

Video Article

Facet-to-facet Linking of Shape-anisotropic Colloidal Cadmium Chalcogenide Nanostructures

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URL: <https://www.jove.com/video/56009>

DOI: [doi:10.3791/56009](https://doi.org/10.3791/56009)

Keywords: Chemistry, Issue 126, Directed assembly, synthesis, colloidal nanocrystals, semiconductor, cation exchange, facet to facet, oriented attachment

Date Published: 8/10/2017

Citation: Ong, X., Gupta, S., Wu, W.Y., Chakraborty, S., Chan, Y. Facet-to-facet Linking of Shape-anisotropic Colloidal Cadmium Chalcogenide Nanostructures. *J. Vis. Exp.* (126), e56009, doi:10.3791/56009 (2017).

Abstract

Here, we describe a protocol that allows for shape-anisotropic cadmium chalcogenide nanocrystals (NCs), such as nanorods (NRs) and tetrapods (TPs), to be covalently and site-specifically linked via their end facets, resulting in polymer-like linear or branched chains. The linking procedure begins with a cation-exchange process in which the end facets of the cadmium chalcogenide NCs are first converted to silver chalcogenide. This is followed by the selective removal of ligands at their surface. This results in cadmium chalcogenide NCs with highly reactive silver chalcogenide end facets that spontaneously fuse upon contact with each other, thereby establishing an interparticle facet-to-facet attachment. Through the judicious choice of precursor concentrations, an extensive network of linked NCs can be produced. Structural characterization of the linked NCs is carried out via low- and high-resolution transmission electron microscopy (TEM), as well as energy-dispersive X-ray spectroscopy, which confirm the presence of silver chalcogenide domains between chains of cadmium chalcogenide NCs.

Video Link

The video component of this article can be found at <https://www.jove.com/video/56009/>

Introduction

The directed assembly of colloidal semiconductor NCs offers a synthetic pathway to the fabrication of nanostructures whose physicochemical properties are either the collective sum of or radically different from their individual NC building blocks^{1,2,3,4}. Among the various approaches to nanoparticle assembly, the method of oriented attachment - in which NCs are essentially fused with each other - stands out as one that allows for interparticle electronic coupling. However, conventional oriented attachment typically requires the delicate balancing of particle dipole-, ligand- and solvent-based interactions that are generally difficult to execute and make applicable to different NC systems.

We have recently developed a wet-chemical method of covalently joining shape-anisotropic cadmium chalcogenide NCs by introducing a reactive inorganic intermediate through a site-selective nucleation process. The particles are subsequently linked by the spontaneous fusion of the reactive inorganic intermediate domains⁵. Although the technique is still based on an oriented attachment mechanism, there is much less need to consider weak interparticle interactions, thus allowing for more flexibility and control. The linking of shape-anisotropic cadmium chalcogenide NCs is carried out by first converting their tip facets to silver chalcogenide via a partial cation exchange process (in solution); this is followed by the selective removal of ligands passivating the surface. The NCs then come together via the fusion of the exposed silver chalcogenide facets, resulting in assemblies of cadmium chalcogenide NCs that are linked end-to-end.

In this protocol, we demonstrate that the linking technique can be applied to a variety of shape-anisotropic cadmium chalcogenide NCs (*i.e.*, CdSe-seeded CdS NRs and CdSe-seeded CdSe NRs or TPs), yielding long linear NR chains or highly branched TP networks. These results suggest that the technique can be extended to a wide variety of NC shapes and metal chalcogenides amenable to silver cation exchange.

Protocol

1. Preparation of Precursor Stock Solutions

1. TOP-Se stock solution.

1. In a nitrogen atmosphere glovebox, weigh out 11.84 g of selenium pellets into a 150-mL conical flask and place a magnetic stir bar in the flask.

2. Add 100 mL of tri-*n*-octylphosphine (TOP) to the conical flask and seal the flask with a rubber septum.
3. Stir the mixture overnight at 800 RPM.
NOTE: Once the selenium pellets have dissolved fully into the TOP, the TOP-Se stock solution (1.5 M) is ready to be used in further reactions.

2. TOP-S stock solution.

1. Weigh out 0.611 g of sulfur powder into a 20-mL single-necked round-bottom flask (RBF) and place a magnetic stir bar in the flask.
2. Add 10 mL of TOP to the sulfur powder and seal the RBF with a rubber septum. Place it under a nitrogen atmosphere and stir at 800 RPM.
3. Once the sulfur powder has dissolved and the solution is clear, use the TOP-S stock solution in further reactions.

