

Electric Field Assisted Assembly of Perpendicular Oriented Nanorod Superlattices

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ABSTRACT

We observe the assembly of CdS nanorod superlattices by the combination of a DC electric field and solvent evaporation. In each electric field (1 V/um) assisted assembly, CdS nanorods (5 X 30 nm) suspended initially in toluene were observed to align perpendicularly to the substrate. Azimuthal alignment along the nanorod crystal faces and the presence of stacking faults indicate that both 2D and 3D assemblies were formed by a process of controlled super crystal growth.

KEYWORDS Nanorod, Superlattice, assembly

Self assembly or directed assembly of discrete nanostructures into organized patterns provides a new route to the formation of functional materials. Colloidal nanocrystals are suitable building blocks as they can be synthesized with size and shape control.¹ The assembly of symmetrical nanospheres and nanocubes into superlattices is known; and in the case of silver nanocrystals, 3 nm in diameter, an insulator to metal transition is observed to occur as a function of sphere size and interparticle separation.²⁻⁴ In effect, the superlattice functions as a novel nanocrystal solid where it is possible to control the electronic coupling by manipulating the size and position of the quantum confined structural units. The coupling can further be modified through exchange of the insulating organic ligands on the nanocrystal surface with low barrier organics e.g. hydrazine. Talapin and Murray used this approach to convert poorly conducting PbSe nanocrystal solids into n-and p-channel field effect transistors.⁵ The ability to direct anisotropic structures such as cylindrical nanorods into superlattices is less well developed but also interesting. In organized nanorod superlattices, it may be possible to simultaneously and independently optimize quantities which depend on the diameter (such as band gap) from quantities which depend on length (total absorption, cross section or conductivity).

Superlattice formation with spherical nanocrystals is strongly correlated to size monodispersity and their entropy driven packing under slow evaporation conditions. While dimensional control and monodispersity in nanorods has been achieved, their organization into superlattices is restricted as both positional and orientational ordering is required during assembly. Some progress has been made in preferred nanorod alignment in single layers with nematic and smectic ordering achieved from gentle evaporation of low boiling point solvents.⁶⁻⁹ The rods align parallel to substrate in small domain sizes. There is further evidence for the preferred orientation of anisotropic nanostructured-rods, tubes and wires along electric field lines. The strength of the interaction is greatest in metallic nanostructures followed by nanostructures with permanent dipole moments e.g. CdSe, CdS nanorods.^{10,11} Anisotropic structures with low polarizability such as silicon nanowires and carbon nanotubes can also be induced to align when the electric field induced torque is greater than the thermal excitation energy (kT).^{12,13} The

effect is usually observed when a solution of 1D nanostructures is deposited between interdigitated electrodes resulting in orientation along field lines parallel to the substrate with no positional order. In our research, we have used the combination of a DC electric field and slow evaporation of solvent (toluene) to generate superlattices of II-VI semiconductor nanorods with orientation perpendicular to a substrate [Footnote].

CdS nanorods (30 nm x 5 nm) were formed by the injection of sulphur/tri-n-octylphosphine solutions at high temperature into hot cadmium oxide/surfactant mixtures.¹⁴ The solution of size monodisperse CdS nanorods in toluene is trapped between parallel electrodes (figure 1) and allowed to dry under a DC electric field of $1\text{V } \mu\text{m}^{-1}$. Gentle evaporation is achieved through near-saturation of the entire assembly in a toluene atmosphere. The solvent evaporation gradually decreases the diameter of the meniscus, packing the nanorods into a 2D supercrystal. In this study, we observe that for, slower rates of the solvent evaporation, a higher degree of positional order is present in our nano-rod assemblies. Figure (2 a,b) shows a 2D nanorod array evaporated from toluene in the absence of an electric field. The centre of the domains consist of perpendicularly aligned rods in a 2D hexagonal array. The outer layers of nanorods progressively tilt towards the centre, aligning parallel to the substrate at the domain edge. This tilting of the nanorods from perpendicular to parallel at the edges is in good agreement with alignment observed in condensed 3D nanocrystal solids reported by Weller¹⁵. In that work the progressive perpendicular to parallel tilt over hundreds of multilayers from edge to centre was sufficient to rotate the polarization of light as verified using crossed polarizers. Assuming that transmitted polarized light is directed normal to the substrate, the observed birefringence changes with both tilting and rotation of the nanorod with respect to the substrate plane. The densely packed rods in figure 2 a,b demonstrate good positional order with 180 degree range of disorder in planar orientation across the nanorod aggregate.

