Nanostructures

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End-to-End Self-Assembly of Semiconductor Nanorods in Water by Using an Amphiphilic Surface Design

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Abstract: *One-dimensional (1D) self-assemblies of nanocrystals are of interest because of their vectorial and polymer-like dynamic properties. Herein, we report a simple method to prepare elongated assemblies of semiconductor nanorods (NRs) through end-to-end self-assembly. Short-chained water-soluble thiols were employed as surface ligands for CdSe NRs having a wurtzite crystal structure. The site-specific capping of NRs with these ligands rendered the surface of the NRs amphiphilic. The amphiphilic CdSe NRs self-assembled to form elongated wires by end-to-end attachment driven by the hydrophobic effect operating between uncapped NR ends. The end-to-end assembly technique was further applied to CdS NRs and CdSe tetrapods (TPs) with a wurtzite structure.*

The last decade has witnessed tremendous development in the controlled synthesis of semiconductor nanocrystals (NCs) with tailored shapes, compositions, and properties.[1,2] In combination with their robust nature and scalability, applications of NCs in diverse technologies have been intensively investigated.[3,4] In addition to such developments, interest in the self-assembly of NCs has been driven by the desire to mimic life systems, such as protein assemblies and their functions,[5,6] and the ability to build nanostructures with collective and enhanced properties.[3,6,7] Among various types of NC assemblies, 1D assemblies are of particular interest because of their vectorial properties, such as directional carrier transport and energy-transfer properties.

Unlike template-directed assembly which employs DNA and peptides as external templates,[8,9] self-directed assembly utilizes directional interparticle forces,[10] including electric or magnetic dipole interactions, to obtain 1D assemblies.[11,12] At the same time, amphiphilic modifications on the NC surface can be a versatile strategy to obtain anisotropic NC assemblies,[13,14] since the hydrophobic effect is ubiquitous and a guiding principle for the organization of biological molecules.[15] The reorganization of weakly binding ligand molecules induces the anisotropic distribution of ligands, or patchiness on the surface of NCs, leading to amphiphilic self-assemblies.[14] In this context, inorganic nanorods (NRs) have an anisotropy in terms of exposed facets, since the difference in the affinity of organic ligands to the specific crystallographic facets directs the anisotropic growth of NCs.[1,16] The selective binding of thiolated molecules to the (111) facet at both ends of Au NRs led to the development of various approaches for the end-to-end assembly of NRs through Au–thiol chemistry.[13,16,17] On the other hand, template-free self-directed end-to-end assemblies of semiconductor NRs are rather limited,[18,19] which could be as a result of strong van der Waals and dipole–dipole forces in a lateral direction preferentially leading to side-by-side assemblies.[20] The higher reactivity of the tips of wurtzite CdSe NRs afforded the selective deposition of gold nanoparticles on the ends of the NRs, bridging two or more NRs together through welding of the gold tips to give end-to-end assemblies.[18] Very recently, Kim, Lee, and co-workers obtained a two-dimensional end-to-end network of CdSe NRs at the air/toluene interface by means of tip-selective etching in toluene.[19] The etching changed the surface property of the ends and brought NRs to the air/toluene interface, at which the capillary attraction force between the NR ends led to the formation of end-to-end assemblies. Thus the facet-selective binding of ligands is a key feature in the introduction of anisotropy at the NR surface. However, the design of self-directed end-to-end self-assemblies in solution remains a challenge for semiconductor NRs.

In this study, we propose a simple method toward the 1D self-assembly of semiconductor wurtzite NRs through ligand exchange. CdSe NRs synthesized in a hot mixture of alkylphosphonic acids and trioctylphosphine oxide (TOPO) were subjected to ligand exchange with short-chained water-soluble thiols with an ionic head group. The weaker binding of ionic thiolate ligands to the end surface of NRs compared to the side face[21] causes the frequent desorption of ligands, leaving the ends uncapped and hydrophobic with high surface energy.[14] The amphiphilic NRs with the hydrophilic sides and hydrophobic ends self-assembled in an end-to-end manner as a result of the hydrophobic effect occurring between the ends of NRs.

