A Versatile Bottom-up Assembly Approach to Colloidal Spheres from Nanocrystals

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S. Figure 1 Representative images of the experimental assembly process.

Emulsification process by ultrasonic a) Mixture of oil phase and water phase: 1ml Ag₂Se NCs cyclohexane solution (10 mg/ml) was added to 10 ml water containing 35 mg CTAB, b) The formation of microemulsion system: emulsion obtained by ultrasonic treatment, c) Evaporation of the low boiling-point solvent in oil microemulsion droplets at a designed rational temperature, the resulted 3-D colloidal spheres dispersed in water.
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S. Figure 2 a) TEM BaCrO$_4$ nanocrystals; b) Size distribution of BaCrO$_4$ (6.9 ± 0.3 nm; sd = 4.3%) c) TEM image of 3-D colloidal spheres assembled from BaCrO$_4$ nanocrystals, the area in white window is same with Figure 2a; d) HRTEM of 3-D colloidal spheres; e) Zeta potential of BaCrO$_4$ colloidal spheres
S. Figure 3  a) TEM Ag\(_2\)Se nanocrystals; b) Size distribution of Ag\(_2\)Se (9.8 ± 0.5 nm; sd = 4.8%); c) TEM image of 3-D colloidal spheres assembled from Ag\(_2\)Se nanocrystals, the area in white window is same with Figure 3d; d) HRTEM of 3-D colloidal spheres; e) Zeta potential of Ag\(_2\)Se colloidal spheres
S. Figure 4 a) TEM PbS nanocrystals; b) Size distribution of PbS (10.3 ± 1 nm; sd = 9.7%); c) TEM image of 3-D colloidal spheres assembled from PbS nanocrystals, the area in white window is same with Figure 4c; d) high resolution images of the selected area from corresponding TEM images
S. Figure 5 a) TEM NaYF₄ nanocrystals; b) Size distribution of NaYF₄ (14.6 ± 1.4 nm; sd = 9.6%); c) TEM image of 3-D colloidal spheres assembled from NaYF₄ nanocrystals, the area in white window is same with Figure 3e; d) high resolution images of the selected area from corresponding TEM images
S. Figure 6 a) TEM Bi$_2$S$_3$ nanocrystals; b) Size distribution of Bi$_2$S$_3$ (12.7 ± 1.1 nm; sd=8.7%); c) TEM image of 3-D colloidal spheres assembled from Bi$_2$S$_3$ nanocrystals, the area in white window is same with Figure 3f; d) high resolution images of the selected area from corresponding TEM images
S. Figure 7 a) TEM PbSeO$_3$-rod nanocrystals; b) TEM image of 3-D colloidal spheres assembled from PbSeO$_3$-rod nanocrystals, the area in white window is same with Figure 3g; c) high resolution images of the selected area from corresponding TEM images
S. Figure 8 LaF$_3$-nanoplate assembly, LaF$_3$ NCs was same with the result reported in reference [1], TEM of LaF$_3$-nanoplate is Fig 1D in reference [1]

a) TEM image of 3-D colloidal spheres assembled from LaF$_3$-nanoplate nanocrystals, the area in white window is same with Figure 3h; b) high resolution images of the selected area from corresponding TEM images
In order to get colloidal spheres with different size, we used systematic variation of the experiment parameters. The diameter of the assemblies mainly depended on emulsification process, NCs concentration, surfactant concentration and oil to water ratio. In general, CdS assemblies with diameter larger than 500 nm (S Figure 17a) were obtained by the mechanical stirring, and spheres with diameter smaller than 300 nm were obtained by sonication emulsification. We tuned the NCs concentrations between 2.5-10 mg/ml, surfactant (SDS) concentration between 2.8-11.2 mg/ml, and oil to ratio between 1:5-1:20. And the CdS assembly diameter increased with increasing NCs concentration in oil, decreasing surfactant concentration in water, or increasing oil to water ratio (S. Table 1, S Figure 17b-f).

S Table 1 The diameter of CdS 3-D colloidal spheres and the experiment parameters

<table>
<thead>
<tr>
<th>Emulsification process</th>
<th>NCs in oil phase (mg/ml)</th>
<th>Surfactant concentration (mg/ml)</th>
<th>Oil to water ratio (vol:vol)</th>
<th>Diameter of assemblies (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a mechanical stirring</td>
<td>2.5</td>
<td>2.8</td>
<td>1:10</td>
<td>200-1000 nm</td>
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<tr>
<td>b ultrasonic</td>
<td>2.5</td>
<td>2.8</td>
<td>1:10</td>
<td>40-80</td>
</tr>
<tr>
<td>c ultrasonic</td>
<td>5</td>
<td>2.8</td>
<td>1:10</td>
<td>~120</td>
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<tr>
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<td>10</td>
<td>2.8</td>
<td>1:10</td>
<td>150-250</td>
</tr>
<tr>
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<td>5</td>
<td>5.6</td>
<td>1:10</td>
<td>60-110</td>
</tr>
<tr>
<td>f ultrasonic</td>
<td>5</td>
<td>2.8</td>
<td>1:5</td>
<td>100-250</td>
</tr>
</tbody>
</table>
S Figure 9 TEM of 3-D colloidal spheres assembled from CdS NCs at different experiment conditions

Reference: