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Cylindrical Superparticles from Semiconductor Nanorods

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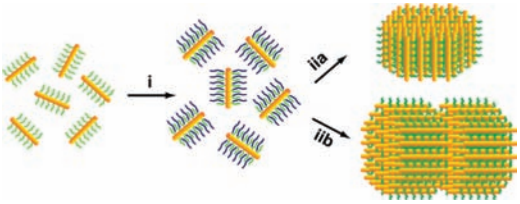
The ability to control the formation of nanoparticle superlattices may allow for the synthesis of new materials with desired chemical and physical properties.[1−3] In the past decades, efforts have been focused on the preparation of nanoparticle superlattices with various compositions and/or supercrystalline structures,[1,2] from which several nanoparticle collective properties have been discovered.[3] Recently, several approaches have been reported for making nanoparticle superlattices in the form of colloidal particles [called superparticles (SPs)].[4] These SPs are spheres with well-controlled sizes ranging from tens to hundreds of nanometers, and their properties can be tailored by varying the size and composition of the nanoparticle building blocks or doping with functional organic molecules.[4] In addition, these spherical SPs can be assembled into close-packed solid structures, demonstrating their potential as a new class of building blocks in nanoscience.[4]

Herein, we report a synthesis of anisotropic SPs from CdSe/CdS semiconductor nanorods. The resulting SPs are cylindrical disks or stacked-disk arrays, and they exhibit photoluminescence (PL) that is linearly polarized along their axial direction. In this work, CdSe/CdS nanorod building blocks were prepared using a literature method.[5] The anisotropic SPs were synthesized using the approach of controlling solvophobic interactions. With this approach, we previously synthesized spherical SPs from spherical nanoparticles of various sizes and compositions.[4a,b] This SP synthesis includes two major steps (Scheme 1): (i) preparation of water-soluble nanorod micelles, and (ii) growth of SPs using nanorod micelles in ethylene glycol, in which an annealing treatment (at 80 °C) is required in order to improve the supercrystallinity of the resulting SPs.[4a,b]

Scheme 1. Synthesis of Anisotropic SPs: (i) Preparation of Nanorod Micelles and (ii) Formation of (a) Cylindrical Disks and (b) Bilayer Stacked-Disk Arrays



In this annealing treatment, suitable capping ligands are critical for stabilizing the SPs. Poly(vinyl pyrrolidone) and gelatin were found to be appropriate ligands for making stable spherical SPs.[4a,b] However, these ligands cannot effectively passivate the surface of CdSe/CdS nanorod SPs, and their use often produced SP samples with aggregation and poor solubility (Figure S1 in the Supporting Information).[6] These results arose, in part, because the ligands have a weak affinity for the (100) facets of the CdSe/CdS nanorods. To overcome this difficulty, we used dual-interaction ligands (e.g., dithiol-functionalized Tween-20, Tween-SH) to passivate these anisotropic SPs in the growth step.[6] These dual-interaction ligands have a strong affinity for CdSe/CdS nanorods, because the ligands bind to the surface of the nanorods through both coordinate bonding and hydrophobic van der Waals interactions. Indeed, the use of these ligands led to the formation of stable cylindrical supercrystalline SPs (Figure 1).

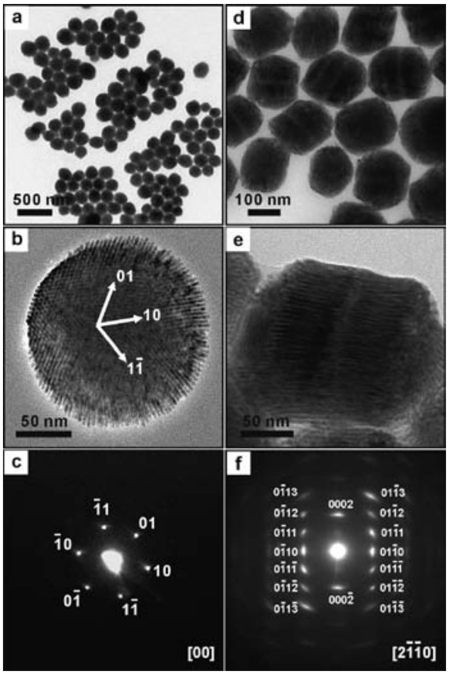


Figure 1. TEM images of cylindrical SPs: (a, b) single-layer disks and (d, e) bilayer stacked-disk arrays. (c) Small-angle ED pattern of the SP shown in (b). (f) Wide-angle ED pattern of the bilayer SP shown in (e).

In a typical synthesis, a chloroform solution of CdSe/CdS nanorods (55.4 ± 2.6 nm in length and 4.4 ± 0.2 nm in diameter, 10 mg/mL, 1.0 mL) was mixed with an aqueous solution of dodecyl trimethylammonium bromide (65 mM, 1.0 mL) under stirring. Chloroform was removed from the mixture using bubbling Ar, yielding a clear aqueous solution of nanorod micelles. This nanorod micelle solution was injected into a three-neck flask containing ethylene glycol (5.0 mL) under vigorous stirring. After this mixture was stirred for 10 min, a Tween-20-SH aqueous solution (0.1 mM, 1.0 mL) was injected into the flask, and the resulting mixture was heated to 80 °C at a rate of 10 °C/min. This temperature was maintained for 1 h, and then the reaction solution was cooled to room temperature. Colloidal SPs were precipitated from the synthesis solution by centrifugation, with a typical yield of ∼70%.

