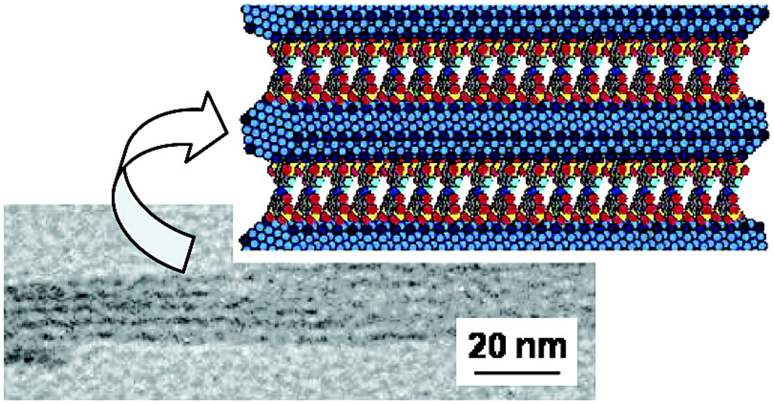
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Bundle-like Assemblies of Cadmium Hydroxide Nanostrands and Anionic Dyes

Yan-Hong Luo, Jianguo Huang, and Izumi Ichinose

J. Am. Chem. Soc., **2005**, 127 (23), 8296-8297• DOI: 10.1021/ja052189q • Publication Date (Web): 17 May 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Bundle-like Assemblies of Cadmium Hydroxide Nanostrands and Anionic Dyes

Yan-Hong Luo, Jianguo Huang, and Izumi Ichinose*

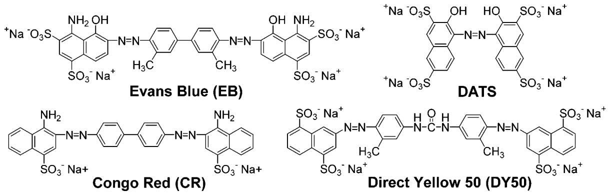
Advanced Materials Laboratory, National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

Received April 5, 2005; E-mail: ichinose.izumi@nims.go.jp

One-dimensional (1-D) nanostructures, such as wires, rods, tubes, and belts, have received increasing interest from various fields of science.[1] 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 nanoelectronics, ultra small optical devices, biosensors, etc. The challenge is how to build desired architectures from long and rigid 1-D nanostructures. In the past, isotropic nanoparticles were used as building blocks of superlattices[2] and 3-D microspheres.[3] DNA templates, biotin−streptavidin interaction, Langmuir−Blodgett technique, etc. were employed to obtain ordered arrays of short nanorods.[4] It was possible to manipulate micrometer- and millimeter-sized objects by controlling their surface and magnetic properties.[5] However, few researches have aimed at assembling inorganic 1-D nanostructures at surface and in solution.[6]

Yang et al. reported that 1-D inorganic nanowires were obtainable by exchanging lithium ions of $LiMo_3Se_3$ with cationic surfactants. The mesostructures of the nanowires were changed from hexagonal to lamellar ones by choosing the structure of surfactants. They reported that these nanowires tend to form bundles with a width of 10−200 nm.[6b,c] Recently, we found that extremely long nanostrands of cadmium hydroxide were spontaneously formed in water just by increasing the pH of dilute cadmium nitrate solution.[7] The nanostrand had a constant width of 1.9 nm and an astonishing number of positive charges on its surface. These properties were applied to the effective separation of short DNA fragments from the dilute aqueous solutions.[8] The nanostrand strongly adsorbed anionic dye molecules, too. In the present study, we employed the organic dyes as "*molecular fasteners*" for the cadmium hydroxide nanostrands. Their bundle-like assemblies with unique UV−vis absorption properties were systematically investigated for the molecules listed in Scheme 1.