The electric field directs the perpendicular orientation of the rods along the field lines during the assembly process.¹⁶ The CdS nanorods (30 nm x 5 nm) are estimated to have a permanent dipole moment of ~ 220 Debye because of the non-centrosymmetric Wurtzite lattice.^{17,18} The electric field will act on the nanorods producing rotation about its axis while the evaporating solvent laterally

confines them into an array. The net effect is a 2D superlattice of semiconductor nanorods with all the c-axes aligned normal to the substrate. Figure 2(b) shows a typical TEM image of a single layer of hexagonally packed nanorods 30 nm x 5 nm showing both positional and orientational order that is extraordinarily resolute throughout the entire domain. The space between the nanorods, 3nm, is occupied by interdigitated phosphonic acid surfactants. Clearly in the approach described here, the electric field is acting on the nanorods during evaporation to direct high orientational order. Close analysis of the nanorods figure 1b under higher magnification shows the hexagonal faceted ends of the zinc blende nanorod structure. The 2D assembly of the nanorods is also affected by the particle shape where the nanorods demonstrate positional and orientational order as well as azimuthal alignment along their [100] and [111] crystal faces. This azimuthal alignment strongly suggests that super crystallization of hexagonally faceted nanorods is entropy driven where the total growth rate is slow and each nanorod can dynamically add to or subtract from the growing supercrystal face before locking in. The electric field electrostatically interacts with the nanorod during packing ensuring that orientational order perpendicular to the substrate is preserved. All nanorods will be parallel aligned under the electric field which suggests that the collective force due to the applied field overcomes the single-particle field alignment energy that favours an antiparallel dipolar arrangement. In addition, the diminished solvent volume due to evaporation, helps to overcome the dipole-dipole repulsion as each nanorod is continually drawn (entropically) into the remaining solvent by its surfactant layer.

This mechanism for superlattice growth is further evidenced in figure 3b where slower evaporation of nanorods resulted in the formation of superlattice domains $> 0.5 \mu\text{m}^2$. The superlattice crystal structure is defect free throughout the entire domain and electron diffraction inset shows sharp maxima indexed to the diffraction planes of a hexagonal lattice.

The stacking fault observed in the domain imaged in figure 3b is further evidence for the controlled sequential addition of nanorods to the growing crystal face of the 2D nanorod superlattice during evaporation. The domain consists of $\sim 4 \times 10^3$ nanorods normal to the substrate. The Fourier transform

shows the effective electron diffraction from selected regions of the domain with spot sizes of 200 nm^2 . The electron diffraction from region 1 shows a hexagonal superlattice with sharp scattering maxima. Similarly, the electron diffraction from region 3 reflects a hexagonally ordered lattice. The stacking fault is observed in region 2 where the Fourier transform of the image shows two sharp maxima at each position evidencing rotation in the azimuthal alignment occurring at this location. The arrows shown in the magnified image of the defect region are aligned with the [100] crystal planes of the nanorod superlattice clearly showing the stacking fault.

CdS nanorods deposited under an electric field with slow evaporation also demonstrate alignment in three dimensions (figure 4). 3D nanorod arrays were obtained where the incoming nanorod selectively sits in the interstitial spacing between the nanorods in the underlying layer creating an AB layered 3D superlattice. Figure 4 b is a schematic showing how this effect manifests itself as the periodic structure seen in figure 4a when the two layers are viewed simultaneously in transmission mode. Typically 3D stacking of nanorods is routinely observed when the concentration of nanorods in solution is high.

The approach described here for assembling superlattices of anisotropic, size and shape controlled nanorods normal to a substrate is generally applicable. This level of directional control may prove helpful in the formation of nanorod-polymer solar cells with increased charge transport efficiencies¹⁹.

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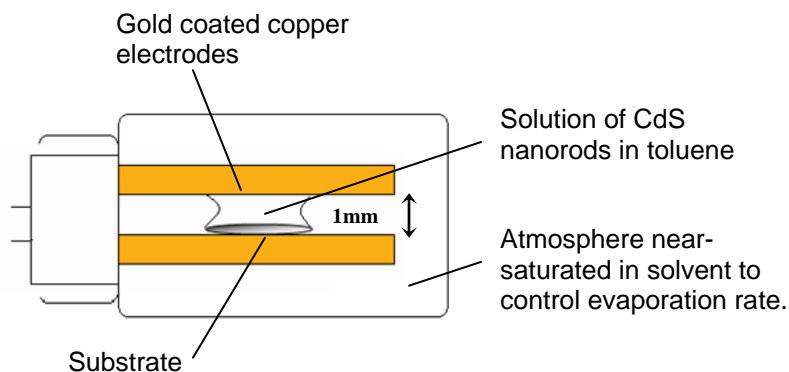


Figure 1. Schematic of electrode assembly for nanorod alignment. A substrate (carbon coated electron microscopy grid or silicon nitride membrane window) and CdS nano-rod solution with toluene is placed between two gold coated copper electrodes. Setup is contained with a reservoir of toluene solvent which is present to provide a near saturated environment to help slow the rate of evaporation.

