Electronic Supplementary Material (ESI) for Soft Matter.

Controlling the assembly of CdS nanorods via solvent and acidity

L. Jan Anton Koster, Saghar Khodabakhsh, and Neil C. Greenham*

Experimental Details

Materials

Cadmium oxide (99.99+%), trioctylphosphine oxide (TOPO) (99%), elemental sulfur (99.98%), benzenethiol (BT, ≥98%), 4-aminothiophenol (ATP, 97%), 4-mercaptobenzoic acid (MBA, 90%), and *p*-benzenediamine (BDA ≥97%), and buffer tablets (pH 4.0 and pH 9.2) were purchased from Sigma-Aldrich. Tetradecylphosphonic acid (TDPA, 98%) and *p*-benzenedithiol (BT, 97%) were purchased from Alfa-Aesar. Trioctylphosphine (TOP, 97%) was obtained from Strem Chemicals. All chemicals were used as received.

Synthesis of CdS nanorods

CdS nanorods were synthesized by decomposing 115 mg CdO in the presence of a mixture of 3.50 g TOPO and 0.62 g TDPA at 320 °C under an argon atmosphere. The resulting solution was kept at 300 °C. Separately, a solution of 90 mg elemental sulphur in 8 ml TOP was prepared. This solution was injected drop-wise over a time span of 80 minutes into the decomposed CdO mixture with a syringe pump. When the injection was finished, the reaction mixture was cooled to room temperature and toluene was added to avoid solidification of the reaction mixture. The nanorods were washed by repeated precipitation with methanol, followed by centrifugation, decanting the solution and redispering the nanorods in toluene.

To exchange the TDPA ligands for other ligands, approximately 5 mg of CdS nanorods were washed three times and redispersed in 7 ml ethanol containing 100 mg of the ligand in question. The resulting reaction mixture was refluxed under an inert atmosphere for 4 hours at 78 °C.

Calculation of the van der Waals and electrostatic interactions

For nanorods of length L and radius R, the van der Waals coupling terms are calculated from[1]

$$V_{RS} = -\frac{AL\sqrt{R}}{24d^{3/2}}, \tag{S1}$$

where d = 1 nm is the nanorod spacing and A is the CdS/solvent/CdS Hamaker constant. For CdS interacting with CdS across water the Hamaker constant is 0.224 eV.[2] For toluene we calculate this value by using the combination formula for media 1 and 2 interacting across medium 3[3]

$$A_{132} \approx \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)\left(\sqrt{A_{22}} - \sqrt{A_{33}}\right) \tag{S2}$$

where $A_{11} = A_{33}$ = 0.686 eV is the CdS Hamaker constant.[4] The toluene Hamaker constant A_{22} is estimated to be 0.37 eV from[3]

$$\gamma = \frac{A_{22}}{24\pi d_0^2}, \tag{S3}$$

where d_0 = 0.165 nm[3] and the surface tension γ = 28.5 mN/m.[5]

The face-to-face interactions are given by[1]

$$V_{RF} = -\frac{AR^2}{12}\left(\frac{1}{d} - \frac{1}{(d+L)^2} - \frac{2}{(d+2L)^2}\right). \tag{S4}$$

The coupling to the substrate is given by[1]

$$V_{SS} = -\frac{A_S LR^2}{6(d_S(2R+d_S))^{3/2}} \tag{S5}$$

and[1]

$$V_{SF} = -\frac{A_S R^2}{12}\left(\frac{1}{d_S^2} - \frac{1}{(d_S+L)^2}\right), \tag{S6}$$

where A_S is the Hamaker constant for the coupling to the carbon substrate and d_S = 1 nm is the distance between the nanorod and the substrate. A_S is calculated from Eq. (S2) and the Hamaker

constant of the carbon substrate (1.36 eV),[6] the Hamaker constant of toluene and that of water (0.23 eV).[7] The hexagonal cross section of CdS nanorods increases the van der Waals coupling energy by 40% for R = 3 nm.[1] We have modified Eqs (S1) and (S5) accordingly.

Calculation of the dipole-dipole interactions

To estimate the dipole-dipole interactions between neighboring nanorods, they were treated as cylinders each containing permanent dipoles. By integrating the dipole contributions over both cylinders the total interaction can be obtained:

$$V_{DD} = \iint_{V1,V2} \frac{-3(\vec{\mu}_1 \cdot \hat{r})(\vec{\mu}_2 \cdot \hat{r}) + \vec{\mu}_1 \cdot \vec{\mu}_2}{4\pi\varepsilon_r\varepsilon_0 r^3} \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2, \qquad \text{(S9)}$$

where ρ_d is the dipolar density, $\mu_{1,2}$ are the dipole vectors in cylinders 1 and 2, and $r_{1,2}$ is the position of the local dipoles within these cylinders. The dipolar density of CdS is approximately twice[8] that of CdSe nanorods[9] and is approximately 1.1 D/nm^3. The relative dielectric constant ε_r poses a problem as its values for the inside of the rods (CdS), and the various solvents (toluene, ethanol and water) are vastly different, making the application of Eq. (S9) less than exact. Nevertheless, the calculated dipole interactions amount to $0.2/\varepsilon_r$ eV for face-to-face orientations and $0.13/\varepsilon_r$ eV for side-to-side orientation (without offset along the rods). For the relative dielectric constant considered here, these interactions are significantly less than the van der Waals and electrostatic interactions.

References

1 A. V. Titov and P. Král, *Nano Lett.,* 2008, **8**, 3605.

2 J. M. Fernández-Varea and R. Garcia-Molinay, *J. Coll. Interface Sci*., 2000, **231**, 394.

3 J. N. Israelachvili, *Intermolecular & Surface Forces*, Academic Press, San Diego, CA, 1991.

4 L. Bergstrom, *Adv. Coll. Interface Sci*. 1997, **70**, 125.

5 D. R. Lide Ed., *CRC Handbook of Chemistry and Physics 72nd Edition*, CRC Press, Inc., Boca Raton, FL, 1991.

6 J. Visser, *Adv. Coll. Interface Sci.,* 1972, **3**, 331.

7 J. Ren, S. Song, A. Lopez-Valdivieso, J. Shen and S. Lu, *J. Coll. Interface Sci.,* 2001, **238**, 279.

8 T. S. Jurgen, *Chem. Phys. Lett.,* 2003, **384**, 150.

9 L.-S. Li and A. P. Alivisatos, *Phys. Rev. Lett.,* 2003, **90**, 097402.