Wurtzite CdSe NRs were synthesized using a well-established procedure using mixtures of alkylphosphonic acids and TOPO.[22] By varying the alkyl chain length of phosphonic acid, the length of NRs was controlled (see the Supporting Information, Figure S1). The NR surface ligands were exchanged by thiolate molecules having an ionic moiety such as 2-(dimethylamino)ethanethiol hydrochloride (DMAET) by a simultaneous phase-transfer method.[23] To carry out the ligand exchange, the purified CdSe NRs with alkylphosphonic acid ligands were dispersed in chloroform. To this mixture, an aqueous solution containing 0.5 M of thiolate was added and the solution was vigorously mixed for 1 h at 80 °C in the presence of a small amount of acetone. The

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NRs transferred into the aqueous phase were purified by repetitive dispersion–reprecipitation cycles using water and ethanol, respectively. The purification gave a clear aqueous dispersion of CdSe NRs, which was subjected to static aging at room temperature in the dark.

TEM measurements revealed that the lipophilic CdSe NRs with *n*-tetradecylphosphonic acid (TDPA) as the ligand prepared from a chloroform solution underwent dense packing in a side-by-side manner during solvent evaporation (Figure S1a). After the ligand exchange, the DMAET-capped CdSe NRs were stably dispersed in water without changing the aspect ratio. In contrast to the CdSe NRs before ligand exchange, the DMAET-capped NRs were uniformly spaced apart with a certain distance, suggesting electrostatic repulsion between the cationic NRs (Figure 1 a). The static aging of the aqueous solution for 4 days at room temperature gave a cotton-like precipitate. Just before the precipitate formation, the NRs formed dimers and trimers through end-to-end attachment (Figure 1 b). The precipitate was then examined by TEM and SEM, by which it was found to be composed of a network of end-to-end NR assemblies (Figure 1 c). The fibrous 1D assemblies further aggregated by strong interchain interactions, leading to the formation of 3D-network polymer-gel-like precipitates (Figure 1 d). The network contained branching points corresponding to the end-to-end linkages, while side-by-side packing along the 1D assemblies was suppressed. Closer examination of the cross points (by examination of expanded portions of these images) suggests that the ends of the NRs interact directly with each other without spacing (Figure S2). Further aging led to the fusion of the NRs at the ends to form nanowires.[11] A few of these fusion points possess a continuous crystal lattice, indicating that an oriented attachment mechanism[24] is partially involved. These results suggest that DMAET ligands desorb from the NR ends, giving uncapped inorganic surfaces during the self-assembly. It should be noted that the cryo-TEM measurement clearly demonstrated that the end-to-end self-assembly occurs in solution (Figure S3).

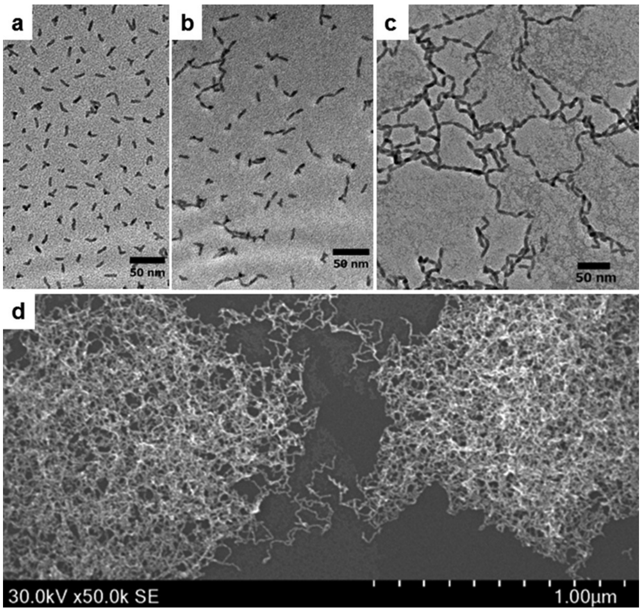

Figure 1. a–c) TEM and d) SEM images of DMAET-capped CdSe NRs: a) soon after the dispersion in water, b) after aging for 3 days, and c, d) after aging for 4 days at room temperature in water. Scale bars in (a–c) = 50 nm.