Scheme 1. Structures of Sulfonated Dye Molecules



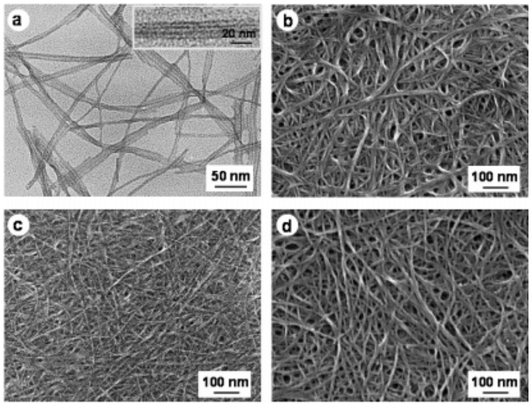


Figure 1. TEM (a) and SEM (b−d) images of the nanostrand/dye composites. The composites were prepared at the concentrations of 10 μM EB (a, b), 80 μM EB (c), and 10 μM DATS (d). The inset in (a) shows a higher magnification image of the nanostrand/EB composite.

An aqueous solution of $CdCl_2$ (4.0 mM) was quickly mixed with an equal volume of aminoethanol (0.8 mM). In this condition, about 10% of Cd^{2+} ions were converted to cadmium hydroxide nanostrands within a few minutes. The pH of the solution was 8.2. Then, a given amount of Evans Blue (EB) solution (1.0 mM) was added under constant stirring. The blue precipitates immediately formed were centrifuged, washed with deionized water, and dried. Figure 1a shows a TEM image of the nanostrand/EB composite prepared at the dye concentration of 10 μM, about $^{1}/_{20}$ of cadmium ions in the nanostrands formed. A few nanostrands started to assemble parallel to each other. The width of the bundle-like assemblies was in a range of 8−20 nm. The enlarged image is shown in the inset of Figure 1a. Distances between the nanostrands were 4.5 nm or more. Considering the diameter of the nanostrand (1.9 nm), the minimum interval of 2.6 nm was consistent with the molecular size of EB (27.4 ± 1.1 Å in length).[9] It is clear that the dye molecules are inserted between the inorganic nanostrands. The elemental composition was estimated to be 52.3 wt % for cadmium and 10.7 wt % for carbon, separately, from ICP measurements and elemental analyses. From these values, atomic ratio (Cd/C) and composite ratio (Cd/EB) were calculated to 0.52 and 17.8, respectively. The latter was close to the mixing ratio of EB in the nanostrand solution.

The bundle-like assemblies were readily immobilized on porous substrates by suction filtration. The film formed on a polycarbonate membrane filter is shown in Figure 1b. A highly entangled network structure of the flexible assemblies was observed in a large area. When the assemblies were prepared at the high concentration of EB (80 μM), the significant narrowing of the width was observed (Figure 1c). The whole surface of the cadmium hydroxide nanostrand is probably coated with an excess number of dye molecules. In fact, we found that a major part of the dye molecules remained in the filtrate after suction filtration. Figure 1d shows the bundle-like assemblies prepared by using DATS at the concentration of 10 μM. The morphology of the nanostrand/DATS composite appeared to be somewhat rigid as compared with that of EB. Other polysulfonated dyes, Congo Red (CR) and Direct Yellow 50 (DY50), gave very similar morphology to the nanostrand/EB composite. We should stress here that these fibrous assemblies are 10−100 times narrower than the polymer fibers prepared by an electrospinning process.[10]

Figure 2a shows an enlarged TEM image of a nanostrand/DATS assembly. The cadmium hydroxide nanostrands aligned in parallel

10.1021/ja052189q CCC: $30.25

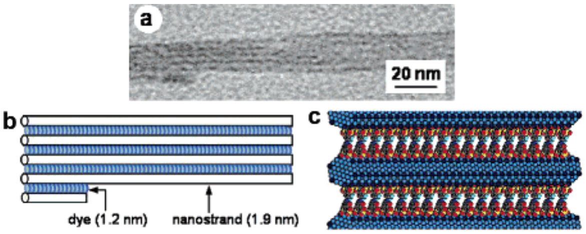


Figure 2. TEM image of nanostrand/DATS composite (a) and the schematic illustrations (b, c). In the cadmium hydroxide nanostrands in (c), positively charged cadmium atoms and neutral ones are colored dark blue and blue, respectively.

