Supplementary Material (ESI) for Chemical Communications

Directing semiconductor nanorod assembly into 1D or 2D supercrystals by altering the surface charge

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Electronic Supporting Information (ES1)

Synthesis of semiconductor nanomaterials:

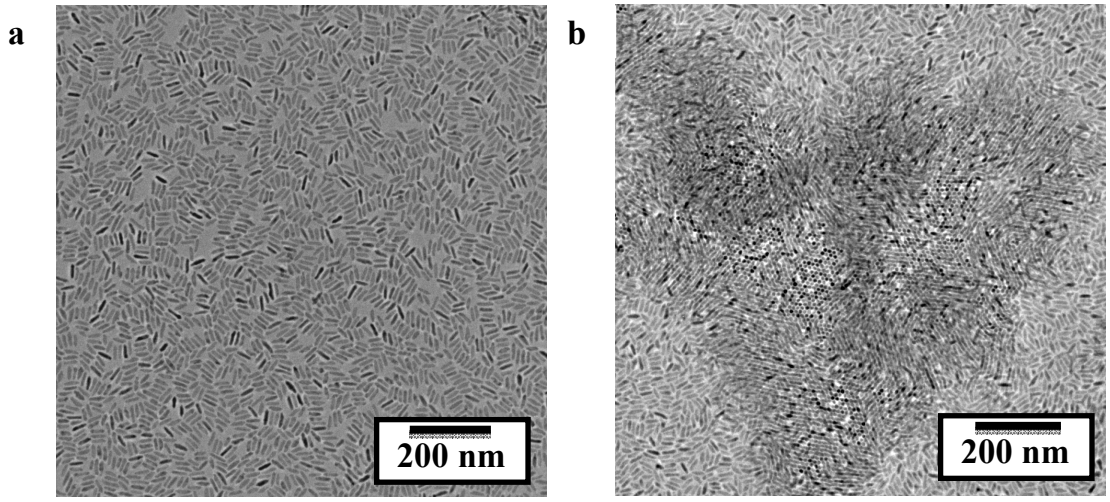
Materials: Cadmium oxide (>99%) was purchased from Fluka, Trioctylphosphine (TOP, 90%), trioctylphosphine oxide (TOPO, 99%), selenium (99.98%) were purchased from Aldrich, n-tetradecylphosphonic acid (TDPA) and *n*-hexylphosphonic acid (HPA) was obtained from PolyCarbon Industries Inc (PCI).

Synthesis of CdSe nanorods: CdSe nanorods were synthesised according to known procedure in an inert atmosphere using standard air free techniques.[1] Briefly, Cadmium oxide (CdO, 0.2g), n-tetradecylphosphonicacid (TDPA, 0.71g), n-Hexylphosphonic acid (HPA, 0.16g) and tri-n-octylphosphine oxide (TOPO, 3.00g) was loaded in 25 ml three-neck flask equipped with a condenser, septum and a thermocouple adapter. The mixture is heated to 120º C in an atmosphere of Ar/N_2 and then evacuates for 1 hour (pressure range between 100 – 300 mTorr) and followed by heating at 300ºC under Ar/N_2 atmosphere, during which the CdO decomposed and the colour of solution change from brown to optical clear. At this point 1.5 g of Trioctylphosphine (TOP) was injected to the mixture, and the temperature was further raised to 310ºC. Next inject rapidly the pre dissolved Selenium in TOP solution (0.073g Se + 0.416 g TOP) in the flask and the resulting nanocrystal were further allowed to grow for 5-10 min at 310ºC and then it was cooled to room temperature under Ar/N_2 flow. The nanorods were purified by dispersion in anhydrous toluene and precipitation from anhydrous isopropanol. They were cleaned thrice with toluene and isopropanol mixture and redispersed in toluene for further measurements.

