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

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Coulomb repulsion due to the surface charge on semi-conductor nanorods works against the dipole-dipole attraction that tends to direct the nanorods to self-assemble; the nature of this self-assembly for CdSe nanorods can be thus altered by pyridine washing, which charges the rods surface – thereby allowing the Coulomb repulsion to tailor the alignment.

The ordered patterns from a drying dispersion of particles offer an insight into the interplay of processes that direct self-assembly.^[1] In the case of dispersions of mono-disperse, spherical nanocrystals, the inter-particle interactions can be tuned to form highly ordered supercrystals in the solid state when the correct balance between nanoparticle diffusion rate, solvent volatility and seeding rate is struck.^[2] Of recent interest are semiconductor nanorods (NRs) where assembly allows individual properties such as single electron charging, linearly polarised emission and absorption to be collectively tuned and upscaled for application in electronics, photonics and solar energy conversion.^[3-4] The long axis of NRs, however, complicates assembly from solution. Early reports countered the anisotropy restriction^[5] with external fields directing perpendicular orientation of the rods while drying in a droplet.^[6-7] Experiments without fields showed that with optimal aspect ratio and concentration, perpendicular assemblies of CdS NRs could form.^[8] However, under similar conditions end to end (CdS) and side by side assemblies (CdSe and CdS) have also been observed, suggesting an intricate balance in the forces that direct organisation.^[9-12] Here we show that nanorods can be manipulated to form either side-by-side (1D) or vertically aligned (2D) assemblies by altering the capping ligand.

The 2D assemblies in Fig. 1a occur only when the concentration of phosphonates/TOPO capped CdSe (pT-CdSe) NRs in toluene is 7×10^{-7} mol l⁻¹ (Electronic Supporting Information ES1 for synthesis and concentration optimisation). The NRs are packed into hexagonal 2D perpendicular arrays that extend to μm -sized domains. A partial exchange of the pT ligand (phosphonates/TOPO) for pyridine results in side by side (rail-track) assemblies in addition to the 2D assemblies (Fig.1 b-d). Increasing the pyridine concentration elongates the chains and increases their relative density (Fig.1c and 1d). TEM (Fig.1) and STEM (ES2) confirm that the rail-tracks deposit atop the 2D assemblies in all cases suggesting a sequential deposition.

Complete exchange of the pT-CdSe rods for the pyridine capped CdSe NRs (Py-CdSe) NRs gives ring patterned deposits (Fig. 2a, ES3). The rings can occur due to the random

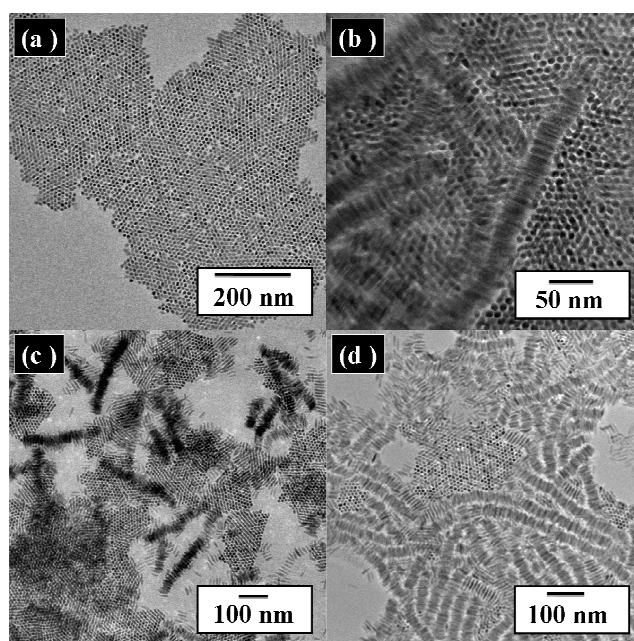


Fig. 1 (a) TEM image showing 2D superlattice of pT CdSe NRs (b) TEM image of the Py-CdSe NRs showing the vertical assembled NRs laying below the aligned (rail-track) Py-CdSe NRs. (c, d) TEM images at a 1:1 and 3:1 volume ratio of Py- to pT-CdSe NRs respectively.

