Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2009

Supporting Information (SI)

S. Ahmed and Kevin M. Ryan^{*} University of Limerick, Ireland

Experimental details

Materials. Cadmium oxide (CdO, >99%, Fulka), Trioctylphosphonic oxide (TOPO, 99%, Sigma-Aldrich), n-Octadecylphosphonic acid (ODPA, Polycarbonate Industries Inc.), Sulphur (S, 99.5%, Sigma Aldrich) and Trioctylphosphine (TOP, >90%, Fulka).

Nanorod Synthesis. 0.21g of CdO, 1.08 g of ODPA and 2.73 g of TOPO were loaded into a 25 ml three-neck flask and heated to 110 °C under Ar- gas flow at which ODPA and TOPO were dissolved (mixture becomes a brown colour). The mixture is degassed at 110°C for 30 minutes followed by switching from gas to vacuum line with a vacuum range of 150-200 mTorr. The mixture is heated to 300°C under Ar-gas at which CdO completely dissolves and the solution becomes clear. The Mixture is cooled to 110°C and further degassed for another 30 minutes under similar vacuum range (150-200 mTorr). After this second degas, the apparatus is switched back to Ar-gas line and mixture was heated to 300°C at which 0.8 g of Sulphur stock solution (0.65 g of Sulphur powder dissolved in 8.25 g of TOP) was injected. After injection, nanocrystals grew at 300°C for 30 minutes to reach desired size.

Washing Step to Remove Excessive Surfactant. Typically as-synthesised nanorods were dispersed 1:1 ratio of acetone to toluene followed by 60 s agitations and 120 s sonication. The solution was then centrifuged at 3000 rpm for 180 s and the sediment was decanted from the supernatant. A single step of the above procedure means a wash with acetone/toluene and the above process repeated for additional number of wash steps. However, this acetone/toluene has almost no significant effect after four washes. Therefore, to remove or exchange the nanorod surfactant (ODPA+TOPO), we used different concentration of pyridine. The terminology: mild, moderate and excess refer to the quantities of 10, 100 and 200 mL of pyridine respectively, which were injected into 20 mL toluene solutions containing 1 mg of dispersed CdS nanorods. During pyridine wash similar procedure as discussed above for acetone/toluene wash was followed with an exception of different sonication time (300s).

Electrophoretic deposition. For electrophoretic deposition, nanorods are further re-dispersed in a toluene solution (5% w/v) and using the set-up (Fig. 1a) CdS nanorods are deposited into v-aligned superlattices. During Electrophoretic deposition, electrodes are completely immersed in a deposition bath and a positive potential of 200V was applied to the substrate using a high voltage power supply unit (TECHNIX SR-5-F-300, S/N: BU08/04971) and voltage was monitored using Black star 3225 MP multimeter.

Substrate and deposition set-up. The substrates (10 mm \times 10 mm) were attached onto the positive electrode (negative electrodes, if the nanorods are pyridine washed) of a two parallel gold coated copper electrodes which are separated at 2 mm apart. Before attachment, the wafers were cleaned in sequence with acetone (300 s), methanol (300 s) and toluene (600 s) using an ultrasonic bath and then dried in an oven (Gallenkamp hot box oven) at $115 \pm 5^{\circ}$ C for 600 s.

For electrophoretic deposition of CdS nanorods directly on to the carbon coated TEM Grids (Carbon type B on 200M Cu, PELCO INTERNATIONAL), a custom made working electrode where a shallow hole of 3.25 mm diameter with a very fine and thin clamp to hold the TEM grid was used. A very dilute re-dispersed nanorods solution (0.5 % w/v) was used for direct deposition of nanorods on TEM grids.

Characterization. The images of the v-aligned nanorods after electrophoretic deposition of the CdS nanorods layers were acquired using high resolution scanning electron microscopy (Hitachi S-4800 HRSEM). Direct assembly of CdS nanorods on TEM grids by electrophoretic deposition were examined (after deposition) using JEOL 2011 transmission electron microscope (TEM). Zeta-potential was measured using Zeta PALS (Zeta Potential Analyzer, Brookhaven Instruments Corporation, US) using low and high electric-field, $E = 137 \text{ Vcm}^{-1}$ and 274 V cm⁻¹, across the palladium electrodes and measured zeta-potential values was constant from two fields which was averaged from 10 repeated experiments.

SI1

Isolated region of nanorod accumulation during solvent evaporation due to the pinning effect: Self-assembly of nanorods drop cast from solution is an entropically driven phenomenon where vertical alignment of each nanorod starts when the evaporation of solvent randomly pins with the subsequent accumulation of nanorods which usually gives short range ordered domains as shown by arrow in Fig.SI1 (a) – (d). (e) shows vertically aligned CdS nanorod assembly over 2 μ m² area.



Figure SI1: (a) to (d) shows short range order in vertically aligned nanorod domains obtained from a drop-cast solution as the evaporating solvent randomly pins at successive points on the surface. (e) shows vertically aligned CdS nanorod assembly over $2 \ \mu m^2$ area.

[SI2]



Figure SI2: No accumulation occurs between the pin points (a) large area image (scale bar = $30 \mu m$) (b-e) shows individual pin point and (f) shows the space between the rod assemblies is typically absent of nanorods.

[SI3]

When CdS nanorods were synthesised using a combination of ODPA and TOPO surfactant, it was shown that the absorbed surfactant layers on the CdS nanorod surfaces were mainly ODPA. Lifei Xi et al further confirmed this using a TGA study of the CdS nanorods. Zeta potential measurement shows that CdS nanorods are negatively charged (-51.48 \pm 1.44 mV). This data indicates that the nanorods are dispersed in the solution which is presumably due to the inter-nanorod repulsive action. As synthesised CdS surfaces are covered with ODPA and the net negative charge of the CdS nanorod is most likely due to the anionic forms of absorbed ODPA (shown bellow). Thus cationic hydrogen in solution acts as counter balance ions and thus the nanorods remain dispersed.



The possibility of dielectrophoresis is ruled out using both uniform and non-uniform electric-field. In case of uniform electric-field, we have changed the electrode polarity and seen that the nanorods are only deposited to the positive electrode as it has net negative charge. Furthermore, in case of non-uniform electric-field, i.e. using two different dimensions of electrode A (L=25 mm × W=25 mm × d= 3 mm) and B (L = 10 mm × W = 5 mm and d = 3 mm). This experiment also shows that the nanorods deposit on the positive electrode. The polarity of the electrode A and B have switched to positive and negative and vice versa and always we found that as synthesised nanorods are deposited to the positive electrode. In case of dielectrophoresis, the particles should be attracted to regions of stronger electric-field when their permittivity exceeds that of the suspension medium. When permittivity of the medium is greater than that of particles, the result would be motion of

Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2009

particles to the lesser electric-field. In our case, the dielectric constant (ϵ/ϵ_0) of toluene is 2.4 ⁽¹⁾ and bulk CdS is 5.4 ⁽²⁾ shows that the permittivity of CdS nanorod is greater than the toluene medium in which they are suspended and thus we would expect migration towards the stronger electric-field (small electrode B) if dielectrophoresis is occurring. However, we experimentally observed that CdS nanorods always migrate and deposited to the positive electrode irrespective of the electrode geometry. Zeta potential measurement under electric-field E= 177.68 V/cm of as synthesised CdS nanorods in toluene, where instrument has equal and parallel electrode, shows that the CdS nanorods are negatively charged and the mobility of the nanorods are 0.15 $\pm 0.01 (\mu m/S)^2 \text{ cm}^{-1}$. It can therefore be postulated that due to the net charge of the nanorod, under electric field the migration velocity as well as force (F =qE where F is force, q is charge and the E is electric-field) of nanorod towards its oppositely polarized electrode is high and thus always deposited to the oppositely polarized electrode irrespective to the electrode geometry and hence the deposition of the nanorod was observed under the electric-field is not due to the dielectrophoresis but it is due to the electrophoretic deposition.

[1]. http://www.sigma aldrich.com/ chemistry/ solvents/ toluene-center.html.

[2]. S.M. Sze, Physics of semiconductor devices, 2nd edition, John Wiley & Sons, 1981.]



Figure SI5: Tensile stress at the substrate/deposit interface can result in crack propagations after the film is removed from solution and dried (a). HRSEM images were acquired from a crack propagation site (a) and (b) and clearly shown that perpendicularly aligned assembly of nanorods has occurred regardless of the area of inspection.

SI5

SI6

Mild pyridine (C_5H_5N : 10 µl, $C_6H_5CH_3$: 20 ml; CdS nanorod: 1 mg) wash gives crack free deposits: As synthesised nanorods (NR) show an excess of surfactant after the first wash with 1:1 mixture of toluene/acetone. During electrophoretic deposition (EPD) this excess surfactant is co-deposited along with nanorods and the resultant EPD layer forms cracks due to the tensile stress developed at the substrate/deposit interface (Fig. SI5a). This cracking can be avoided by removing/exchanging long chain (ODPA+TOPO) surfactant with short chain pyridine surfactant. Figure SI6 shows a crack-free EPD layer of nanorods after mild stripping and/or exchange of (ODPA+TOPO) by the short chain ligand pyridine (scale bar 100 micrometer) and inset zoomed image (scale bar 100 nm) showing ~ 75% vertically aligned nanorods in this assembly.



Figure SI6: A macro-scale SEM image (scale bar = 100 micron) of electrophoretically deposited crack-free nanorod assembly and inset HRSEM image (scale bar = 100 nm) shows ~ 75% nanorods are vertically aligned in this deposited layer.]



Figure SI7: (a) HRSEM image of a different sample and (b) cross-section TEM image of a lift out sample randomly extracted using FIB milling of a CdS nanorod monolayer deposited on Au/TaN/Si substrate.