CdSe NRs with different aspect ratios prepared in the presence of *n*-decylphosphonic acid (DPA) or *n*-octadecylphosphonic acid (ODPA) were also subjected to the ligand exchange with DMAET. The DPA-capped CdSe NRs had an average length of 30 nm, while the ODPA-capped NRs had shorter lengths of 7.5 nm and 6.4 nm, depending on the ODPA/TOPO ratio (Figure S1). The end-to-end assemblies were also detected for these CdSe NRs regardless of the original alkylphosphonic acids used for the NR growth (Figure S4). The NRs with shorter lengths required a longer aging period for self-assembly, probably because of the smaller contribution of van der Waals and dipole–dipole forces to the stabilization of end-to-end assemblies.

In the UV/Vis absorption spectrum, the first exciton absorption band was detected at $\lambda = 600$ nm for DMAET-capped CdSe NRs just after dispersion in water (Figure 2). This absorption band was found to shift slightly to a shorter wavelength with aging (Figure 2). This blue shift suggests the slight etching of CdSe NRs. The presence of halogen ions such as Cl^- was reported to cause chemical etching selectively at NR tips.[19,25] It was difficult to detect electronic coupling[26] between NRs by UV/Vis absorption spectroscopy, although TEM measurements showed that the solution aged for 3 days contained oligomers such as dimer and trimers (Figure 1 b). Optical interaction such as energy transfer was difficult to detect because of the weak emission of NRs. Powder X-ray diffraction (XRD) measurements did not produce any noticeable difference between TDPA-capped CdSe NRs and the assemblies of DMAET-capped NRs (Figure S5). The wurtzite crystal structure was maintained through the ligand-exchange and self-assembly processes.

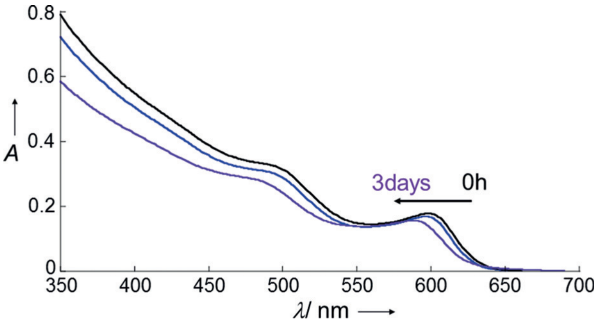

Figure 2. UV/Vis absorption spectra of DMAET-capped CdSe NRs in water showing spectral changes with aging of the NRs.

Considering the experimental results reported above, a mechanism for the 1D assembly of CdSe NRs is proposed in Figure 3. The long-alkyl-chained ligands were replaced with a thiolate molecule (DMAET) with a cationic group to provide water-soluble NRs. We propose that two major mechanistic factors drive the end-to-end assembly of NRs.

