Colloidal Synthesis of Homogeneously Alloyed CdSe$_x$S$_{1-x}$ Nanorods with Compositionally Tunable Photoluminescence

Shalini Singh, Ajay Singh†, Kumaranand Palaniappan, Kevin M. Ryan†*

Materials and Surface Science Institute and Department of Chemical and Environmental Sciences, University of Limerick, Limerick, Ireland.

†SFI-Strategic Research Cluster in Solar Energy Research, University of Limerick, Limerick, Ireland.

* Corresponding authors. E-mail: kevin.m.ryan@ul.ie

Supporting Information

Section S1- Experimental Details-

Experimental Section

Materials

All reagents were used as received without any further purification. Cadmium oxide (>99%) was purchased from Sigma Aldrich, trioctylphosphine (TOP, 90%), trioctylphosphine oxide (TOPO, 99%), selenium (99.98%), sulphur (99%), tellurium (99.9%) were purchased from Aldrich, n-octadecylphosphonic acid (ODPA), tetradecylphosphonic acid (TDPA) and n-hexylphosphonic acid (HPA) was obtained from PolyCarbon Industries Inc (PCI). All solvents and Rhodamine-6G were purchased from Sigma Aldrich.

Synthesis of CdSe$_x$S$_{1-x}$ Nanorods

General synthesis procedure: CdO (0.12g, 1 mmol), TOPO (1.45 g, 3.87 mmol), HPA (concentration as given in Table S1) and ODPA (0.45 g, 1.35 mmol) were weighed into a three-neck round-bottom (RB) flask. The flask was fitted with a condenser, a stainless steel thermocouple and a magnetic stir bar. The apparatus was sealed and brought onto a Schlenk line. Using a heating mantle, the mixture was heated to 120 ºC, evacuated under vacuum for 30 min, refilled with argon, and heated to 300 ºC to form a completely colourless solution. When the temperature reached 300 ºC, TOP (0.84 g, 2.26 mmol) was injected into the flask. When the temperature reached 330 ºC, the Se-S stock solution prepared in 500 µl of TOP (the...
molar amount of Se/S is given in Table S1) was rapidly injected, causing a gradual colour change. After injection, the growth was allowed to continue for 15 min with continuous stirring. Subsequently, the heating mantle was removed and the reaction vessel was allowed to cool to 80 °C. A 2-3 mL portion of anhydrous toluene was added initially to quench the reaction. The nanorods were then washed in a 2:1 ratio of toluene to 2-Propanol and centrifuged at 3000 rpm for 10 min. The washing was repeated three times and the nanorods were stored in toluene for further characterizations.

**Synthesis of Cadmium Sulphide (CdS) Nanorods.** Cadmium Oxide (0.21g), trioctylphosphine oxide (2.73g) and octyldecylphosphonic acid (1.07g) were weighed out in a 25ml 3-neck flask and heated to 120ºC under a flow of argon. The system was degassed for one hour to remove any moisture. It was then heated up to 300ºC and the growth monomer TOP + S were injected in. Growth was continued for 30 minutes before removal of the heating mantel. When the temperature reached 70ºC 3ml of anhydrous toluene was injected in. The nanorods were washed three times in a 1:1 toluene:acetone mix to remove any excess surfactants followed by centrifuging to drop the nanorods out of solution. The nanorods were stored in toluene.

**Synthesis of Cadmium Selenide (CdSe) Nanorods.** CdSe nanorods were synthesized according to previous methods where 710mg TDPA, 160mg HPA, 3g TOPO and 200mg CdO were degassed for 60 minutes at 120°C in a 25ml 3 neck flask. The temperature was raised under a flow of argon until the solution turned colourless when 1.5g of TOP was injected in. The temperature was raised to 300°C and 73mg of selenium in 416mg of TOP was injected in and growth was allowed to continue for 5 minutes until removal of the heating-mantle.

