Synthesis and Assembly of Binary, Ternary and Quaternary Semiconductor Nanorods

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Finally, I wish to thank my parents and family. Their love provided me inspiration and was my driving force. I wish to thank my elder brother, Ramnik Singh for his belief in me and unflagging encouragement to complete this goal.
Abstract

Herein is presented novel routes towards synthesis and assembly of colloidal semiconductor nanorods. A versatile colloidal approach was developed to synthesise complex multicomponent copper chalcogenide \((\text{Cu}_2\text{ZnSnS}_4)\) nanorods with tight control in shape, size and crystal phase. Assembly protocols to control the position and orientation of semiconductor nanorods were significantly progressed in this work leading to controlled approaches for assembly of binary \((\text{CdS}, \text{CdSe})\) to ternary \((\text{CuInS}_2)\) and quaternary \((\text{CuInGaS}_2, \text{Cu}_2\text{ZnSnS}_4)\) nanorods into close packed superstructures.

Specifically, the preparation of highly monodispersed, anisotropic \(\text{Cu}_2\text{ZnSnS}_4\) (CZTS) colloidal nanocrystals is described in chapter 2. The reaction conditions used (selectivity of precursors, addition of anionic precursor at low temperature \((150-160 \, ^\circ\text{C})\), and surfactant/solvent composition) resulted in a tuneable shape from spherical to rod CZTS nanocrystals. The formation of rod shaped CZTS nanocrystal is only possible by stabilising the nuclei of nanocrystal in wurtzite phase by using strong coordination ligands such as thiols, followed by controlled growth in \((002)\) direction. These monodispersed nanorods are further assembled into 2D sheets, consisting of each rod vertically aligned by using drying mediated assembly approach.

A charge based assembly method is introduced in chapter 3 and 4 where a precise control of nanorod orientation \((1D, 2D, 3D)\) in the assembled superstructure is achieved by manipulating the surface charge of nanorods. By optimising the initial concentration of nanorods in solution, it is possible to nucleate the assembly as 2D sheets where each rod is close-packed in the side by side fashion. These 2D sheets are further deposited on the substrate by gravity sedimentation and give interesting Moiré pattern when analysed with TEM/STEM as discussed in chapter 5. These Moiré interference patterns arise from rotational offsets between respective monolayer 2D sheets and the exact degree of rotational offsets can be measured by SAED and FFT.

In Chapter 6, the reversible assembly de-assembly method is shown for ternary and quaternary nanorod \((\text{CuInS}_2\) and \(\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2)\) in solution. The monodispersed nanorods are self-assembled into micron size 3D superstructure over time. These superstructures attain the perfect hexagonal close-packing which is predominantly entropy driven. These superstructures were de-assembled by a facile ligand exchange; reverting the solution to a random nanorod dispersion. As these nanorods have a modified ligand environment which
influence the net charge, their vertical assembly were then controlled by either optimizing the solution concentration to form micron size free floating 2D sheets or on the conductive substrate by electrophoresis.

Chapter 7 discussed the influence of external field such as DC field on the nanorod assembly. The use of DC field in the nanorod solution enables the uniform vertical alignment of nanorods on a square-centimetre conductive substrate. The precise control on the number of layers is shown.

*The research work summarized in this thesis describes both synthetic and assembly techniques that enable a fine control on shape/size morphology and composition at nanoscale level that is extendable to the device-scale.*
Declaration

The work described in this thesis is the result of my own work carried out in the University of Limerick except for the assistance mentioned in the contribution section and the collaborative work with other people for publication.

This dissertation has not been submitted previously in whole or in part for the award of a degree at this or any other university.

Ajay Singh
List of Publications

This thesis is based on the following first author papers (1-6), which have been reproduced exactly as published as chapters from 2 to 7 in the thesis. For ease of reading, the supporting information of each paper is incorporated in the text. The table of contents of each paper is added in the appendix.


The following articles are not included in the thesis


**Conference Proceedings**


Comments on my contributions

This work from synthesis, assembly and characterization planning and data analysis has been carried out at the Materials and Surface Science Institute, University of Limerick. I have had primary responsibility for all experimental work, data analysis and manuscripts in all publications from 1-6 and the contributions of co-authors is outlined below for each paper.

In all publications K. M. Ryan has secured funding, planned research proposals and contributes from experimental planning through results discussion to manuscript preparation.


H. Geaney contributed towards XRD data analysis and F. Laffir contributed on XPS data analysis.


R. D. Gunning contributed towards modelling of nanorod assembly and A. Sanyal provided insight during discussing of the experimental results.


