

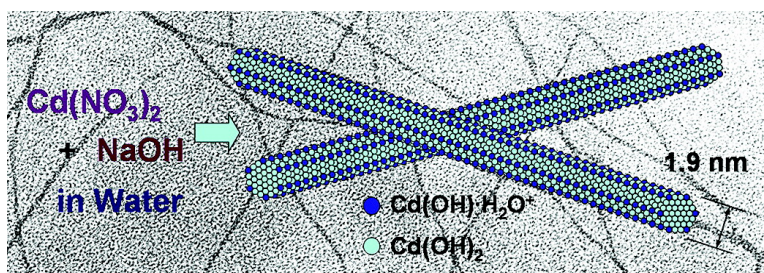
Communication

## Spontaneous Formation of Cadmium Hydroxide Nanostrands in Water

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## Spontaneous Formation of Cadmium Hydroxide Nanostrands in Water

Izumi Ichinose,<sup>\*,†</sup> Keiji Kurashima,<sup>†</sup> and Toyoki Kunitake<sup>‡</sup>

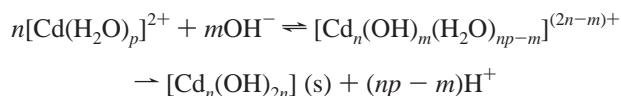
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Biological architectures such as phospholipid membranes and proteins are known to be organized principally by the balance of hydrophobicity and hydrophilicity of the components in aqueous media. Not just for organic molecules, the water occasionally gives aesthetic structures for inorganic materials.<sup>1,2</sup> In fact, imogolite, a natural aluminosilicate, has a fascinating structure very similar to that of carbon nanotube.<sup>3,4</sup> Nanometer-sized capsules and wheels are spontaneously formed from polyoxometalates in water.<sup>5,6</sup> We report herein cadmium hydroxide nanostrands with an extremely narrow diameter of 1.9 nm that are formed by just raising the pH of a dilute Cd(NO<sub>3</sub>)<sub>2</sub> solution. The length reaches a few micrometers and the aspect ratio exceeds 1000. The crystallographic structure was successfully elucidated by high-resolution electron microscopy.

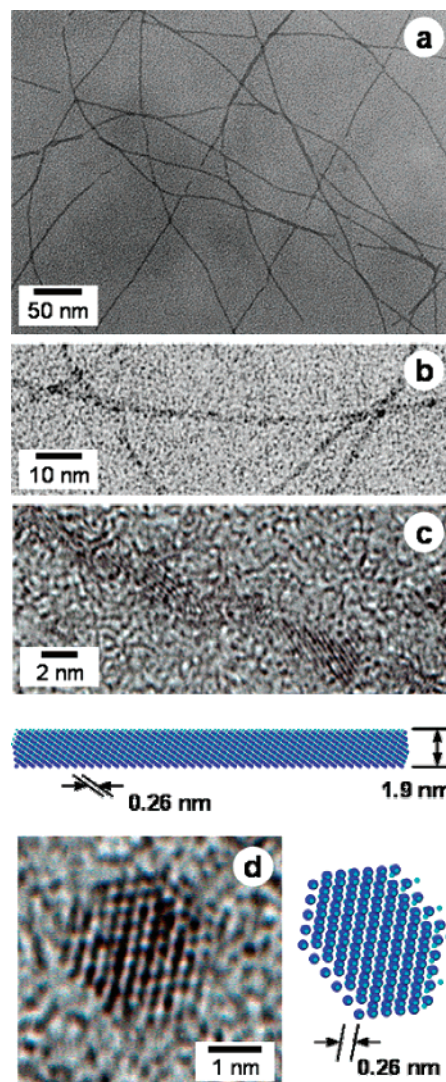
A given amount of a dilute NaOH solution was quickly added into aqueous Cd(NO<sub>3</sub>)<sub>2</sub> (2.0 mM, pH 5.44) with stirring. The pH of the mixed solution became 8.19 when the concentration of NaOH was 0.8 mM. The value rose slightly up to 9.09 by the addition of 4.0 mM NaOH, twice the molar amount against Cd(NO<sub>3</sub>)<sub>2</sub>, and then suddenly increased after that. White precipitates of cadmium hydroxide were formed in solutions of more than pH 9.0 after a while. We recognized that solutions containing a small amount of NaOH were weakly scattering light-blue. Metal hydroxide nanostrands were abundantly observed in these solutions, as confirmed by transmission electron microscopy (TEM).