The resulting colloidal SPs were dispersible in polar solvents such as ethanol and water. Transmission electron microscopy (TEM)

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observations revealed that the SPs are cylindrical disks rather than spheres. These cylindrical disks were mainly vertically oriented on the TEM substrate (Figure 1a), but a small number of the disks were still laterally oriented on the substrate, giving a side view of these SPs (Figure S2).[6] The diameter of these disks was 160 nm with a relative standard deviation (σ) of 11% (Figure 1a). A typical side-view image of these SPs showed that the height of the disks was ~56 nm and that the disks are single-layer assemblies of CdSe/CdS nanorods.[6]

The supercrystalline structure of these cylindrical SPs was characterized by TEM and small-angle electron diffraction (ED) studies. Because they are single-layer nanorod assemblies, these SPs possess a two-dimensional (2D) structure. A typical TEM image (Figure 1b) shows that the SPs exhibit a superlattice fringe pattern, which is the [00] zone projection of a *P*6 2D lattice structure with a lattice constant of 6.0 ± 0.2 nm.[7] The [00] projection image displays the characteristic hexagonal cross-fringes with a spacing of 5.2 nm, which can be indexed as the (01), (10), and (1$\bar{1}$) crystal lines in the 2D superlattice (Figure 1b). The interline spacing and angles obtained from the TEM image are consistent with the corresponding small-angle ED pattern (Figure 1c). The ED pattern shows a sharp-spot array, which demonstrates the perfection of the 2D superlattice.

The formation of cylindrical disks is likely driven by two major forces: anisotropic interparticle interactions between the CdSe/CdS nanorods and repulsive solvophobic interactions between an SP and ethylene glycol solvent molecules. The anisotropic interparticle interactions favor hexagonal close packing of the CdSe/CdS nanorods along their *c* axis inside an SP; this packing characteristic can maximize the volume free energy of this SP. The repulsive solvophobic interactions favor an SP with a round shape, which minimizes the SP's surface free energy.[8] Therefore, SPs made from nanorods appear as cylindrical disks. In contrast, when spherical nanoparticles are used as building blocks, the interparticle interactions are isotropic, and thus, the resulting SPs normally adopt a spherical shape.[4]

An interesting question is how the shape of the SPs changes with a further increase in their size (or volume). To answer this question, we managed to grow larger-sized SPs using a synthesis protocol similar to the one described above but with a more concentrated nanorod micelle solution (25 mg/mL, 1.0 mL). TEM measurements showed that these larger-sized SPs consist of stacked-disk arrays with very clear fine lines between nanorod layers (Figure S3 and Figure 1d).[6] Such a shape change should also be the consequence of a compromise between the anisotropic interparticle interactions and the repulsive solvophobic interactions, because stacked-disk arrays have a smaller surface area than single-layer disks at the same total volume. Although these larger-sized SPs had a broad size distribution ($\sigma \approx 31\%$; Figure S3),[6] we obtained a sample of bilayer-stacked SPs with a narrow size distribution ($\sigma \approx 9\%$) using careful size-selective separation via centrifugation (Figure 1d). These bilayer SPs had a diameter of 155 ± 13 nm and a length of 112 ± 8 nm, and nearly all of the SPs were laterally oriented on the substrate (Figure 1d,e). In addition, the SPs exhibited a typical wide-angle ED pattern, which can be indexed corresponding to the [2$\bar{1}\bar{1}$2] zone diffraction of wurtzite CdS (Figure 1f).[9] The single-crystal-like diffraction spots in the pattern indicate that the alignment of nanorod building blocks in an SP is ordered at the atomic level.

Moreover, these cylindrical SPs possess an anisotropic PL property. In a typical experiment, the PL from single-disk SPs did not have a significant linear polarization, but individual bilayer SPs exhibited much more strongly linearly polarized emissions (Figure 2). This result is consistent with the orientation and structure of the two types of SPs in the TEM observations (Figures 1 and 2), and the linearly polarized emissions of the SPs should originate from those of single CdSe/CdS nanorod building blocks.[5a,10] The result also corresponds with the fact that the total PL intensity of a typical bilayer SP is more than an order of magnitude larger than that of a typical single-disk SP, while their volume difference is only a factor of ~2 (Figures 1 and 2).[6]

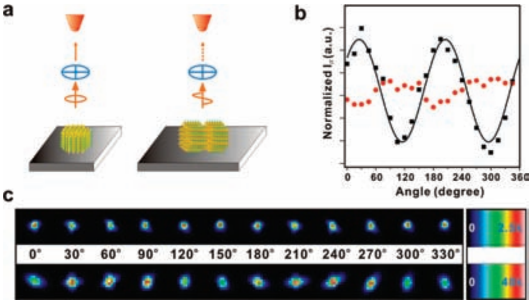

Figure 2. (a) Scheme for polarized PL measurements. (b) Normalized $I_{\|}$ as a function of polarizer angle for (red) a single disk and (black) a single stacked-disk array. $I_{\|}$ is the PL intensity measured in the direction parallel to the optical axis of the polarizer. The values of $I_{\|}$ are normalized with their mean, and solid line is a $\cos^2$ fit. (c) PL images of SPs as a function of polarizer angle for (top) a single disk and (bottom) a single stacked-disk array.

In conclusion, we have reported a synthesis of cylindrical supercystalline SPs from CdSe/CdS nanorods. We have demonstrated that anisotropic interparticle interactions between nanorods as well as solvophobic interactions between an SP and the surrounding solvent play the major roles in controlling the shape of the SPs. According to their sizes (or volumes), the SPs adopt either single- or multilayered structures. In addition, these SPs, which exhibit linearly polarized emissions, would be useful as functional components in devices such as polarized light-emitting diodes and electrooptical modulators.[5a,11]

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Supporting Information Available: Detailed synthetic procedures, additional TEM images, and complete ref 5a (as ref S1a). This material is available free of charge via the Internet at http://pubs.acs.org.

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