2. Synthesis of CdSe Quantum Dot (QD) Stock Solution

1. Wurtzite CdSe QDs.

Note: See⁵.

1. Mix 9 g of tri-*n*-octylphosphine oxide (TOPO), 6 g of hexadecyl amine (HDA), and 0.25 mL of diisooctylphosphonic acid (DIPA) in a three-necked RBF. Add a magnetic stir bar to the mixture and insert a temperature probe into the RBF through a punctured rubber septum.
 1. Mount a reflux condenser over the RBF and connect it to a Schlenk line via an adapter. Apply high vacuum grease at all glass-to-glass joints.
2. Degas the solution at 100 °C for 2 h under constant stirring at 800 RPM.
3. Separately, mix 0.320 g of cadmium acetylacetonate ($\text{Cd}(\text{acac})_2$), 0.570 g of hexadecanediol (HDDO), and 6 mL of 1-octadecene (ODE) in a single-necked RBF. Add a magnetic stir bar and degas the mixture under constant stirring over an oil bath for 2 h at 120 °C and 800 RPM.
4. After degassing for 2 h, increase the temperature of the three-necked RBF to 345 °C. Concurrently, let the cadmium precursor mixture cool to room temperature and add 4 mL of TOP-Se stock solution to the single-necked RBF.
5. Swiftly inject the entire cadmium and selenium precursor solution into the three-necked RBF once its temperature reaches 345 °C. Remove the heating mantle immediately after injecting the precursor solution and allow the reaction mixture to cool to room temperature under ambient conditions.
6. Add 15 mL of toluene to the crude reaction mixture and process the synthesized QDs by centrifuging for 3 min at 2,240 x g. Discard the precipitate and add an excess of methanol to the recovered supernatant. Centrifuge the mixture at 2,325 x g for 8 min and discard the supernatant.
7. Add 5 mL of toluene to the precipitate to disperse the QDs. Carry out further processing cycles via the precipitation of the QDs using 30 mL of methanol, centrifuge the suspension at 2,240 x g for 3 min, discard the supernatant, and disperse the QDs in 5 mL of toluene.
 1. Following two cycles of processing, disperse the QDs in a minimal amount (~2-3 mL) of toluene (henceforth referred to as the QD stock solution) for further use.
8. Determine the concentration of QDs in solution by taking 20 μL of the stock solution and adding it to 3 mL of toluene. Measure the absorbance at 350 nm and calculate the concentration using the known molar absorptivity at 350 nm⁶. Scale the concentration accordingly to take into account the dilution of the stock solution.
NOTE: It is important to maintain vigorous stirring of the solution and to immediately remove the heating mantle after the swift injection of the precursor solution in step 2.1.5 to obtain highly size-monodisperse QDs.

2. Zinc-blende CdSe QDs.

Note: See⁷.

1. Mix 0.0384 g of cadmium oxide (CdO), 0.137 g of myristic acid (MA), and 5 mL of ODE in a three-necked RBF. Add a magnetic stir bar to the mixture and insert a temperature probe into the RBF through a punctured rubber septum. Mount a reflux condenser over the RBF and connect it to a Schlenk line via an adapter. Seal the remaining port with a rubber septum. Apply high vacuum grease at all glass-to-glass joints.
2. Degas the solution at 90 °C under constant stirring at 800 RPM.
3. Separately, degas a mixture of 0.05 mL of oleic acid (OA), 0.5 mL of oleylamine (OM), and 2 mL of ODE in a single-necked RBF under constant stirring at 75 °C and 800 RPM.
4. Increase the temperature of the cadmium precursor solution to 250 °C and maintain it for 15 min. Observe a color change in the solution, from dark brown to colorless, indicating the formation of cadmium myristate.
5. Cool the reaction mixture to 90 °C and add 12 mL of ODE. Degas the mixture again for 1 h.
6. Let the reaction mixture cool to room temperature. Add 0.012 g of selenium powder and degas the mixture for 20 min.
7. Increase the temperature of the reaction mixture to 240 °C under N_2 . Observe a color change, from colorless to yellow at 150 °C and then to orange-red upon reaching 240 °C, signifying the formation of zb-CdSe QDs.
8. Grow the QDs for 5 min at 240 °C and then cool the mixture to room temperature. Add the degassed mixture of OM, OA, and ODE dropwise to the reaction solution. Leave the solution to cool to room temperature under ambient conditions.
9. Process the synthesized QDs by adding acetone to the growth solution until the total volume is about 50 mL. Centrifuge the resulting suspension at 2,240 x g for 3 min. Subsequently, discard the supernatant.
10. Add 5 mL of toluene to the precipitate to disperse the QDs. Carry out further processing cycles: precipitate the QDs using 30 mL of methanol, centrifuge the suspension at 2,240 x g for 3 min, discard the supernatant, and disperse the QDs in 5 mL of toluene.
 1. Following two cycles of processing, disperse the QDs in a minimal amount (~2-3 mL) of toluene (henceforth referred to as the QD stock solution) for further use.