**Quantum Yield of CdSe_xS_1-x nanorods** - The quantum yield (Q.Y.) for all the samples were measured using Rhodamine-B (Q.Y.~ 95%) as the standard dye. Rhodamine-6G was
dissolved in ethanol and all the samples were dissolved in toluene. For all the samples, the optical density (O.D.) at the excitation wavelength was kept below 0.1 to avoid reabsorption. The optical density of the dye was matched with that of the samples and P.L. was measured. Q.Y. was calculated by using the formula mentioned below where R represents reference dye.

\[ Q = Q_R \left( \frac{I}{I_R} \right) \left( \frac{OD_R}{OD} \right) \left( \frac{n}{n_R} \right)^2 \]

The quantum yield study showed that the CdSe\textsubscript{x}S\textsubscript{1-x} nanorods were weakly luminescent (0.2-0.6%) consistent with that reported for homogenous nanorods. As we increase the Se content, the quantum yield increases up to 0.6% for the highest Se rich nanorods. In rods, the surface-to-volume ratio is higher than nanodots, which increases the occurrence of surface trap-states and hence leading to increased delocalization of carriers and reducing the luminescence.\textsuperscript{1} The quantum yield was increased dramatically to 5-6% when the CdSe\textsubscript{x}S\textsubscript{1-x} nanorods were capped by a thin layer of higher band-gap material (CdS). The surface capping of the alloyed nanorods lead to the effective removal of surface trap sites and hence, enhancement in the quantum yield.

**Characterization**

The CdSe\textsubscript{x}S\textsubscript{1-x} nanorods and their assemblies were characterized by transmission electron microscopy (TEM), angular dark-field scanning transmission electron microscopy (DF-STEM) by using a JEOL JEM-2011F operating at an accelerating voltage of 200 kV. Nanocrystals were precipitated from the reaction mixture and dissolved in toluene. TEM samples were prepared on 200 mesh carbon-coated copper grids (Ted Pella Inc.). The sample for X-ray diffractograms analysis was prepared by drop-casting the nanorod solution on a glass substrate. The analysis was carried out on a PANalytical X0Pert MPD Pro using Cu K\textalpha radiation source (\( \lambda = 1.5418 \) Å) and a 1-D X’celerator strip detector with a 1-D X0Celerator strip detector. UV-vis spectroscopy of the nanorod solutions was performed on Cary 5000
UV-Vis-NIR spectrophotometer operated at a resolution of 1 nm. Photoluminescence (PL) spectra were measured with a Cary Eclipse Fluorescence Spectrophotometer equipped with a photomultiplier detector. PL spectra of the samples (dispersed in toluene) were measured at room temperature excited at a wavelength of 360 nm.

**Table S1.** Composition and Dimensions of CdSe$_x$S$_{1-x}$ Alloyed Nanorods

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Se/S (mmol) Injected</th>
<th>HPA (mmol)</th>
<th>Length (nm) ±2</th>
<th>Diameter (nm) ±0.5</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.14</td>
<td>0.09</td>
<td>40</td>
<td>7.0</td>
<td>2.03</td>
</tr>
<tr>
<td>2</td>
<td>0.33</td>
<td>0.18</td>
<td>37</td>
<td>7.0</td>
<td>1.97</td>
</tr>
<tr>
<td>3</td>
<td>0.45</td>
<td>0.24</td>
<td>36</td>
<td>7.5</td>
<td>1.95</td>
</tr>
<tr>
<td>4</td>
<td>0.77</td>
<td>0.48</td>
<td>37</td>
<td>8.0</td>
<td>1.9</td>
</tr>
<tr>
<td>5</td>
<td>1.28</td>
<td>0.72</td>
<td>43</td>
<td>8.0</td>
<td>1.87</td>
</tr>
<tr>
<td>6</td>
<td>2.2</td>
<td>0.78</td>
<td>37</td>
<td>8.0</td>
<td>1.825</td>
</tr>
</tbody>
</table>
Figure S1. CdSe$_x$S$_{1-x}$ nanorods composition obtained experimentally from elemental analysis and X-ray diffraction plotted against molar concentration of Se in the stock solution.
Figure S2. (a) DF-STEM image of the Cd(SeₓS₁₋ₓ) nanorods with Se/S ratio of 1.28, (b) HRTEM image showing the wurtzite Cd(SeₓS₁₋ₓ) nanorods with Se/S ratio of 0.45 showing interplanar (002) d-spacings (perpendicular to c axis) is constant throughout the length of the nanorod. (c) STEM image of the Cd(SeₓS₁₋ₓ) nanorods with Se/S ratio of 0.45 showing the area where EDS line scan was preformed (d) EDS line scan graph.
Section S2- Selection of Ligands for CdSe$_{x}$S$_{1-x}$ Nanorods Synthesis and Comparison of Different Ligand Systems for CdSe and CdS Nanorods Formation