Ligand exchange CdSe nanorods with pyridine:

To prepare pyridine covered CdSe nanorods, 1 ml of as synthesised phosphonates/TOPO covered CdSe nanorods (0.0082g/ml) were dissolved in anhydrous pyridine (5 mL) followed by vortex for 5-10 min and then sonicated for 30 min. The solution was then centrifuged at 13000 rpm for 10 min following which the filtrate was discarded and the resulting residue was redispersed in toluene

Concentration Effect on Nanorod Alignment



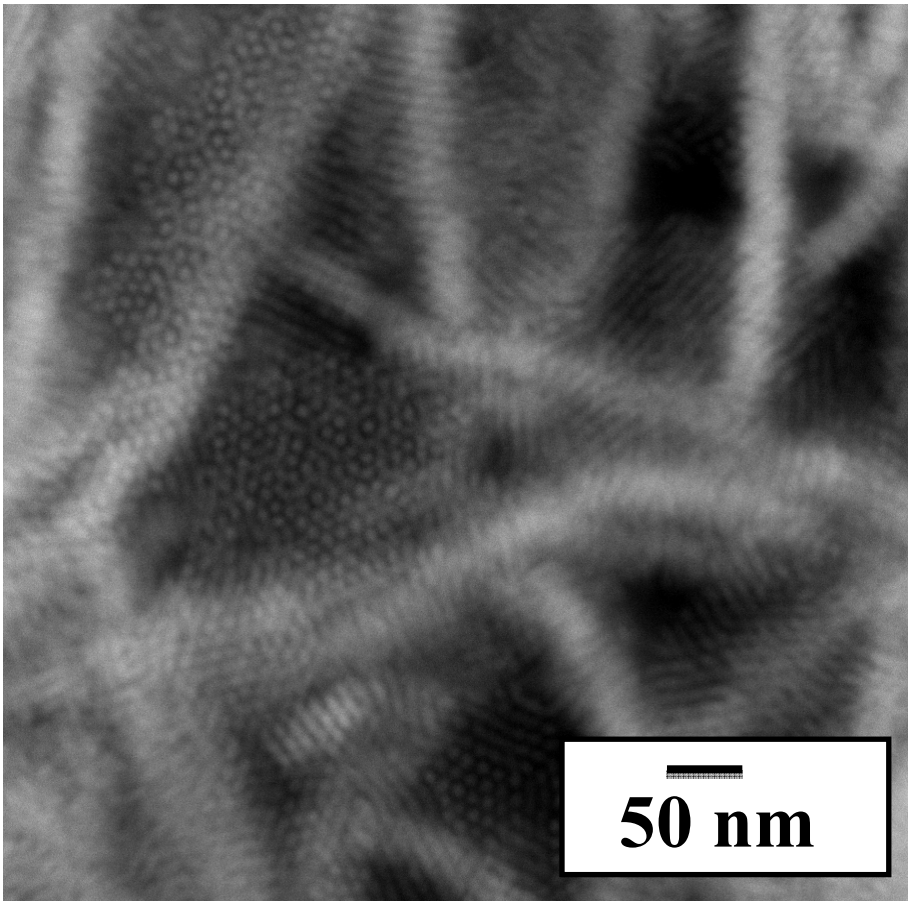
The effect of nanorod concentration on as-synthesized nanorod alignment was investigated by drop-casting solutions of various concentrations on to TEM grids. The optimum concentration was found to be 7×10^{-7} mol l^{-1}. Concentrations below this resulted in randomly deposited nanorods, shown in (a),

with no obvious ordering. Concentrations above the optimal resulted in two-dimensionally aligned cores overlayed and intercalated with randomly deposited nanorods, as shown in (b).

Reference:-

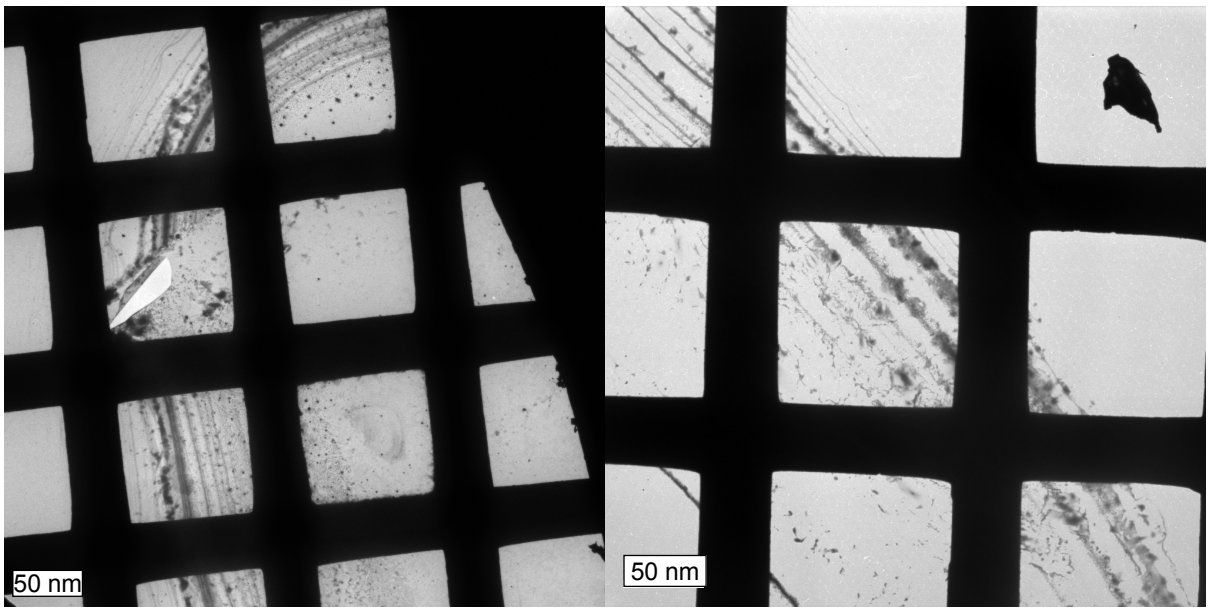
[1] I. Gur, N. A. Fromer, M. L. Geier, A. P. Alivisatos, *Science* 2005, **310,** 462-465; b) Z.A. Peng, X. Peng, *J. Am. Chem. Soc.* 2002, **124**, 3343-3353; c) M. W.Yu, X. Peng, *Angew. Chem. Int. Ed.* 2002, **41**, 2368-237