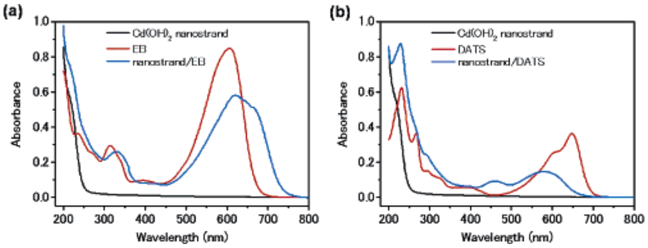


Figure 3. UV−vis absorption spectra of cadmium hydroxide nanostrand (black line), dyes (red line), and nanostrand/dye composites (blue line). The concentration of EB in (a) and DATS in (b) was 10 μM. The concentration of the nanostrands was 2 mM in terms of cadmium ions.

Table 1. UV−Vis Absorption of Organic Dyes and Their Composites

	Absorption Maxima (λ_{max})		
	dye[a]	nanostrand/dye composites	$\Delta\lambda_{max}$
EB	606	620 (670)[b]	14 (64)[b]
CR	498	510	12
DY50	397	423	26
DATS	648	579	−69

[a] Aqueous solution of 10 μM. [b] Shoulder peak.

with a distance of 3.1 nm. The interval between the nanostrands was 1.2 nm, which is very consistent with the molecular length of DATS (11.8 Å) estimated for the distance between edges of two naphthalene units. Since this molecule has a trans-conformation, the four sulfonic groups locate symmetrically. We presumed that such molecules stood perpendicular to the nanostrand and were one-dimensionally stacked along with the nanostrand. Interestingly, their assemblies usually appeared to be flat tapes. They are not bundled with a round cross-section. Schematic illustration of the TEM image and the molecular representation are shown in Figure 2b,c.

As in the cases of semiconductor nanoparticles,[11] the cadmium hydroxide nanostrand showed a strong quantum size effect. The UV absorption threshold was at 246 nm, which was blue-shifted by 52 nm from the reported value for cadmium hydroxide powder (298 nm).[12] UV−vis spectra of EB, DATS, and their composites are shown in Figure 3. The aqueous solution of EB showed a strong absorption at 606 nm (red line in Figure 3a) attributed to the $\pi-\pi^*$ transition parallel to the long axis.[13] This peak shifted to 620 nm when the dye formed the nanostrand/EB composite, and a new shoulder appeared near 670 nm (blue line). As shown in Table 1, Congo Red (CR) and Direct Yellow 50 (DY50) also gave red-shifts of 12 and 26 nm, respectively. These dyes with elongated molecular shapes seem to form J-aggregates in the bundle-like assemblies.[13,14] In sharp contrast, the composites of DATS gave a large blue-shift of 69 nm and strong hypochromicity (Figure 3b). This dye must form H-aggregates in the interstitial space between two cadmium hydroxide nanostrands, as illustrated in Figure 2c.

It is apparent that strong $\pi-\pi^*$ interaction exists among the dye molecules. This must significantly contribute to the structural stabilization of the bundle-like assemblies, as well as electrostatic interaction between the nanostrands and the dye molecules.[15] We have estimated that about $^1/_3$ of cadmium atoms located at the surface of nanostrand were positively charged at neutral pH, as shown in Figure 2c.[8] In that case, there are enough excessive positive charges to neutralize the negative charges of dye molecules that are one-dimensionally stacked. It was possible to produce similar assemblies by using sodium dodecylsulfonate (SDS). In this case, however, we needed to use SDS solution near the critical micelle concentration (see Supporting Information). In contrast, bundle-like assemblies of nanostrand/dye composites were obtainable from the dye solutions at the concentration of 5 μM or less. These indicate how strong the interaction between the nanostrands and stacked dye molecules is.