CdSe$_{x}$S$_{1-x}$ nanorods were prepared using different ligand systems in order to choose the ligand system which works well for alloy formation and aspect ratio control. It was found that mixture of a short chain phosphonic acid and a long chain phosphonic acid works better in formation of 1-D nanorods in comparison to individual phosphonic acids. The morphology of CdSe$_{x}$S$_{1-x}$ nanorods obtained by using different ligand systems are shown in Fig. S3. The formation of gradient alloys (having different Se and S rich zones in individual nanorod) occurred when ODPA+OPA and HDPA+HPA ligands systems were used (Fig. S3(b) and
(e)). Flower shaped branched structures were obtained with ODPA+ DPA ligands (Fig. S3(c)). Mixture of short length nanorods and nanoparticles were obtained when DDPA+ HPA system was used as shown in Fig. S3(d). Formation of homogeneous alloyed nanorods was obtained only when ODPA and HPA were used as ligands. ODPA is used in the formation of conventional CdS nanorods, whereas ODPA and HPA are used together in the formation of CdSe nanorods. This fact supported the formation of CdSe$_{x}$S$_{1-x}$ nanorods when ODPA and HPA were used together in optimized concentrations.

During the synthesis of nanocrystals, the cadmium-ligand complex is known to play a crucial role in deciding the growth direction of the nanocrystals. The complexes with longer chain ligands are more stable, and lead to relatively slow active species. On the other hand, shorter chain ligand complexes react faster and generate higher concentration of nuclei upon reaction with the anionic precursor. According to the diffusion model, higher monomer concentration (generated by shorter chain ligand) favours anisotropic growth of the nanocrystals. Since, Se is bigger and heavier atom in comparison to S; as we replace S with Se in the stock solution, higher diffusion speed would be expected to allow for proper growth of nanorods. To maintain diffusion speed and high reactivity of monomers, the increase of the ratio of short chain ligand facilitates anisotropic growth of the nanorods as the concentration of Se increases.
**Figure S4.** TEM images of CdSe$_{x}$S$_{1-x}$ nanorods synthesized with different Se/S compositions as given in Table 1.
Section S3- ODPA Concentration Effect on Nanorods Shape Evolution

The effect of concentration of ODPA was studied via the synthesis of CdSe$_{x}$S$_{1-x}$ nanorods with varied molar concentration of ODPA (keeping the total ligand concentration constant). It was observed that ODPA has control on the overall morphology of the nanocrystals. When the nanocrystals were synthesized in the absence of ODPA, the crystals were small psedo-spherical crystals without any defined c-axis of growth. When low concentration of ODPA (0.1-0.25 mmol) was introduced in the reaction flask as surfactant, the overall growth rate was slow which lead to the formation of irregularly-spherical, multi-faceted shaped nanocrystals. These nanocrystals were 10-11 nm tri-/tetrapods with short arms. The occurrence of tri-/tetrapods in the flask was observed until there was enough ODPA in the reaction flask to control the growth of the nanocrystals in one particular direction i.e., the c-
axis. The formation of nanorods started when the concentration of ODPA was 0.3 mmol. Increasing the concentration of ODPA gradually resulted into much longer nanorods with reduced diameters. This observation strongly suggested the role of ODPA in the overall shape evolution of the nanocrystals as 1-D nanorods.

References-