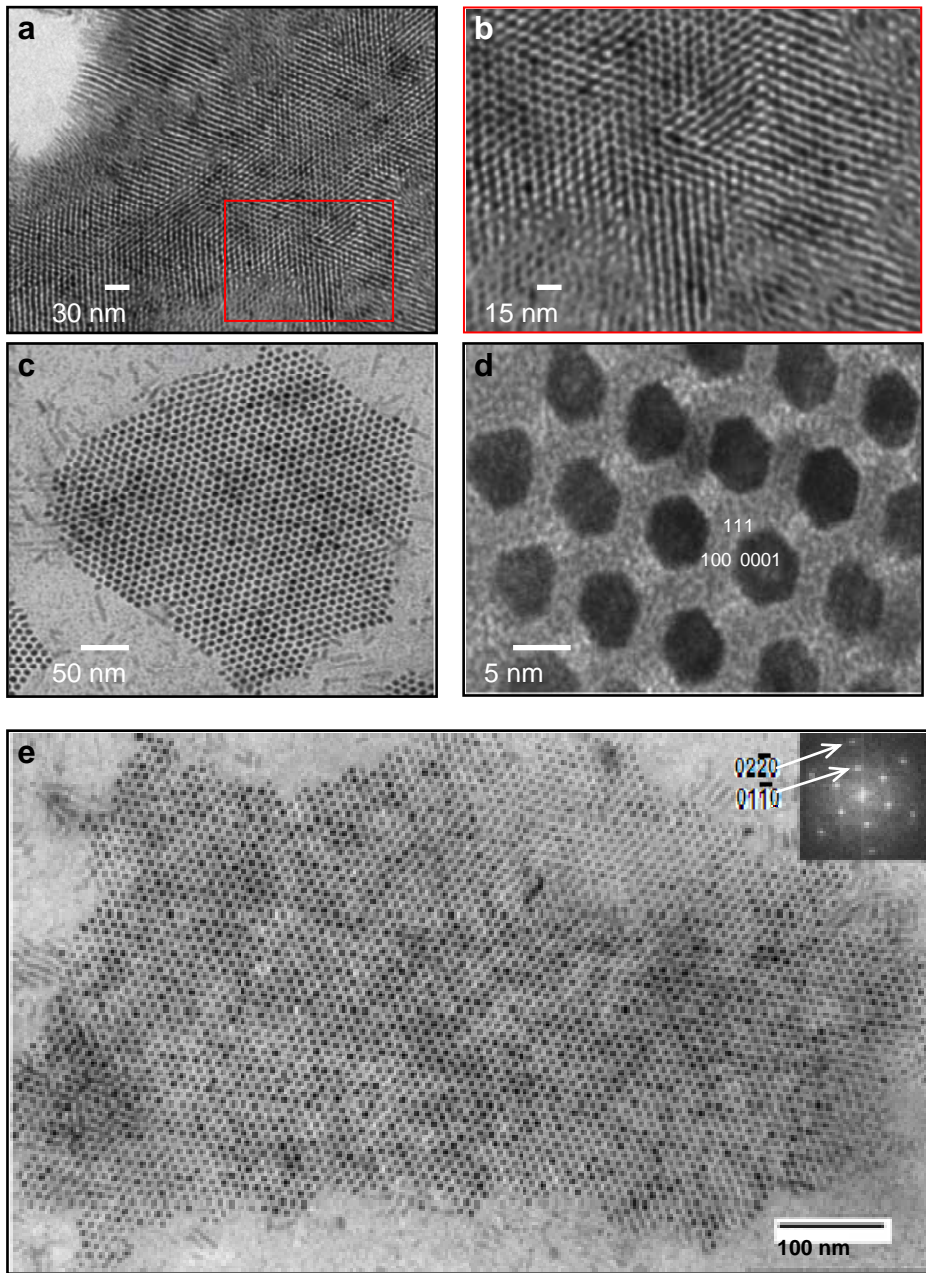


Figure 2. TEM images of perpendicularly aligned nanorod superlattices: a, Section of CdS nanorod (30 nm x 5 nm) domain in absence of electric field, scale bar = 30 nm; b, Magnified section of a, showing parallel to perpendicular alignment from edge to centre (scale bar = 10 nm); c, CdS nanorods aligned under a field of 1 V/(um); d, azimuthal alignment of the nanorods; e, 30 nm CdS nanorod superlattice with domain size $> 0.5 \mu\text{m}^2$, inset Fourier transform of image showing electron diffraction from hexagonally ordered 2D array. Maxima highlighted from [01-10] and [02-20] diffraction planes with

remaining planes $[10-10]$, $[1-100]$, $[0-110]$, $[-1010]$, $[-1100]$ and $[20-20]$, $[2-200]$, $[0-220]$, $[-2020]$, $[-2200]$ clockwise from these positions respectively .