ES2 – STEM



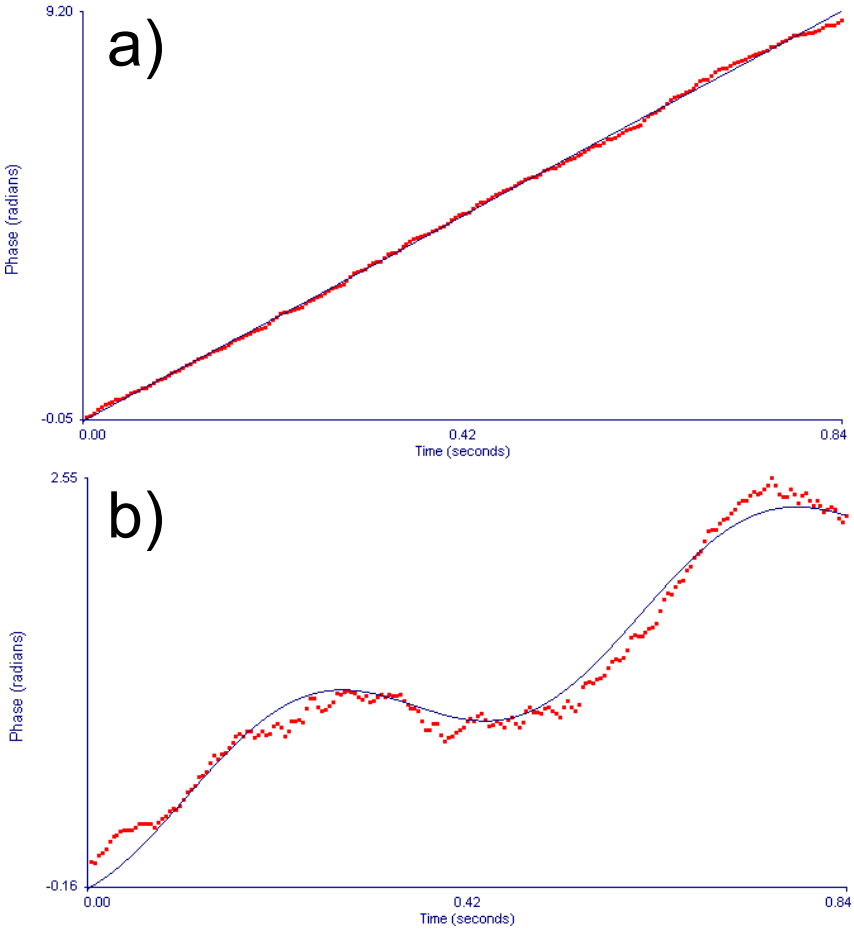
Scanning Transmission Electron Microscopy (STEM) clearly shows the sequential nature of the deposition. The hexagonal pattern of the two dimensional array can be seen below the one-dimensional rail-track assemblies.

ES3 – Low Magnification Ring Images



The TEM image show the nature of the receding evaporation line of the drying solvent as it deposits nanorods.

ES4 – Zeta Potentiometry



The zeta potential of the as-synthesized pT-CdSe nanorods, shown in (a), was found to be 1 ± 4 mV. The as-synthesized nanorods therefore have a charge that is below the detection limits of the equipment used.
The Py-CdSe has, on the other hand, a charge that is measurable, having a value of 23 ± 3 mV.

