SUPPORTING INFORMATION

Bundle-like Assemblies of Cadmium Hydroxide Nanostrands and Anionic Dyes

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1. Formation of cadmium hydroxide nanostrands

Discovery of cadmium hydroxide nanostrands have been described in our previous report, *J. Am. Chem. Soc.*, *126*, 7162-7163 (2004), and the crystallographic structure was demonstrated in another report, *Nano Letters*, *5*, 97-100 (2005), and in the supporting information. The nanostrands have a constant width of about 2 nm, as shown in Figure S1. The structure is thought to be made of hexagonal plates of cadmium hydroxide with a diameter of 1.9 nm, which are piled up each other after shifting by one unit cell because of the electrostatic repulsion. One-third of cadmium atoms located at the surface are positively charged due to the protonation of a hydroxyl group coordinated to the cadmium atom to give a composition of $[Cd_{37}(OH)_{68}(H_2O)_n]^{6+}\cdot 6X^-$ (X; counter-anion).

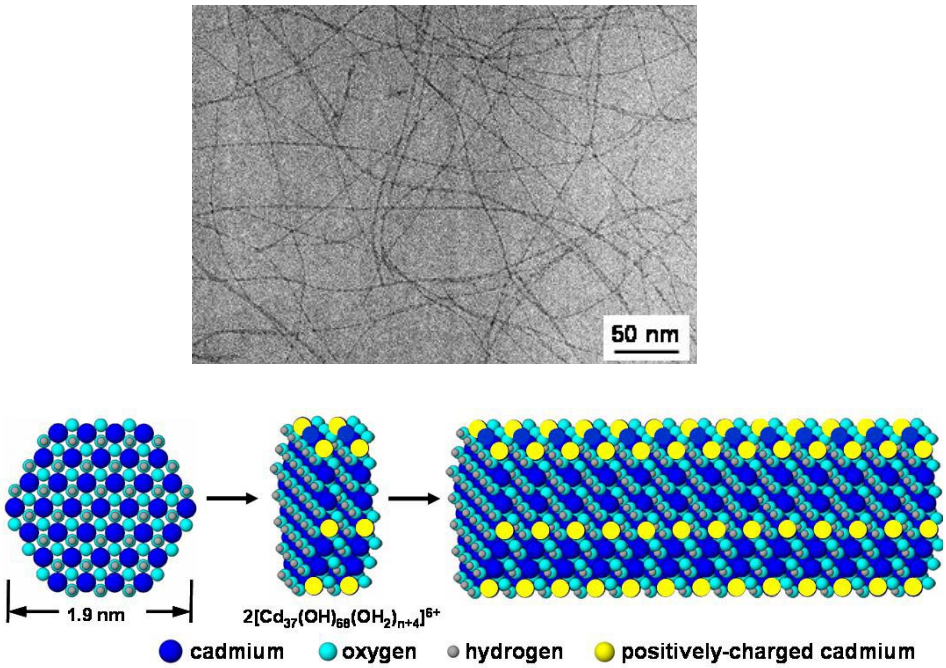

Figure S1. TEM image of cadmium hydroxide nanostrands and the structural model. TEM specimen was prepared by quickly mixing 20 mL of 4 mM $Cd(NO_3)_2$ and 20 mL of 2 mM NaOH.

Cadmium hydroxide nanostrands are spontaneously formed in water just by raising pH of the solution.

When sodium hydroxide (NaOH) was used, the formation was very dependent on the molar ratio against cadmium salt. Figure S2 shows the titration curve of $Cd(NO_3)_2$ by NaOH. At the beginning, pH increased with small amount of NaOH, and then very slowly increased until the addition of 10 mL, twice molar amount against $Cd(NO_3)_2$, and then turned upward again. Extremely narrow nanostrands were abundantly observed at the mixing ratio indicated by "**a**". Besides the nanostrands, globular particles of about 200 nm in diameter were occasionally observed at "**b**". The particles developed into hexagonal crystals of cadmium hydroxide at "**c**". The nanostrands were dominantly produced at the mixing ratio of NaOH far smaller than the amount required for the stoichiometric formation of bulk cadmium hydroxide.