11. Determine the concentration of CdSe QDs in the stock solution by taking 20 μ L of the processed nanoparticles and adding it to 3 mL of toluene. Measure the absorbance at 350 nm and calculate the concentration using the known molar absorptivity at 350 nm⁶. Scale the concentration accordingly to take into account the dilution of the stock solution.

NOTE: For the successful synthesis of monodisperse QDs, it is critical to ensure that all the selenium powder is added to the reaction mixture and that none of it is left stuck to the neck and sidewalls of the RBF.

3. Synthesis of CdSe-seeded CdS NRs

Note: See⁸.

1. Mix 3 g of TOPO, 0.90 g of CdO, 0.80 g of hexylphosphonic acid (HPA), and 0.29 g of octadecylphosphonic acid (ODPA) in a 50-mL three-necked RBF. Add a magnetic stir bar to the mixture and insert a temperature probe through a punctured rubber septum.
2. Mount a reflux condenser over the RBF and connect it to a Schlenk line via an adapter. Seal the remaining port with a rubber septum. Apply high vacuum grease at all glass-to-glass joints. Heat the RBF to 150 °C and place it under a vacuum for 1.5 h to degas, with stirring at 800 RPM.
3. Place 1.8 mL of the TOP-S stock solution into a 10-mL single-necked RBF and seal it with a rubber septum. Add 80 nmol of wurtzite CdSe QDs in toluene to the TOP-S solution and subsequently remove the toluene under vacuum at 70 °C. Allow the solution to degas under stirring at 800 RPM for a further 30 min.
4. Place the RBF containing the Cd precursor under nitrogen and raise the temperature to 350 °C. At 320 °C, add 1.8 mL of TOP to the RBF through the rubber septum.
5. At 350 °C, draw the TOP-S solution containing the w-CdSe QDs into a syringe and rapidly inject it into the RBF containing the Cd precursor. Allow the solution to stir at 800 RPM for an additional 6 min to allow for the growth of the NRs. Subsequently, remove the heating mantle and cool the solution to room temperature under ambient conditions.
6. To process the solution of NRs, add 2 mL of toluene to the growth solution and place the entire mixture into a 50-mL centrifuge tube. Add 30 mL of methanol. Subsequently, centrifuge the resulting suspension at 2,240 x g for 3 min and then discard the supernatant.
7. Add 5 mL of toluene to the precipitate to disperse the NRs. Carry out further processing cycles: precipitate the NRs using 30 mL of methanol, centrifuge the suspension at 2,240 x g for 3 min, discard the supernatant, and disperse the NRs in 5 mL of toluene.
 1. Following 2-3 cycles of processing, disperse the NRs in 5 mL of toluene (henceforth referred to as the NR stock solution) for further use.
8. Prepare the sample for TEM analysis.⁵
 1. Place a drop of the NR solution onto a 300-mesh copper grid covered with a continuous carbon film for electron microscopy analysis.
 2. Remove the excess solution with an adsorbent paper and dry the sample at room temperature.
9. Perform TEM imaging (and analysis) to obtain the dimensions of the NR so that the average volume of the NR and the number of moles of CdS per NR can be determined.
 1. Determine the concentration of CdSe-seeded CdS NRs in the stock solution by taking 20 μ L of the processed NRs and adding it to 3 mL of toluene. Measure the absorbance at 350 nm and calculate the concentration of NRs using the known molar absorptivity at that wavelength (assumed to be dominated by CdS)⁹. Scale the concentration accordingly to account for the dilution of the stock solution.