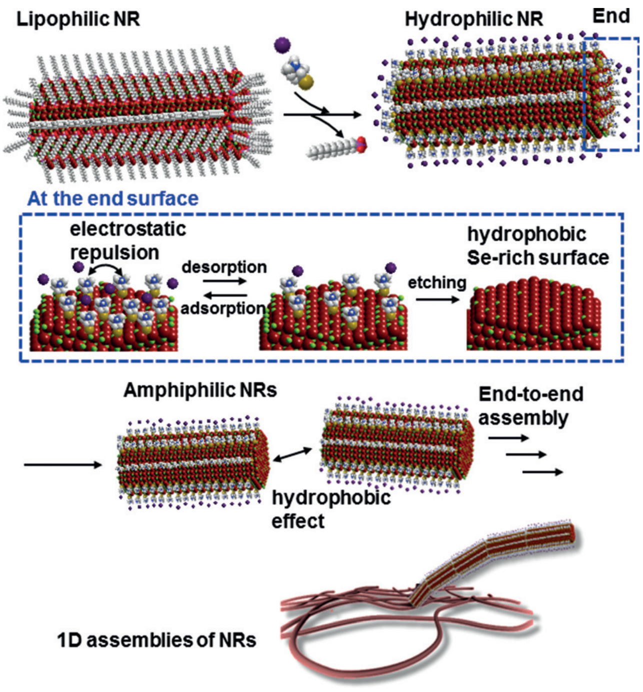

Figure 3. Schematic mechanism for the 1D assembly of CdSe NRs. The thiol end of the DMAET ligand is shown as a gold sphere, the amino fragment as a blue sphere, and the chloride counterion as a purple sphere.

First, a desorption/adsorption equilibrium for DMAET exists on the surface of the NRs, which should be facilitated by the electrostatic repulsion between neighboring ligands.[27] This equilibrium is considered to take place both on the side and end faces. However, we propose that the ligand desorption process dominates at the NR ends, which have a weaker binding affinity for thiolate ligands than the side face,[21] leading to the formation of uncapped hydrophobic inorganic ends.[14] Second, one of the ends is considered to have a Cd-rich face with a (001) facet, which is expected to have a higher binding affinity for thiolate ligands.[21] However, the end-selective etching[25] suggested by the UV/Vis absorption data could form a Se-rich surface even for the (001) face with the aid of ligand desorption. Thus, the desorption of ligands and etching of Cd atoms at the ends make both ends hydrophobic. Together with the hydrophilic side face with the stronger affinity for thiolate ligands,[21] the surfaces of the NRs are considered to be amphiphilic. The hydrophobic effect between the ends led to the end-to-end self-assembly of NRs. It should be also noted that the nondirectional hydrophobic effect sometimes leads to branching at the end-to-end attachment point, as demonstrated in Figure 1c. The end-to-end assemblies are most likely stabilized by additional forces such as van der Waals and electric dipole–dipole interactions. The absence of side-by-side assembly may rule out electric dipole coupling as a primary driving force for the end-to-end assembly.[28]

To elucidate the effect of the ligand desorption–adsorption equilibrium at the NR surface on the self-assembly, the purified DMAET-capped CdSe NRs were dispersed in an aqueous solution of 0.1 M DMAET. The aqueous dispersion of CdSe NRs in the presence of excess DMAET ligands showed a better dispersion stability even after aging for a week and no noticeable blue shift was detected in the UV/Vis absorption spectra (Figure S6). It was also found that 1D assemblies were obtained regardless of the nature of the polar group in the short-chained thiolate ligand molecules. An aqueous solution of CdSe NRs prepared through ligand exchange using thiocholine bromide (TCB) and thioglycolic acid (TGA) also afforded end-to-end assemblies of NRs (Figure S7). The use of a long-alkyl-chained ligand, which is expected to suppress the desorption of ligands as a result of stronger interligand interactions, meant that a longer aging period was required to complete the self-assembly (Figure S8). These findings further supported the above proposed mechanism in which the adsorption–desorption equilibrium plays an important role in the self-assembly.