pinning of the receding solvent line depositing the dissolved material, or the formation of “breath patterns”.^[13]

The anisotropy in the outward capillary flow of NRs towards the pinned contact line to compensate the evaporating solvent creates thicker deposits in the outermost ring (track “b”, also Fig. 2b). The next track “c” (Fig. 2c) shows dense wire-like hierarchical structures similar to the “spaghetti-like” structures observed by Nobile et al.^[12] Furthermore, the density of the NR fringes decreases from track “b” to “d” (Fig. 2). The occurrence of discrete 1D or 2D assembly with single surfactants or both with partial exchange suggests that the behaviour of the Py-CdSe and pT-CdSe NRs is different with the two alignments occurring independently.

Understanding both alignments requires consideration of the forces acting on the NRs in the droplet. The dipole-dipole energy between the rods can be approximated by

$$V(R_{ij}, \theta_i, \theta_j, \phi) = -\frac{\mu_i \mu_j}{4\pi\epsilon_0 R_{ij}^3} (2 \cos \theta_i \cos \theta_j - \sin \theta_i \sin \theta_j \cos \phi)$$

where μ_i is the dipole moment of i , R_{ij} is the displacement between i and j , θ_i is the angle between i and the

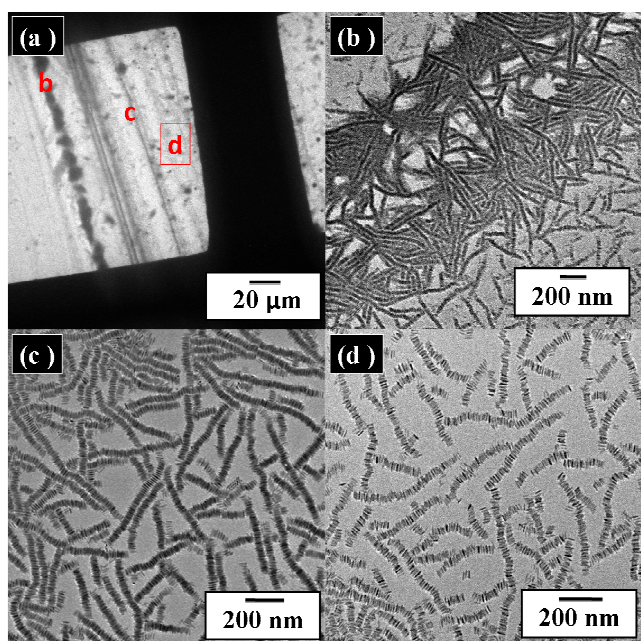


Fig. 2 (a) TEM image showing formation of ring patterns by PyCdSe NRs (b)-(d) TEM images magnified from the corresponding tracks b-d marked in (a), respectively showing the lateral assembly of Py-CdSe NRs.

displacement, and φ is the torsion angle between the dipoles. The dipole moment for CdSe NRs is large, with a value of 250 D (or 8.3×10^{-28} C m in SI units) for a 35×7 nm NR expected.^[14] NRs may also have a net surface charge, so Coulomb repulsion must also be considered. Assuming a negligible ion concentration in toluene, the other electrostatic terms (dipole-charge and Coulomb) can be approximated by

$$V(R_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 R_{ij}^2}, \quad V(R_{ij}, \theta) = -\frac{q_i \mu_j \cos \theta}{4\pi\epsilon_0 R_{ij}^2}$$