NOTE: For a typical synthesis, the yield of NRs is nearly 100%, with very few byproducts such as branched structures.

4. Synthesis of CdSe-seeded CdSe NRs

Note: See⁸.

1. Mix 1.035 g of CdO, 0.1657 g of HPA, 0.1543 g of n-tetradecylphosphonic acid (TDPA), and 3 g of TOPO in a three-necked RBF. Add a magnetic stir bar to the mixture and insert a temperature probe into the RBF through a punctured rubber septum. Mount a reflux condenser over the RBF and connect it to a Schlenk line via an adapter. Seal the remaining port with a rubber septum. Apply high vacuum grease at all glass-to-glass joints.
2. Degas the solution at 150 °C for 1.5 h under constant stirring at 800 RPM.
3. Separately, mix 2 mL of the TOPSe stock solution and 10 nmol of w-CdSe QDs (dispersed in toluene) in a single-necked RBF and degas under constant stirring over an oil bath at 800 RPM and 90 °C until all the toluene is removed.
4. After degassing, increase the temperature of the cadmium precursor mixture to 340 °C. As the temperature increases, observe a color change in the solution, from dark brown to colorless, indicating the formation of the cadmium-alkyl phosphonic acid complex.
5. As the temperature of cadmium precursor reaches 340 °C, swiftly inject 1.8 mL of TOP into the mixture and allow the temperature to recover to 340 °C.
6. Upon reaching 340 °C, swiftly inject 1.8 mL of the TOP-Se/CdSe QD mixture into the three-necked RBF, whereupon the temperature will drop to 320 °C. Upon recovery to 340 °C, maintain the reaction solution at this temperature for ~3 min before removing the heating mantle and allowing the solution to cool to room temperature under ambient conditions.
7. After the reaction solution has cooled to room temperature, add 2 mL of toluene and transfer the entire solution to a 50-mL centrifuge tube. Top up the centrifuge tube with methanol (99%) to 50 mL and centrifuge the resulting suspension at 2,240 x g for 3 min. Subsequently, discard the supernatant.
8. Add 5 mL of toluene to the precipitate to disperse the NRs. Carry out further processing cycles: precipitate the NRs using 30 mL of methanol (99%), centrifuge the suspension at 2,240 x g for 3 min, discard the supernatant, and disperse the NRs in 5 mL of toluene.
 1. Following 2-3 cycles of processing, disperse the NRs in 5 mL of toluene (henceforth referred to as the NR stock solution) for further use.

9. Place a drop of NR solution onto a 300-mesh copper grid covered with a continuous carbon film for electron microscopy analysis. Remove the excess solution with an adsorbent paper and dry the sample at room temperature.
10. Perform TEM imaging and analysis to obtain the dimensions of the NRs so that the average volume of the NR and the number of moles of CdSe per NR can be determined.
 1. Determine the concentration of NRs in solution by taking 20 μL of the stock solution and adding it to 3 mL of toluene. Measure the absorbance at 350 nm and calculate the concentration using the known molar absorptivity at that wavelength⁶. Scale the concentration accordingly to take into account the dilution of the stock solution.

NOTE: For a typical synthesis, the yield of NRs is close to 100%, with very few byproducts such as branched structures.

5. Synthesis of CdSe-seeded CdSe TPs

Note: See¹⁰.