SI8

A comparison of the FTIR transmission spectrum of as synthesised ODPA ($C_{18}H_{39}O_3P$) and TOPO ($C_{24}H_{51}OP$) capped CdS nanorod before and after pyridine wash is shown in Figure .SI8a-c. Infrared absorption peaks characteristics of phosphine oxide (P=O) and hydroxide (P-OH) with details in Figure SI8a indicate that the surface of nanorod is covered with ODPA and TOPO surfactant. The characteristics symmetric and anti-symmetric absorption bands of P=O stretching of bulk ODPA at ca. 1054, 1228 cm⁻¹ and ca.1150 cm⁻¹ for bulk TOPO were shifted to the lower wave numbers with broaden peak in the range of 1000-1190 cm⁻¹ suggests the possible interaction between the P=O moiety and the CdS surface. This broaden peak contains the signature of P=O stretching peaks from TOPO and ODPA at 1155, 1083, 1035 cm⁻¹. Similar blue shift of the P-OH stretching frequency of as prepared CdS nanorods at ~ 910 cm⁻¹ in comparison to that from pristine ODPA/TOPO (ca. 950 cm⁻¹) was observed. After pyridine wash, the IR spectrum shows weak intensity of P=O stretching peak at ~1035 cm⁻¹ and P-OH stretching peak at ~910 cm⁻¹ as compared to the as synthesis ODPA and TOPO caped CdS nanorod indicates that a considerable amount of ODPA and TOPO ligands were removed by the mass action of pyridine. Furthermore, new peaks characteristics of pyridine molecules appeared at 3100-3500 cm⁻¹ (this broaden peak is due to the merging of asymmetric (3417 cm⁻¹) and symmetric (3244 cm⁻¹) peaks of N-H stretching), 1608, 1495, 1465, 1175 cm⁻¹ which can be attributed due to the N-H bending vibration, symmetric and asymmetric ring breathing, C=C stretching and C=N stretching modes in the pyridine rings. A slight shift of these characteristics peaks as compared to the bulk pyridine indicates that there is a strong interaction between the CdS surface and the attached pyridine molecules which possibly have protonated in the presence of phosphonic acid groups. It can also be noted that after pyridine washes, The FTIR spectrum shows sharp peaks with smaller FWHM as compared to the FTIR spectrum of ODPA+TOPO caped CdS nanorods (SI8a and SI8b) suggesting the formation of a closed-packed, dense and ordered structure by the remnant ligands that are present after the ligand wash. IR results suggested that due to the pyridine treatment considerable surfactant molecules of ODPA and TOPO on the surface of CdS nanorods were replaced by pyridine molecules. Thus the surface of CdS nanorod assemblies after pyridine washed has better electron transport properties than ODPA and TOPO caped nanorods since pyridine should favour electron transport due to its aromatic character, while ODPA and TOPO are much more insulating due to its aliphatic character which is eventually confirmed by our electrical data. The FTIR spectrum of bulk ODPA, TOPO and Pyridine is also shown along with as synthesised and pyridine washed CdS nanorods in SI8c for comparison.





Figure SI8a: FTIR spectrum of as synthesised and pyridine washed CdS nanorod zoomed $(600 - 1750 \text{ cm}^{-1})$ to see the details effect after being washed with pyridine.



Figure SI8b: FTIR spectrum of as synthesised and pyridine washed CdS nanorod zoomed $2500 - 5000 \text{ cm}^{-1}$) to see the details effect after being washed with pyridine e.g. N-H bending etc.



Figure SI8c: Characteristic FTIR spectrum of (a) ODPA/TOPO capped as synthesised CdS nanorods (b) nanorods after pyridine washed (c) bulk Pyridine (d) bulk TOPO and (e) bulk ODPA

SI9

Capacitance vs. voltage data analysis using Mott-Schottky model:

Capacitance vs. voltage data was acquired at 150 Hz from a two electrode configuration using a CH-Instruments 650A workstation. The data was then analysed in the framework of the mott-Schottky model. Figure SI9 shows a plot of $1/C^2$ versus applied voltage for silver/parallel aligned CdS nanorods/indium Schottky diode. The straight line region of this Mott-Schottky plot is well described by the simple equation:

$$\frac{1}{C_{sc}^2} = \left(\frac{2}{eN_D \varepsilon \varepsilon_0}\right) \left(-\Delta \phi - \frac{kT}{e}\right)$$

and thus the slope $\frac{2}{eN_D \varepsilon \varepsilon_0} = 4 \times 10^{13}$ and using $\varepsilon_s / \varepsilon_0$ of CdS is 5.4, permittivity in vacuum, $\varepsilon_0 = 8.85418 \times 10^{14}$ F/cm and $e = 1.60218 \times 10^{-19}$ C the intrinsic doping density of n-CdS, N_D = 6.517×10^{-17} cm⁻³ was calculated.



Figure SI9: Plot of 1/C² versus applied voltage for silver/parallel aligned CdS nanorods/indium Schottky diode.