The end-to-end self-assembly is expected to be applicable generally to other NRs with the same wurtzite crystal structure. The TDPA-capped CdS NRs (Figure S9) were subjected to ligand exchange with DMAET. After aging for 3 days in an aqueous solution, a cotton-like precipitate of CdS NRs formed in a similar manner to CdSe NRs. TEM images revealed that the CdS NRs, with a width of 2.8 nm and an average length of 20 nm, self-assembled in an end-to-end manner to form nanofibers (Figure 4a). We further extended this method to CdSe tetrapods (TPs) with wurtzite arms.[1] The surface ligand of CdSe TPs (Figure S10a)[29] was also replaced with DMAET, giving an aqueous dispersion of TPs without changing the shape and length of the arms (Figure S10b). The CdSe TPs showed less dispersion stability in water and aggregated to form an irregularly structured 3D network with high porosity (Figure 4b) after aging for only one night as a result of strong interparticle interactions. Careful examination of the less densely aggregated region in the network suggests that the interconnection of TPs was dominated by tip-to-tip attachment (Figure 4c). The coassembly of CdSe NRs and TPs was carried out as a preliminary experiment to introduce 3D branching points into end-to-end assemblies. The DMAET-capped CdSe TPs were mixed with the corresponding NRs in an approximate mole ratio of 1:4. The mixture also gave gel-like precipitates, which were deposited on a TEM grid or suspended in water and subsequently investigated by using cryo-TEM. The TEM image of the deposited aggregates showed the coassembly of CdSe NRs with TPs in a random manner (Figure 4d). The inset image in Figure 4d shows that multiple arms in TPs are attached to NRs or other TPs through tip-to-tip contacts, so that they serve as 3D branching points. The random coassembly of NRs and TPs was also detected by cryo-TEM measurement, which suggested that the tip-to-end or tip-to-tip attachments were not formed during drying but instead took place in aqueous solution (Figure S11).

In summary, we propose a simple route to the end-to-end self-assembly of semiconductor NRs through ligand exchange with a short-chained thiolate molecule. The heterogeneous nature of the surfaces of wurtzite NRs with a face-dependent affinity for thiolate ligands plays a crucial role in the amphiphilic surface design. Given that the present mechanism was demonstrated for anisotropic NCs with a wurtzite

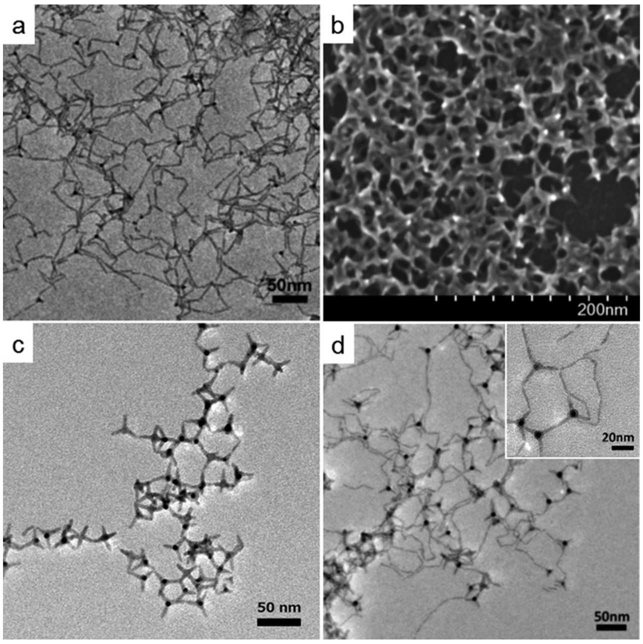

Figure 4. a) TEM image of the end-to-end assemblies of DMAET-capped CdS NRs, b) SEM image of porous 3D aggregates of CdSe TPs, c) TEM image of the tip-to-tip assembly of CdSe TPs, and d) TEM image of the coassembly of CdSe NRs and TPs. Inset in (d): enlarged portion of (d) showing the connection between TPs and NRs (scale bar = 20 nm). Scale bars in (a, c, d) = 50 nm.

structure and considering that the hydrophobic effect is universal, it should be possible to apply this technique to obtain a range of diverse coassembled NCs, similar to copolymerization.[13] Heterojunction NRs with an ABA-type triblock composition[30] or a core/shell structure could be a promising component to provide a nanowire formed through sequence-controlled NC assembly.

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