1. Mix 0.43 g of CdO, 3.8 mL of OA, 2.2 mL ODE, and 0.3 mL of TOP in a three-necked RBF. Add a magnetic stir bar to the mixture and insert a temperature probe into the RBF through a punctured rubber septum. Mount a reflux condenser over the RBF and connect it to a Schlenk line via an adapter. Seal the remaining port with a rubber septum. Apply high vacuum grease at all glass-to-glass joints.
2. Degas the solution at 90 °C for 1 h under constant stirring at 800 RPM and then increase the temperature to 265 °C. As the temperature reaches 265 °C, observe the color of the solution changing, from dark brown to colorless, indicating the formation of the cadmium oleate complex.
3. Reduce the temperature to 50 °C and add 1.7 mL of 2 M TOPSe (separately prepared by sonicating, at 37 kHz and 320 W, a mixture of 0.316 g of Se powder in 2 mL of TOP in an 8-mL glass vial) and 0.017 g of hexadecyltrimethylammonium bromide (CTAB).
4. Separately, mix 7 mL of ODE, 0.025 g of CTAB, 0.5 mL of TOP, 0.75 mL of OA, and 100 nmol of zinc-blende CdSe QDs (dispersed in toluene) in a three-necked RBF. Add a magnetic stir bar to the mixture and insert a temperature probe into the RBF through a punctured rubber septum.
 1. Mount a condenser over the RBF and connect it to the Schlenk line via an adapter. Seal the remaining port with a rubber septum. Apply high vacuum grease at all glass-to-glass joints.
5. Degas the mixture prepared in step 5.4 at 90 °C and 800 RPM under constant stirring for ~45 min until all the toluene is removed.
6. Increase the temperature of the reaction mixture containing the zinc-blende CdSe QDs to 260 °C. When the temperature reaches 260 °C, add 8 mL of the cadmium precursor solution to the mixture containing zinc-blende CdSe QDs at an injection rate of 0.25 mL/min using a syringe pump. After the addition is completed, allow the solution to cool to room temperature under ambient conditions.
7. After the solution has cooled to room temperature, transfer it to a 50-mL centrifuge tube. Add 40 mL of acetone (99%) to precipitate the TPs and centrifuge the suspension at 1,340 \times g for 10 min. Subsequently, discard the supernatant.
8. Add 5 mL of toluene to the precipitate of TPs to disperse them. Carry out further processing cycles: precipitate the TPs using 30 mL of methanol (99%), centrifuge the suspension at 2,240 \times g for 3 min, discard the supernatant, and disperse the TPs in 5 mL of toluene.
 1. Following 2-3 cycles of processing, disperse the TPs in 5 mL of toluene (henceforth referred to as the TP stock solution) for further use.
9. Place a drop of the TP solution onto a 300-mesh copper grid covered with a continuous carbon film for electron microscopy analysis. Remove the excess solution with adsorbent paper and dry the sample at room temperature.
10. Perform TEM imaging and analysis to obtain the dimensions of the TPs so that the average volume of the TP and the number of moles of CdSe per TP can be determined.
 1. Determine the concentration of QDs in solution by taking 20 μL of the stock solution and adding it to 3 mL of toluene.
 2. Measure the absorbance at 350 nm and calculate the concentration using the known molar absorptivity at that wavelength⁶. Scale the concentration accordingly to account for the dilution of the stock solution.

Note: For a typical synthesis, the yield for the TPs is ~80%, with ~20% being bipods and tripods.

6. Facet Activation and the Linking of Nanostructures

1. **Preparation of a dodecylamine (DDA) stock solution.**
 1. Prepare a DDA stock solution by adding 0.140 g of DDA to 5 mL of ethanol. Sonicate the solution at 37 kHz and 320 W for ~5 min to ensure that the DDA is fully dissolved.
2. **Cation exchange and linking.**
 1. Prepare a 1-mL solution of NC (NR or TP) at the appropriate concentration (see **Table 1**). Add 6 mg of ODPa to the 1 mL of NC solution and sonicate for 10 min at 37 kHz and 320 W.
 2. Separately, mix 1 mL of DDA stock solution and 1 mL of Ag^+ solution at the appropriate concentration (see **Table 1**) in a vial. Add a magnetic stir bar and stir the solution vigorously at 800 RPM.
 3. While stirring, add 1 mL of the NC solution to the vial and allow the reaction to proceed for the corresponding amount of time, as listed in **Table 1**.
 4. At the end of the reaction, stop the stirring and allow the solution to phase-separate. Extract and remove the bottom aqueous layer. Add 5 mL of methanol to the organic layer, to precipitate out the NCs. Centrifuge the vial for 3 min at 2,240 \times g.
 5. After centrifugation, discard the supernatant and add 1 mL of toluene to re-disperse the product for further characterization.

NOTE: The cation exchange reaction occurs at different rates for different materials. **Table 1** summarizes the set of conditions under which the synthesis of linked nanostructures of other materials and morphologies are synthesized. The volume of NC solution (1 mL), aqueous Ag^+ solution (1 mL), and ethanol-DDA solution (1 mL) and the amount of ODPa (6 mg) added are kept the same, as mentioned above, for each set of reactions.