In the past, mesoscopic structures of inorganic materials have been created with the help of surfactants.[6,16] The use of organic dyes of peculiar molecular configuration will be a way to design new supramolecular architectures with strong absorption for visible light. Furthermore, morphological features of the immobilized membranes of the fibrous nanocomposites will be an advantage for future applications.

Supporting Information Available: Formation of cadmium hydroxide nanostrands. Photo images of nanostrand/dye composites. TEM image of bundles formed from cadmium hydroxide nanostrands and SDS. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Adv. Mater.* **2003**, *15*, 353−389. (b) Peng, X. G.; Manna, L.; Yang, W. Y.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59−61. (c) Iijima, S. *Nature* **1991**, *354*, 56−58. (d) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, *291*, 1947−1949.
(2) (a) Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. G. *Science* **1996**, *273*, 1690−1693. (b) Li, M.; Schnablegger, H.; Mann, S. *Nature* **1999**, *402*, 393−395.
(3) (a) Boal, A. K.; Ilhan, F.; DeRouchey, J. E.; Thurn-Albrecht, T.; Russell, T. P.; Rotello, V. M. *Nature* **2000**, *404*, 746−748. (b) Jin, J.; Iyoda, T.; Cao, C.; Song, Y.; Jiang, L.; Li, T. J.; Zhu, D. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2135−2138.
(4) (a) Dujardin, E.; Hsin, L. B.; Wang, C. R. C.; Mann, S. *Chem. Commun.* **2001**, 1264−1265. (b) Caswell, K. K.; Wilson, J. N.; Bunz, U. H. F.; Murphy, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 13914−13915. (c) Kim, F.; Kwan, S.; Akana, J.; Yang, P. D. *J. Am. Chem. Soc.* **2001**, *123*, 4360−4361.
(5) (a) Park, S.; Lim, J. H.; Chung, S. W.; Mirkin, C. A. *Science* **2004**, *303*, 348−351. (b) Grzybowski, B. A.; Stone, H. A.; Whitesides, G. M. *Nature* **2000**, *405*, 1033−1036.
(6) (a) Kimizuka, N. *Adv. Mater.* **2000**, *12*, 1461−1463. (b) Messer, B.; Song, J. H.; Huang, M.; Wu, Y.; Kim, F.; Yang, P. *Adv. Mater.* **2000**, *12*, 1526−1528. (c) Messer, B.; Song, J. H.; Yang, P. *J. Am. Chem. Soc.* **2000**, *122*, 10232−10233.
(7) Ichinose, I.; Kurashima, K.; Kunitake, T. *J. Am. Chem. Soc.* **2004**, *126*, 7162−7163.
(8) Ichinose, I.; Huang, J.; Luo, Y. H. *Nano Lett.* **2005**, *5*, 97−100.
(9) Inglesby, M. K.; Zeronian, S. H.; Elder, T. J. *Textile Res. J.* **2002**, *72*, 231−239.
(10) (a) Doshi, J.; Reneker, D. H. *J. Electrostat.* **1995**, *35*, 151−160. (b) Bognitzki, M.; Czado, W.; Frese, T.; Schaper, A.; Hellwig, M.; Steinhart, M.; Greiner, A.; Wendorff, J. H. *Adv. Mater.* **2001**, *13*, 70−72.
(11) (a) Brus, L. E. *J. Chem. Phys.* **1984**, *80*, 4403−4409. (b) Murray, C. B.; Norris, D. J.; Bawemdo, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706−8715.
(12) *Gmelins Handbook of Inorganic Chemistry*, system number 33, Cadmium, Verlag Chemie: Weinheim, Germany, 1959; p 442.
(13) Cooper, T. M.; Stone, M. O. *Langmuir* **1998**, *14*, 6662−6668.
(14) A shoulder peak observed for the nanostrand/EB composite should be attributed to the highly tilted J-aggregate. This is probably due to the excess adsorption of the dye molecules.
(15) Guan, Y.; Antonietii, M.; Faul, C. F. J. *Langmuir* **2002**, *18*, 5939−5945.
(16) Faul, C. F. J.; Antonietti, M. *Adv. Mater.* **2003**, *15*, 673−683.

JA052189Q