Fig. 3a shows the combined energy, ΔE , versus rod displacement, R_{ij} . For rods with a zeta potential, $\zeta < \sim 15$ mV, the repulsion can be easily overcome by the thermal energy. Therefore the dipole-dipole force would be sufficient to cause rods to align and assemble in solution. When ζ is higher, the Coulomb repulsion maintains the dispersion such that no aggregation occurs. There will be, however, a critical inter-dipole distance at which the thermal energy is sufficient to overcome the repulsive barrier, roughly 23 and 47 nm for NR with $\zeta = 20$ mV and 25 mV, respectively. Once within the attractive potential, the dipoles can align and assemble. Thus, there is a critical concentration whereby assembly of NRs with a high ζ can align. End-to-end assembly unaided by any other factor can be overcome by the thermal energy, and as such, side-by-side alignment is favoured. Therefore, assembly in the solution is predicted to occur for low ζ at an optimal concentration. The experimentally determined zeta potential data (ES4) shows pT-CdSe NRs at (1 ± 4) mV in comparison to Py-CdSe NRs at (23 ± 3) mV. Consequently, there is no repulsive Coulomb barrier preventing the pT-CdSe NRs from aligning due to the dipole-dipole force and thereby assembling in the bulk solution (Fig. 3b). These growing supercrystals will precipitate out by gravity sedimentation onto the grid as

the 2D assemblies. The dipole-dipole attraction is the driving force for alignment and is assisted by the affinity of surface ligands to interdigitate to reduce interfacial energy.^[15-16]

The higher ζ Py-CdSe rods will not assemble in solution as the Coulomb repulsion maintains a barrier to aggregation. Through the combination of fluid flow and diffusion the higher ζ Py-CdSe rods will migrate to and get trapped at the liquid air interface.^[2] The rods will act to minimize surface tension by orienting with their long axis parallel to the droplet surface. The energy potential of the NR at the droplet surface is calculated by a modified equation following He et al.,^[17]

$$\Delta E = -wl[(\pi - \theta) \times (\gamma_{CdSe-Air} - \gamma_{CdSe-Toluene}) + \gamma_{Air-Toluene} \sin \theta]$$

where l and w are the basal width and the length of the NR, respectively; γ_{x-y} is the interfacial tension between phases x and y ; and θ is the contact angle between the rod surface and the toluene-air interface, given by $\cos \theta = (\gamma_{CdSe-Toluene} - \gamma_{CdSe-Air}) / (\gamma_{Air-Toluene})$. $\gamma = 15.0, 33.0$ and 28.1 mT m⁻¹ for the CdSe-toluene, the CdSe-air and the toluene-air interfaces, respectively;^[18-20] this gives a potential of $450 k_B T$, well in

excess of the electrostatic potentials involved. This removes the possibility of any electrostatic forces pushing the rods back into the volume. Thus, the droplet surface will be a two-dimensional manifold with rods confined to move within it (Fig. 3b). The surface concentration will increase as droplet size reduces and can trap more rods while reducing the surface area. At critical concentration for high ζ rods, the rods align due to the dipole-dipole attraction and form the 1D arrays. These arrays precipitate off the surface, forming rings with a diameter equal to that of the droplet. Increasing the average charge should increase the relative density of the 1D arrays, as is observed with increase in pyridine concentration.

The dimensionality of the arrays reveals their origins. Due to ligand attachment and dipole attraction energy, the NRs will not align into arrays along their long axis. Thus, arrays forming from a 3D space (the droplet volume) will be two-dimensional; the inability to align along the NR axis deprives the crystallization of one of its dimensions. Likewise, arrays forming from a 2D manifold (the droplet surface) will be one-dimensional. Thus, the vertical assemblies come from the volume and the rail-tracks come from the droplet surface. The vertical assemblies deposit before the rail tracks as sedimentation occurs before receding contact line deposition.

Solvent volatility can affect assembly size^[1,2]. For NRs are dissolved in a higher volatility solvent, cyclohexane, much shorter domain sizes are observed. Highly polar solvents, such as dichloromethane and methanol, do not dissolve the rods due to the poor solubility of the ligands. Using a solvent with an intermediate dielectric constant such as chloroform leads to an absence of the highly-ordered assemblies. This is due to the larger dielectric permittivity screening the electrostatic interaction forces and inhibiting the assembly (ES5).

