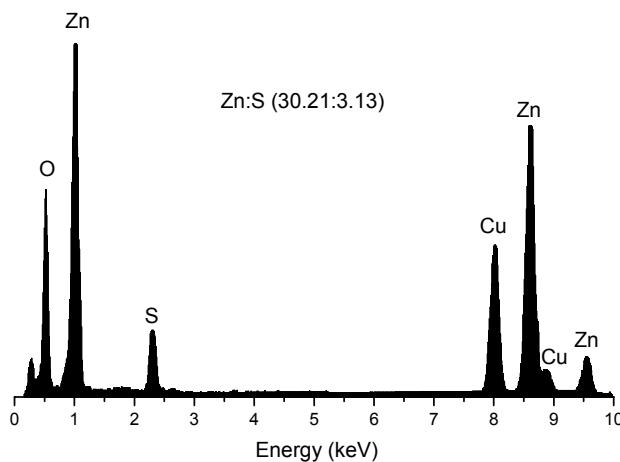


Figure S6. Energy dispersive X-ray spectrum of the precipitates of zinc hydroxide nanostrands and Evans Blue (EB) at the molar ratio of 125/1 for zinc atoms against EB.

In order to verify the above estimation, we measured EDX spectra of the precipitates of the nanostrands with Evans Blue. As shown in Figure S6, the molar ratio of zinc and sulfur atoms was estimated to 30.2 : 3.1 for the precipitates obtained from the mixture of 1/125 for EB/Zn²⁺. The first decimal digit of the molar ratio may contain some uncertainty. However, the observed value is in very good agreement with the composition, in which about one-tenth of zinc atoms in the nanostrand are positively charged and these charges are compensated with negative charges of Evans Blue.

Comparison of Cadmium, Copper, and Zinc Hydroxide Nanostrands:

Typical preparation conditions of metal hydroxide nanostrands and their properties are summarized in Table S2.

Cadmium hydroxide nanostrands are often prepared by mixing equivolume of 4 mM CdCl₂ and 0.8 mM AE. Under this condition, nanostrands of a few micrometres in length and 1.9 nm in width are selectively produced within 10 min. This nanostrand is stable in the aqueous solution for about one day. About one sixth of the cadmium atoms in the nanostrands are positively charged. This value is corresponding to one third of the surface cadmium atoms. Copper hydroxide nanostrands are usually prepared from 4 mM Cu(NO₃)₂ and 1.6 mM AE. The width of this nanostrand (2.5 nm) is a little larger than that of cadmium hydroxide nanostrand. The length reaches a few tens of micrometres after aging the reaction mixture for a few days. Copper hydroxide nanostrand is highly positively charged. About half of the surface copper atoms are assumed to be positively charged. This nanostrand is stable for about one month. In sharp contrast with copper ions, zinc ions give unstable nanostrands. We observed almost all the nanostrands converted into other morphology after aging one hour. This is probably due to the low charge density on its surfaces. At the aging time of 30 min, zinc hydroxide nanostrands of a few micrometres were selectively obtained by filtering with a polycarbonate membrane filter.

Table S2. Comparison of metal hydroxide nanostrands.

| nanostrand | concentration (mM) | | AE / metal ion | pH | diameter (nm) | positive charge density ^b | stability |
|---------------------|-------------------------|-----|----------------|-----|---------------|--------------------------------------|-----------|
| | metal salt ^a | AE | | | | | |
| Cd(OH) ₂ | 4.0 | 0.8 | 0.2 | 8.2 | 1.9 | 1/3 | < 1 day |
| Cu(OH) ₂ | 4.0 | 1.6 | 0.4 | 6.2 | 2.5 | 1/2 | < 1 month |
| Zn(OH) ₂ | 4.0 | 2.4 | 0.6 | 6.6 | 2.0 | 1/4 | < 1 hour |

^a The metal salts used for cadmium, copper, and zinc hydroxide nanostrands are CdCl₂, Cu(NO₃)₂, and Zn(NO₃)₂, respectively. ^b Positive charge density denotes the ratio of positive charges against the metal atoms on the surfaces of the nanostrand.

Cadmium ions tend to be stored in human body for about 30 years and give rise to serious diseases. Therefore, cadmium hydroxide nanostrands are highly toxic. Copper hydroxide nanostrands are not so harmless, as compared with those of cadmium. However, the growth speed is very slow, probably due to the Jahn-Teller effect of copper ion. In general, it takes a few days to obtain the nanostrands stoichiometrically. The slow growth will prevent us from designing the production processes in flow reactors. In sharp contrast, zinc ions that have been used as a nutritional supplement are intrinsically non-toxic and the nanostrands grow quickly. These are favorable for the consecutive large-scale production in industry.