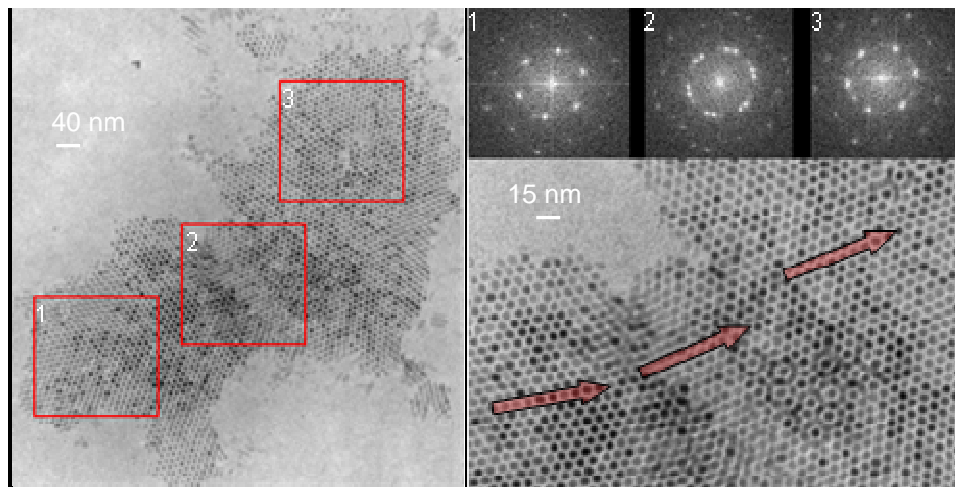


Figure 3. Electron diffraction from selected regions of electric field assisted perpendicularly aligned nanorod domain showing superlattice stacking fault

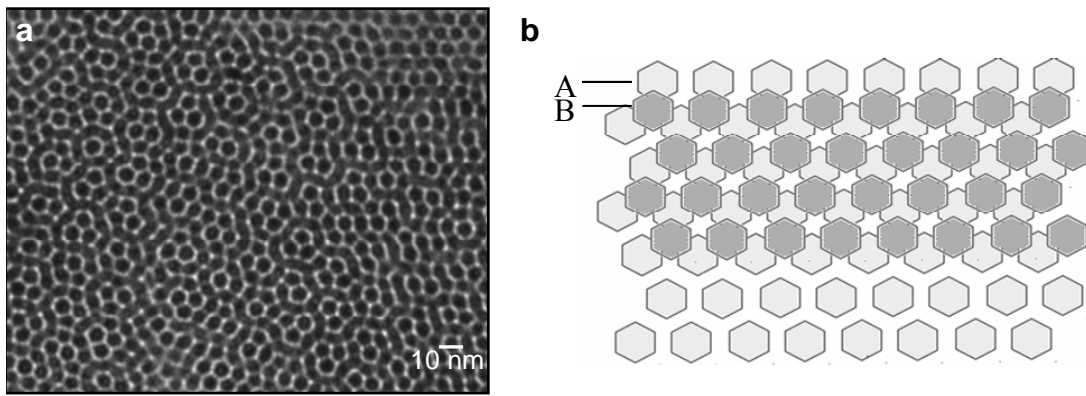


Figure 4. a, 3D superlattice of CdS nanorods 30 nm x 5 nm scale bar = (10 nm), b Schematic showing the top down view of perpendicular arrangement of nanorods with AB stacking

FOOTNOTE: As this work was in progress, we received notice of similar unpublished work from the laboratories of Professor T. Russell and T. Emrick of U. Mass. Amherst.

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(14) To a three-neck flask was added tri-n-octylphosphine oxide (Aldrich, g., n-octadecylphosphonic acid (Polycarbon, 1.07 g, 3.19 mmol), and CdO (Aldrich, 0.205 g, 1.60 mmol). The mixture was degassed at 120 °C for 30 min before it was heated to 320 °C under Ar to dissolve CdO. The temperature was then lowered to 300 °C and solution of sulfur in tri-n-octylphosphine (7.9% w/w, 0.60 g, 1.5 mmol of sulfur) was swiftly injected to the flask via syringe. The nanorod was grown at 290 °C for 30 min. After the reaction, the temperature was lowered to 100 °C and toluene (3-4 mL) was added to dissolve the reaction mixture. The toluene solution was centrifuged at 2500 g to give a yellow precipitate. This precipitate was redissolved in toluene and the nanorod was precipitated with acetone.

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(16) A dilute solution of nanorods was trapped between a substrate and the upper electrode of a parallel assembly separated at a distance of 1 mm. The assembly was covered in a glass vial and solvent is added to the vial to effect a near saturation of the atmosphere. A DC electric field of 1000V is applied using a power generator and the solvent is allowed to evaporate over a period of several hours.

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SYNOPSIS TOC