ES5 – Different Solvents

Methanol

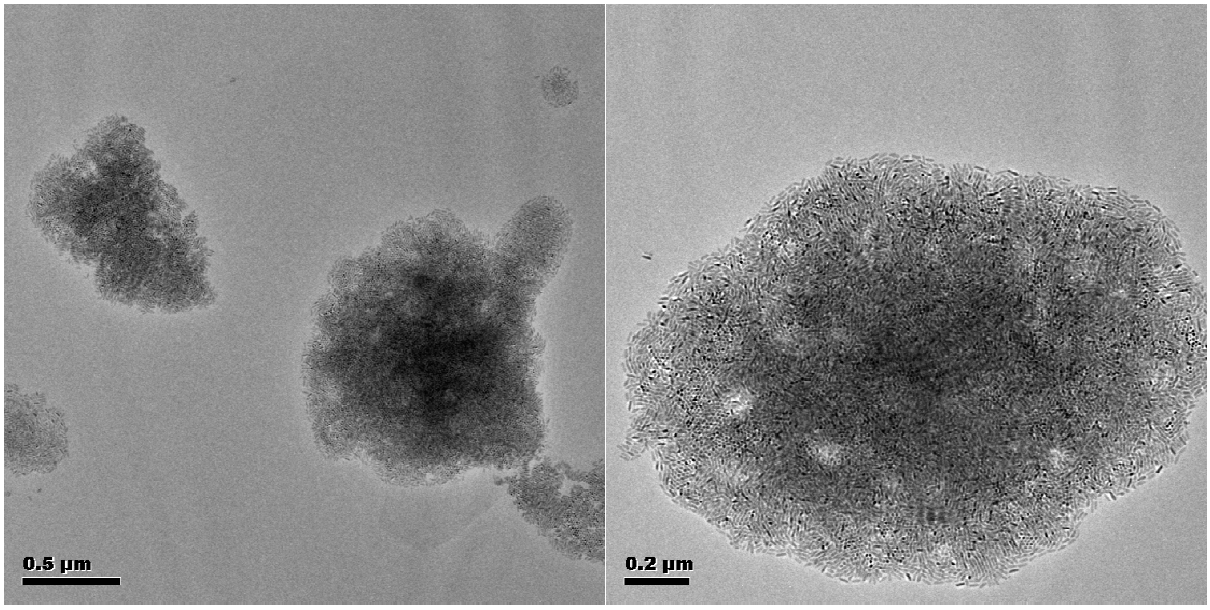


Figure ES5.1 – Drop casting of nanorods in methanol

Methanol is a polar solvent with a relative permittivity of $\varepsilon_r = 32.66$ and a boiling point of 64.7 °C. The agglomerates observed from the methanol drop-casting experiments are shown in Figure ES5.1. The agglomeration is attributed to the poor solubility of the ligand-capped rods in the methanol.

Dichloromethane (DCM)

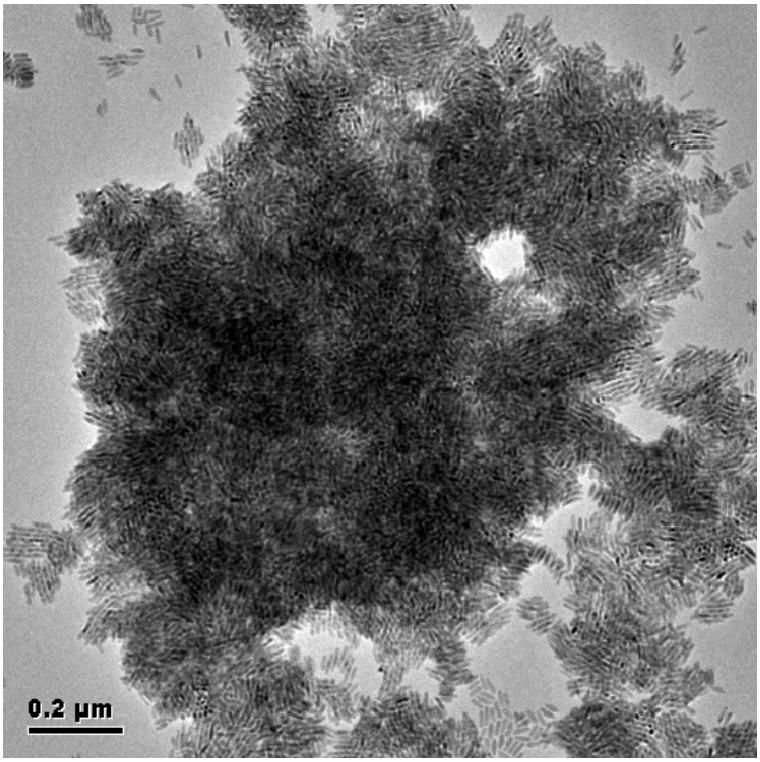


Figure ES5.2 - Drop casting of nanorods in dichloromethane

Dichloromethane (DCM) is a polar solvent with a relative permittivity of $\varepsilon_r = 9.08$ and a boiling point of 40 °C. The agglomerates observed from the methanol drop-casting experiments are shown in Figure ES5.2. The agglomeration is also attributed to the poor solubility of the ligand-capped rods in the DCM.