Representative Results

Using CdSe-seeded CdS NRs as a model system, as illustrated in **Figure 1(a)**, we demonstrated that we can use a partial Ag^+ exchange process to specifically transform the facets at the NR tips to Ag_2S . The Ag_2S facets are capped by DDA, which reacts with ODPa via an acid-base reaction to form an insoluble salt⁵. This causes the DDA ligands to be removed from the Ag_2S facets, causing them to fuse with each other upon contact and to form linked NR chains, as shown in **Figure 1(b)**. To ascertain whether the individual NRs are fused within the chain or are simply held together by Van der Waals forces, HRTEM analysis on the joint regions was carried out. As illustrated in **Figure 1(c)**, there is a distinct domain in the epitaxial contact with two NRs. An FFT analysis of the HRTEM image (inset of **Figure 1(c)**) reveals the existence of two different lattice constants that can be ascribed to the (001) facets of Ag_2S and CdS. Additionally, point energy-dispersive X-ray spectroscopy (EDX) analysis on the linkage region prominently shows the presence of Ag and the absence of Cd (**Figure 1(d)**), which corroborates our notion of Ag_2S -tipped CdSe-seeded CdS NRs bridged via the fusion of the Ag_2S domains. The yield and statistical nature of the linking process can be visualized via a histogram (**Figure 1(e)**) that shows the number of rods linked within a NR chain.

The mechanism for linking was previously reported by Sabyasachi *et al.*⁵ and will not be described in detail in this work. It is observed that, without the addition of ODPa, no linking takes place as seen in **Figure 2(a)**, in accordance with the view that the addition of ODPa causes the native surface ligands of the Ag_2S tip to come off. This can clearly be seen in **Figure 2(c)**, as the histogram for the reaction shows a large proportion of single, unlinked NRs. The presence of dimers might be due to residual ODPa left over from the NR synthesis reaction, allowing a small amount of linking to occur. Aside from ODPa, the concentration of AgNO_3 was also found to be extremely important, as illustrated in **Figure 2(b)**, where only short chains were obtained under non-optimal concentrations of AgNO_3 . Where the Ag^+ concentration used was too low, the histogram shows that the distribution was heavily weighted towards shorter chain lengths. Indeed, the linking statistics for the chains shown in **Figure 2(b)** feature a substantial proportion of dimers, followed by monomers, as seen in **Figure 2(d)**.

In addition to CdSe-seeded CdS NRs, we show that the Ag^+ -mediated linking process can be extended to CdSe-seeded CdSe NRs and TPs, which are shown in **Figure 3(a)** and **(b)**, respectively. Under the reaction conditions summarized in **Table 1**, we show that we can achieve similar chained networks of CdSe-seeded CdSe NRs and TPs, as exemplified in **Figure 3(c)** and **(d)**. As in the case of Ag_2S -linked CdSe-seeded CdS NRs, the CdSe-seeded CdSe nanoparticles are linked via Ag_2S intermediates.