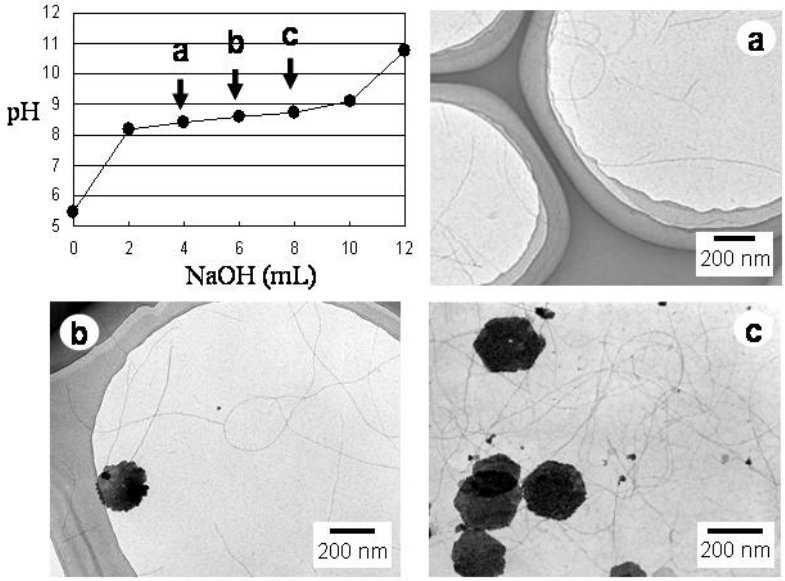

Figure S2. Titration curve of $Cd(NO_3)_2$ by NaOH and TEM images obtained at different pH (**a**, **b**, **c**). To obtain the titration curve, a given amount of NaOH solution (16 mM) was diluted to be 20 mL with water, and then quickly added into 20 mL of 4 mM aqueous $Cd(NO_3)_2$ with stirring. All the solutions contain small amount of poly(allylamine hydrochloride) (0.2 mM for monomer unit).

Formation of the nanostrands was not influenced by counter-anions. In fact, $CdCl_2$, $CdSO_4$, and $Cd(NO_3)_2$ gave the same nanostrands within a few minutes after mixing with NaOH. Ammonia and organic amines (aminoethanol, iminodiethanol, etc.) were also available. The nanostrands were quantitatively produced from 4 mM $CdCl_2$ and an equivolume of 0.8 mM aminoethanol. In other words, about one-tenth of cadmium ions were converted to the nanostrands in this condition. Increase of the mixing ratio of the aminoethanol resulted in the appearance of globular particles after a few hours. The nanostrand was stable at least one day at room temperature. In our experience, 2 mM was the best for the final concentration of cadmium ions in the reaction mixture. In case of iminodiethanol, it took several tens of minutes to give the nanostrands. This delay is probably caused by the coordination of iminodiethanol to cadmium ion.

2. Electrostatic composites of cadmium hydroxide nanostrands and dye molecules

Formation of nanostrand/dye composites. Evans Blue, Congo Red, and Direct Yellow 50 were obtained from Aldrich, and used without further purification. DATS (2,2'-dihydroxy-1,1'-azonaphthalene-3,3',6,6'-

tetrasulfonic acid sodium salt) was obtained from Sigma as the sulfonic acid derivative, and then neutralized by adding aqueous NaOH. Sodium dodecylsulfate (SDS) and cadmium chloride ($CdCl_2 \cdot 2.5H_2O$) were purchased from Kanto Chemical. Polycarbonate (PC) membrane filter is a product of Whatman (Nuclepore®).

Characterization. TEM observations were carried out on a JEOL-1010 at an acceleration voltage of 100 kV. To prepare the specimens, the precipitates of nanostrand/dye composites were dispersed in ethanol, and a drop of the suspension was spread on a carbon-coated copper TEM grid and allowed to stand in air until the solvent completely evaporated. FE-SEM images were obtained by using a Hitachi S-4800 at an acceleration voltage of 25 kV. The specimens were prepared just by filtering the aqueous suspensions of as-prepared nanostrand/dye composites on a PC membrane filter with pores of 0.2 μm in diameter. About 2-nm thick platinum layer was deposited by using a Hitachi e-1030 Ion Sputter to prevent the specimens from electric charge up. UV-vis absorption spectra were obtained by using a Shimadzu UV-3150 spectrophotometer in transmission mode. The spectra of nanostrand/dye composites were obtained from the as-prepared suspensions by using 1-cm cell.

Additional information. Negatively charged organic compounds were strongly adsorbed on the surface of cadmium hydroxide nanostrands. For example, sodium poly(styrene sulfonate) (PSS), sodium benzoate, and anionic surfactants (sodium 4-octylbenzensulfonate, etc.) quickly gave white precipitates after mixing with the nanostrands. On the other hand, rigid double-stranded DNA gave weakly gelled precipitates. Multiply-charged dye molecules showed different precipitation behavior depending on the concentration of the nanostrands. When the concentration was low, the dye molecules slowly formed weakly gelled precipitates. In contrast, an excess amount of the nanostrands quickly gave condensed aggregates, as shown in Figure S3 (**a**, **b**). The latter aggregates were readily separated by filtration using PC membrane filter or porous alumina membrane. The photo images of the filtered composites are shown in Figure S3 (**c**, **d**).