When the nanostrands appear in solution, the pH change due to the addition of alkaline solution is very small. This can be explained by the buffer action of cadmium ions. It is widely believed that hydrated cadmium ions ( $n[\text{Cd}(\text{H}_2\text{O})_p]^{2+}$ ) become solid cadmium hydroxide ( $[\text{Cd}_n(\text{OH})_{2n}]$ ) through the stepwise coordination of hydroxyl ions and the subsequent condensation of hydroxyl groups bound to individual cadmium ions as follows.



This process is often referred to as “olation”. The nanostrands we discovered seem to be one of the morphologies of cadmium hydroxide with a nonstoichiometric composition of  $[\text{Cd}_n(\text{OH})_m(\text{H}_2\text{O})_{np-m}]^{(2n-m)+}$ .

The nanostrands prepared at low pH were examined by high-resolution electron microscopy. The observation was carried out at an acceleration voltage of 200 kV, using a sufficiently narrowed electron beam. As shown in Figure 1, many of the nanostrands had a constant width of about 2 nm. The length reached a few micrometers. There were nanostrands of 3-nm width, but the occurrence was very low. Linear nanostrands were slightly bent or broken at the location where two nanostrands overlapped. Figure



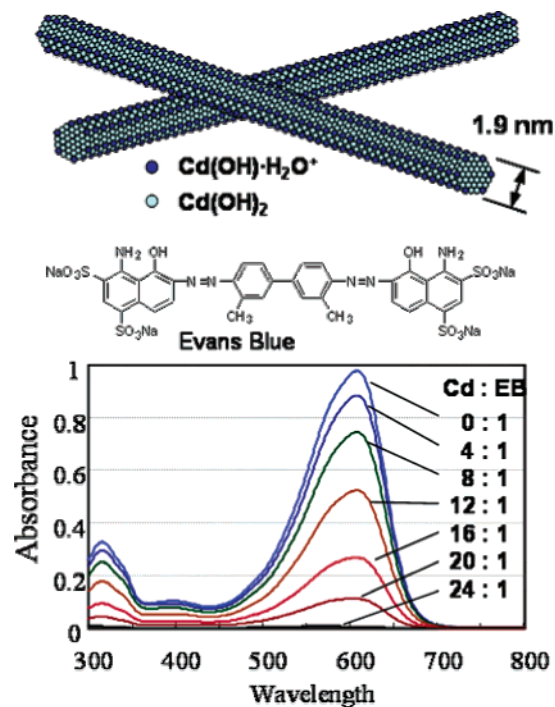
**Figure 1.** TEM (a) and HR-TEM (b–d) images of cadmium hydroxide nanostrands and their structural models.

1c shows a lattice image successfully observed at high magnification. It has a periodicity of 0.26 nm, which appears to be tilted at angles of 15–30°. The lattice image could be observed up to seven lines perpendicular to the nanostrand. The measured width was 1.9 nm. Figure 1d shows an image of a distorted hexagonal object we observed by chance. It is still uncertain whether this is a cross section of a nanostrand or that of a cluster. However, we assumed the image to be a part of the nanostrand, since it gave periodicity of 0.26 nm.

We calculated structural models of the nanostrand from the crystallographic data of cadmium hydroxide (crystal system,

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**Figure 2.** Schematic illustration of the nanostrands with a diameter of 1.9 nm. The cadmium atoms colored deep blue are thought to be positively charged. The bottom is UV-vis absorption changes of Evans Blue solutions after filtering the precipitate weakly gelled by nanostrands.

hexagonal;  $a$ , 3.496;  $c$ , 4.702; space group,  $P-3m1$ ).<sup>7</sup> If the cross section is hexagonal and the diameter is 1.9 nm, the nanostrand can be posited to be made of a plate composed of 37 unit cells. We piled up the hexagonal plates after shifting by one unit cell so as to generate proper periodicity. The results are shown in Figure 1, where cadmium atoms (blue) were drawn two times larger than oxygen atoms (green) to be seen similarly to the TEM image. We could exactly reproduce, in the lateral model of nanostrand, a width of 1.9 nm and periodicity of 0.26 nm tilted at an angle of 30°. The model for the cross section could also well reproduce the distorted-hexagonal shape. These results clearly indicate that nanostrands are made of the same crystallographic unit cells as that of cadmium hydroxide. Our model is schematically illustrated in Figure 2, in which oxygen and hydrogen atoms are not described for simplification. The hexagonal cross section has seven cadmium atoms in the diagonal line and four cadmium atoms in the side. Cadmium atoms located at the surface reach approximately half of the total Cd atoms. It is surprising that such a structure is robust enough to sustain its strand shape no less than a few micrometers.