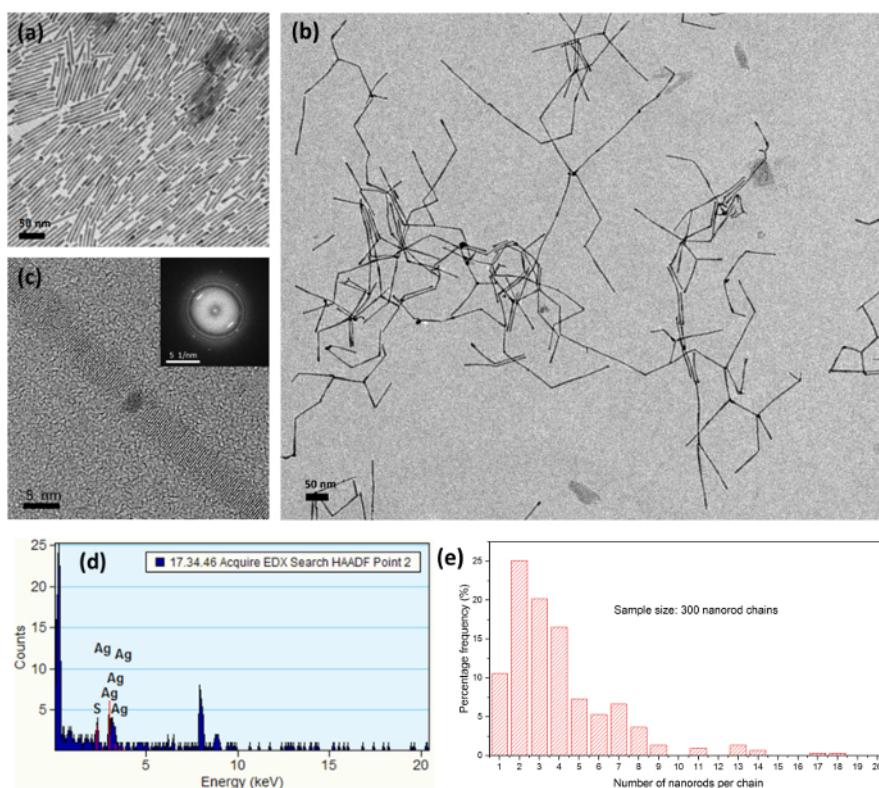


Figure 1. Characterization of linked CdSe-seeded CdS NRs. (a) Low-resolution TEM image showing as-synthesized CdSe-seeded CdS NR. (b) Low-resolution TEM image showing Ag_2S -linked CdSe-seeded CdS NRs. (c) High-resolution TEM (HRTEM) image of a single joint between two NRs. Inset is a Fast Fourier Transform (FFT) of the HRTEM image, showing two different lattice points that are attributed to CdS and Ag_2S . (d) Point EDX analysis on a single linkage point, confirming its composition as Ag_2S . (e) Histogram showing the distribution of the number of NRs per chain in a typical linked NR sample. [Please click here to view a larger version of this figure.](#)

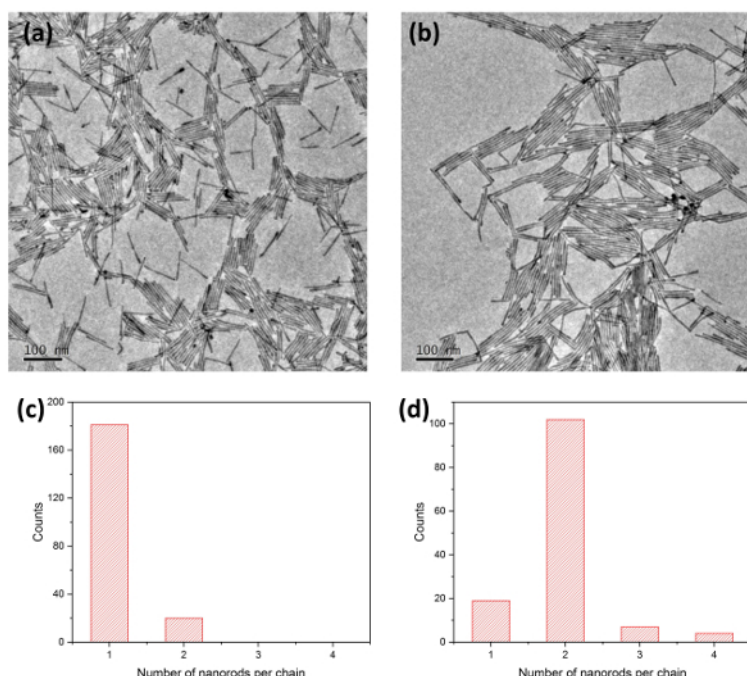


Figure 2. Results of non-optimal reaction conditions. (a) TEM image of CdSe-seeded CdS NRs with Ag_2S tips that underwent the linking procedure, with the exception that no ODPA was used. (b) TEM image showing short chains of Ag_2S -linked CdSe-seeded CdS NRs when the Ag^+ concentration was not optimized. (c) Histogram showing that most of the species present are single NRs when ODPA is absent. (d) Histogram showing that when the Ag^+ concentration is not optimized, only short chains are present. [Please click here to view a larger version of this figure.](#)