Cyclohexane

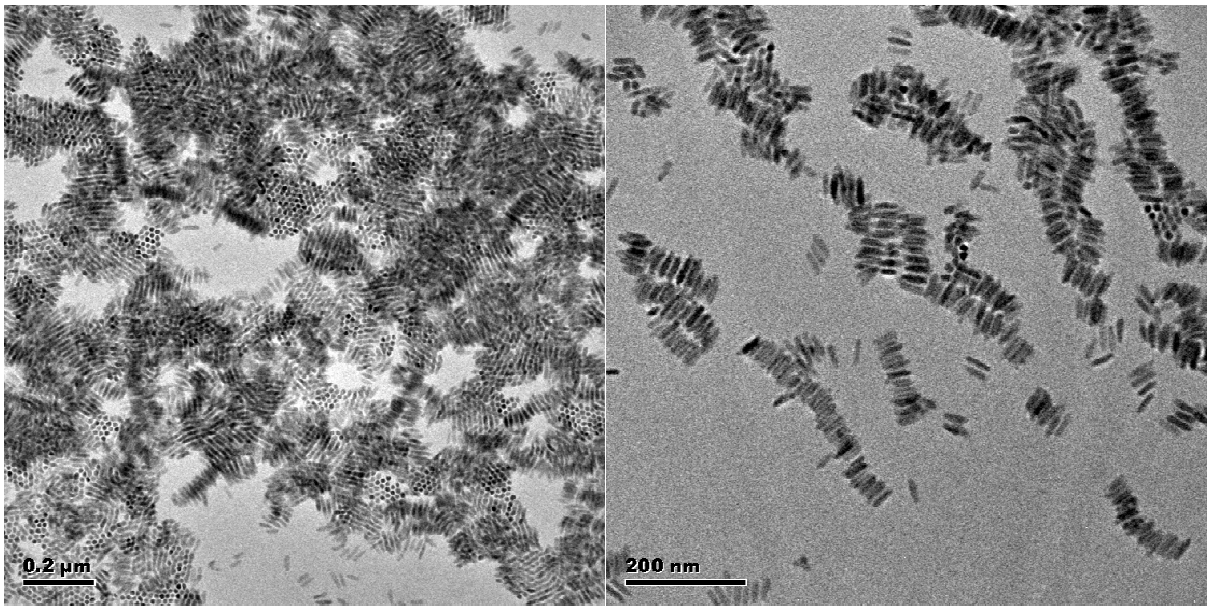


Figure ES5.3 - Drop casting of nanorods in cyclohexane

Cyclohexane is a non-polar solvent with a relative permittivity of $\varepsilon_r = 2.02$ and a boiling point of 80.7 °C. The assemblies observed (Figure ES5.3) are similar to those observed in the toluene, but the domain lengths are much small than those observed in toluene. This is attributed to the higher volatility of cyclohexane, relative to toluene.

Chloroform

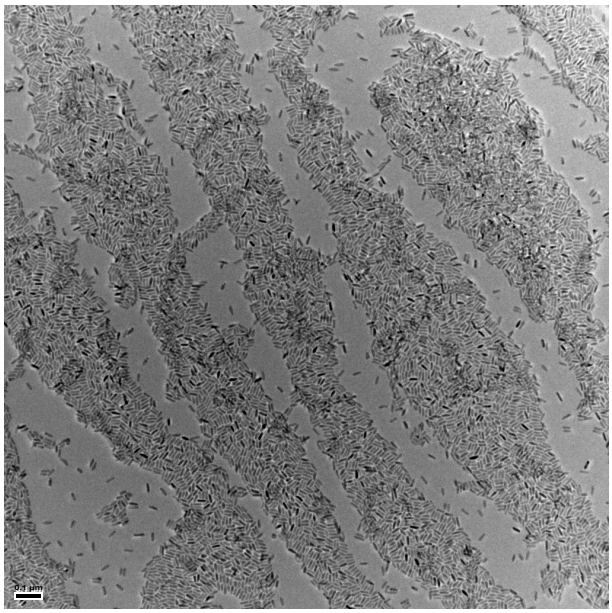


Figure ES5.4 - Drop casting of nanorods in chloroform

Chloroform is a non-polar solvent with a relative permittivity of $\varepsilon_r = 4.9$ and a boiling point of 61.2 °C. No long range assembly in the drop-cast nanorods (Figure ES5.4). This is attributed the screening of the electrostatic interactions by the higher relative permittivity.