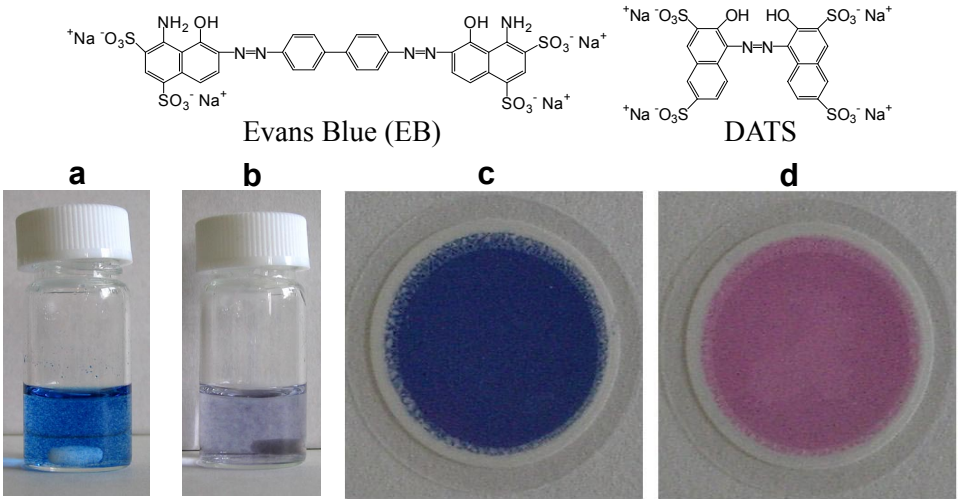

Figure S3. Photo images of electrostatic composites of Evans Blue (**a**) and DATS (**b**) with cadmium hydroxide nanostrands. The composites were prepared by adding 50 μL of 1 mM dye solution (Evans Blue or DATS) into 5 mL of as-prepared cadmium hydroxide nanostrand solution that had been obtained from 4 mM $CdCl_2$ and equivolume of 0.8 mM aminoethanol. Bottom images (**c**, **d**) were alumina membranes with 0.2-μm pores (Whatman) after filtering these composites (**a**, **b**).

3. Bundles of cadmium hydroxide nanostrands induced by SDS

The bundles of cadmium hydroxide nanostrands were obtainable by using aqueous solution of sodium dodecylsulfate (SDS). For example, 1 mL of 40 mM $CdCl_2$ was stirred with 0.4 mL of 200 mM SDS solution for 1 hour, and then 160 mM ammonia was added into the mixture up to the molar ratio of 0.2 for NH_3/Cd^{2+} under continuous stirring. The clear solution turned to white one. After further stirring for 1 hour, the precipitates formed were collected by centrifugation, and washed 3 times with deionized water. As shown in Figure S4, the precipitates were composed of flexible fibers, which had a stripe of 3–4 nm. Probably, individual cadmium hydroxide nanostrands are coated with SDS molecules and assembled to the bundles.

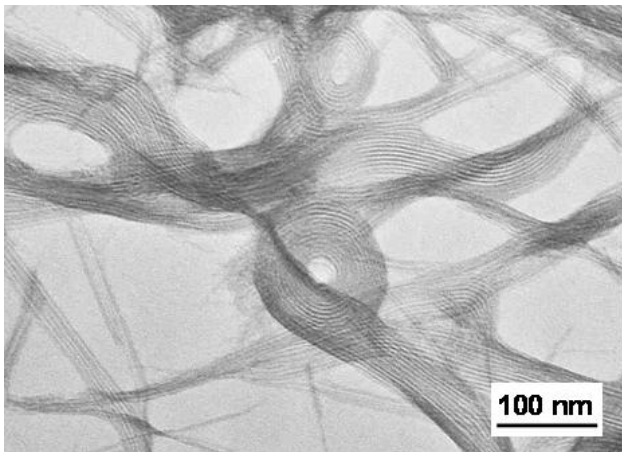

Figure S4. TEM image of bundles of cadmium hydroxide nanostrands induced by SDS. The precipitates of nanostrands/SDS composite were dispersed in ethanol by sonicating for a few minutes. One drop of the suspension was spread on a carbon-coated copper grid, dried, and used for TEM observation.