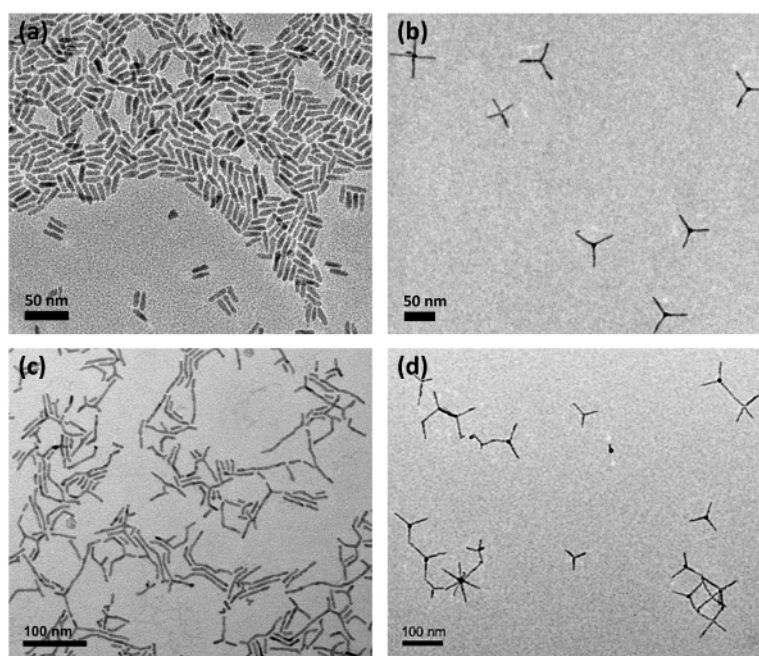


Figure 3. Extension of the linking process to CdSe-seeded CdSe nanostructures. (a) Low-resolution TEM image showing as-synthesized CdSe-seeded CdSe NRs. (b) Low-resolution TEM image showing as-synthesized CdSe-seeded CdSe TPs. (c) Low-resolution TEM image showing the CdSe-seeded CdSe NRs after linking. (d) Low-resolution TEM image showing the CdSe-seeded CdSe TPs after linking. [Please click here to view a larger version of this figure.](#)

Nanoparticle	Concentration of NC solution (mM)	Concentration of Ag ⁺ solution (mM)	Stirring time (hours)
CdSe seeded CdS NRs	3	1	1
CdSe seeded CdSe NRs	5	0.8	1
CdSe seeded CdSe TPs	5	0.6	0.5

Table 1. Summary of the approximate concentrations of the NC solution and the Ag⁺ solution and of the required stirring time.

Discussion

The linking technique described in this work allows for shape-anisotropic cadmium chalcogenide nanoparticles that can undergo cation exchange with Ag⁺ to be joined, facet-to-facet, into assemblies such as linear chains or branched networks. Failure to form well-dispersed, extensive assemblies of facet-to-facet linked nanoparticles is often because of two reasons: (i) the ODPa is not dispersed well in the NR-containing solution, which can be addressed by sonicating the mixture for the prescribed amount of time detailed in the protocol; or (ii) the concentration of Ag⁺ used is non-optimal. When the Ag⁺ concentration used is too low, most of the cadmium chalcogenide nanoparticles do not undergo cation exchange, resulting in little or no linking (as described in the **Representative Results**). When the Ag⁺ concentration used is too high, multiple domains of Ag₂S form on each particle, resulting in severe aggregation upon linking.

Our approach to the facet-to-facet linking of shape-anisotropic inorganic nanoparticles is currently limited to metal chalcogenide nanoparticles that can undergo cation-exchange with Ag⁺ or Cu⁺ (not shown in this work) under mild reaction conditions. Efforts are underway to expand the repertoire of inorganic materials that can be linked directly via our synthetic strategy. We previously demonstrated that the facet-to-facet linked nanoparticle assemblies can undergo further cation exchange processes and can be transformed into other semiconductor materials while retaining their linked architecture⁵. This modified linking procedure, although more tedious, can significantly widen the diversity of semiconductor nanomaterials that can be brought together into facet-linked assemblies.

Because the assemblies of linked semiconductor nanoparticles are joined facet-to-facet, they are electronically coupled to each other. This may be advantageous for applications such as solution-processed optoelectronics, where a major problem is the poor charge transport through insulating ligands surrounding the semiconductor nanoparticles. Further work will be needed to evaluate the efficacy of assemblies of linked semiconductor nanoparticles as the active material in optoelectronic devices.

Disclosures

We do not have anything to disclose.

Acknowledgements

This work was supported by JCO A*STAR Investigatorship grant (Project no. 1437C00135), A*STAR Science & Engineering Research Council Public Sector Funding (Project no. 1421200076), and a JSPS-NUS Joint Research Projects grant (WBS R143-000-611-133).

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