This nanostrand was extremely positively charged, and it adsorbed negatively charged organic molecules. For example, when the nanostrand was mixed with Evans Blue solution, blue-colored weakly gelled precipitates were produced. To evaluate the trapping ability for the dye molecules, we monitored UV-vis absorption changes of Evans Blue solutions after filtering the gelled precipitates. The results are shown in Figure 2, where the concentration of nanostrand was regularly increased, and that of Evans Blue was fixed to 0.04 mM for all mixtures.

The absorption peak at 608 nm, which was attributed to Evans Blue, was quantitatively decreased with increases in the nanostrand concentration. This indicates that the nanostrands and dye molecules generate a stoichiometric complex, which is removed by the filtration. The amount of nanostrands is given in Figure 2 as the ratio of cadmium atoms against Evans Blue molecules (Cd:EB). The dye molecules with four sulfonate groups completely disap-

peared from the filtrate when 24-fold cadmium atoms were mixed to the solution. This means that one-sixth of the cadmium atoms in the nanostrand are positively charged and neutralize Evans Blue electrostatically. This proportion might be deemed too high. However, it is quite convincing, when the six corner cadmium atoms of the hexagonal plate composed of 37 unit cells are positively charged. That is to say, our structural models, TEM images, and results of UV-vis spectroscopic titration are consistent each other.

Formation of cadmium hydroxide nanostrands can be explained as follows. First, a hydroxide ion coordinates to a hydrated cadmium ion and becomes a hydroxyl group. The hydroxyl groups on different cadmium ions ( $[\text{Cd}(\text{OH})(\text{H}_2\text{O})_{p-1}]^+$ ) condense each other, and divalent  $[\text{Cd}(\text{H}_2\text{O})_{p-1}-\text{O}-\text{Cd}(\text{H}_2\text{O})_{p-1}]^{2+}$  ion is formed. In the course of subsequent ololation, positively charged and highly anisotropic cadmium hydroxide clusters are produced, and such clusters would assemble to the nanostrand with a large aspect ratio. From the results of UV-vis titration, the composition should be described as  $[\text{Cd}_{6n}(\text{OH})_{11n}(\text{H}_2\text{O})_n]^{n+}$ .

Recently, we found out that similar nanostrands with a width of a few nanometers were formed during the ololation process of lanthanide ions. Interestingly, lanthanide ions gave very flexible nanostrands. Metal oxide nanostrands are not necessary to be crystalline. More essential might be the fact that the surface has a proper amount of positive charges. Too much positive charge ought to disconnect the nanostrand and too little charge will make the nanostrand precipitate. In other words, the extent of surface charge neutralization by hydroxyl ions and the easiness have a decisive influence on the nanostrand formation. Under proper pH conditions, nanostrands are spontaneously formed as if rodlike micelles of cationic surfactants were formed in water.

It is known that some of metal oxides gave fibrous structures.<sup>8,9</sup> Nevertheless, cadmium hydroxide nanostrand has many unprecedented features that have not been observed in past fibrous metal oxides. It is noteworthy that double-stranded DNA of 6-kbp has a length of 2  $\mu\text{m}$  (1 bp = 0.34 nm) and a width of 2 nm. Cadmium hydroxide nanostrand has the same dimension with a short DNA chain. The nanostrand is a temporal object and eventually becomes a large hexagonal crystal, but the dilute solution is stable at least for a few weeks. It appears to be stabilized by the addition of amines or cationic polymers. Furthermore, the nanostrand quickly disappears by lowering the pH or adding chelate compounds such as EDTA. A remarkable affinity for organic molecules has not been seen for the past nanofibers with inert surfaces. Inorganic nanostrands spontaneously formed in water promise unique molecular functions we have not seen before.

**Supporting Information Available:** Preparation and structural modeling of cadmium hydroxide nanostrands. Photograph of the weakly gelled precipitate with Evans Blue. TEM images of lanthanide oxide nanostrands (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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