The NR centre-to-centre distance in the 1D assemblies is shorter (9.4 nm) than of that of the rods in the 2D assemblies (10.87 nm), representing a reduction of ligand spacing between the rods from 4.0 to 2.6 nm after washing, due to the shorter-length pyridine replacing the longer chain p/TOPO.

This model based on charge and dimensionality rationalises

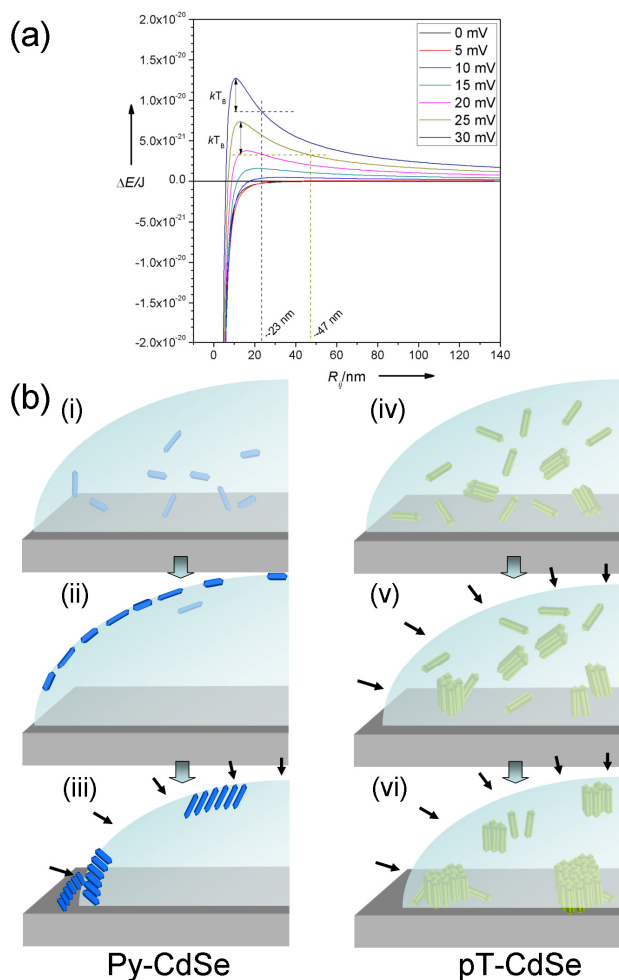


Fig. 3a A plot of energy versus nanorod-nanorod displacement for NRs of different zeta potential. The barrier to assembly is less than the thermal energy for lower higher zeta potentials and can be overcome thermally if the nanorods are placed sufficiently close to one another, shown by the drop-lines from the intersection of the thermal energy with the attraction potential. **3b** A schematic of the two types of NR self-assembly in a drying droplet; Py-CdSe [(i) – (iii)] and pT-CdSe [(iv)–(vi)].

reports where slight modifications of similar systems gave differing results. Querner reported no vertical assemblies – only rail-track assemblies occurred with pT-CdSe NR assembled from hexane/octane.^[10] However, ζ of the pT rods in these solvents is found to exceed that of pT-CdSe rods in our study, which implies 1D assemblies should form. Similarly, in reports of orthogonal assemblies in solution of CdSe/CdS and Au-CdSe, the preassembly of the NRs in the bulk solute is critical to vertically aligned order.^[7,21] In both cases the equilibrium of dispersion and aggregation was deliberately modulated; 2D monolayers and not 3D supercrystals were formed from assembling NRs in the bulk. In summary, correlating both the influence of inter-particle forces (charge and dipole) and the available dimensions (liquid-air 2D, bulk 3D) creates intrinsically tuneable parameters to control NR assembly. Charge can be modified relatively easily by ligand exchange and monitored by zeta potential allowing a general route to predict rod organisation.

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