C. Dickinson contributed towards SAED analysis.

Chapter 6: A. Singh, C. Coughlan, F. Laffir, K. M. Ryan. “Assembly of CuIn$_{1-x}$Ga$_x$S$_2$ Nanorods into Highly Ordered 2D and 3D Superstructures” ACS Nano 2012, 6, 6977

C. Coughlan contributed to material selection for the synthetic experiment, F. Laffir contributed in XPS data analysis.


N. J. English contributed towards molecular simulation.
List of abbreviations:

0D - zero dimensional
1D - one dimensional
2D - two dimensional
3D - three dimensional
ODPA - n-octadecylphosphonic acid
TDPA - n-tetradecylphosphonic acid
HPA - n-hexadecyphosphonic acid
DDT - dodecanethiol
t-DDT - tert-dodecylmercaptan
TOP - trioctylphosphine
TOPO - trioctylphosphine oxide
HDA - hexadecylamine
DDA - dodecylamine
CdO - cadmium oxide
CdSe - cadmium selenide
CdS - cadmium sulphide
PbS - lead sulphide
CZTS - Cu$_2$ZnSnS$_4$
CIGS - CuIn$_{1-x}$Ga$_x$S$_2$
CIS - CuInS$_2$
HOPG - Highly ordered pyrolytic graphite
LB - Langmuir–Blodgett
EPD - electrophoretic deposition
ITO - indium tin oxide
HSAB- hard-soft-acid-base

TEM- transmission electron microscopy

HRTEM- high resolution transmission electron microscopy

STEM- scanning transmission electron microscopy

DFSTEM- angular dark field scanning transmission electron microscopy

EDX- energy dispersive X-ray spectroscopy

FFT- fast Fourier transform

SAED- small angle electron diffraction

SEM- scanning electron microscopy

HRSEM- high resolution scanning electron microscopy

FTIR- Fourier transform infrared spectroscopy

UV-vis- UV-Visible Spectroscopy

XPS- X-ray photoelectron spectroscopy

XRD- X-ray diffraction

ANCs- assembled nanorod cluster
Introduction

1.1 Nanocrystal

Nanocrystals are crystalline particles of semiconductors, metals or magnetic materials comprising of ~ 100 to ~100,000 atoms.\textsuperscript{1,2} The size range can vary from 1-100 nm although typically the most interesting structures are in the 2-10 nm diameter range. Nanocrystals represent an intermediate size regime between molecules and bulk solids and therefore display distinct physical and chemical properties as a function of size.\textsuperscript{3} This allows tuning of the electronic structure and the resultant optical properties leading to new phenomena, such as size dependent band gap. II-VI nanocrystals such as the cadmium chalcogenides (CdE, E= S, Se, Te) are the most extensively investigated colloidal semiconductor materials and serve as an excellent starting point for understanding how nanocrystal size, shape, and composition can be used to govern their physical properties.\textsuperscript{3-7} Figure 1.1 shows how the fluorescence emission of colloidal solutions of CdSe nanocrystals, result in different wavelengths depending on their size. Such control allows tailoring the nanocrystal design for a range of applications including photodetectors, catalysis, biolabeling, energy storage and conversion.

![Figure 1.1: Size-dependent change of the photoluminescence colour of colloidal solutions of CdSe nanocrystals.\textsuperscript{8}](image_url)
1.2 Quantum Confinement Effects

Semiconductors are predominantly crystalline materials which are characterized by a fixed distance between the filled and unfilled electronic bands, which are called the valence and conduction bands, respectively, allowing the flow of electrons upon excitation.\textsuperscript{9} Nanocrystals have an electronic structure that is intermediate between bulk solids and molecules as shown in Figure 1.2.\textsuperscript{10, 11} Material smaller than their natural radius of the electron-hole pair (Wannier exciton), require more energy to “confine” their excitons within the material. This confinement is referred to as quantum confinement which leads to changes in the electronic and optical properties of material compared to their bulk phase.\textsuperscript{10-12} These properties can be tuned by physically changing the size of material in one (quantum well), two (quantum wires such as nanorod and nanowire) and three dimensions (quantum dot).\textsuperscript{10} When the size of the material is much larger than the Bohr radius no quantum confinement effects are observed. The Bohr radii are material dependent and depend largely on the chemical structure of the materials. Table 1.0 shows Bohr radii of a range of semiconductors. The materials used in this thesis are highlighted in grey.

Figure 1.2: Relation between the electronic structure of bulk semiconductor solid and nanocrystal.

Electronic structure of semiconductor material
<table>
<thead>
<tr>
<th>Material</th>
<th>Bohr Exciton Radius (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>4.9</td>
<td>13</td>
</tr>
<tr>
<td>Ge</td>
<td>17.7</td>
<td>14</td>
</tr>
<tr>
<td>CdS</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td>CdSe</td>
<td>5.4</td>
<td>16</td>
</tr>
<tr>
<td>CdTe</td>
<td>7.3</td>
<td>17</td>
</tr>
<tr>
<td>GaAs</td>
<td>14</td>
<td>18</td>
</tr>
<tr>
<td>PbS</td>
<td>20</td>
<td>19</td>
</tr>
<tr>
<td>PbSe</td>
<td>46</td>
<td>19</td>
</tr>
<tr>
<td>CuZnSnS$_4$ (CZTS)</td>
<td>2.6</td>
<td>20</td>
</tr>
<tr>
<td>CuInS$_2$</td>
<td>3.8</td>
<td>21</td>
</tr>
<tr>
<td>CuInSe$_2$</td>
<td>7.6</td>
<td>22</td>
</tr>
<tr>
<td>CuGaSe$_2$</td>
<td>5.1</td>
<td>23</td>
</tr>
<tr>
<td>ZnS</td>
<td>2.5</td>
<td>24</td>
</tr>
</tbody>
</table>

Table 1.0: Table shows the Bohr radii of a range of semiconductor materials.

1.3 Optical Properties of Semiconductor Nanocrystals

The absorption and emission properties of semiconductor nanocrystals are characterized by photoluminescence colour, photo-stability and photoluminescence quantum yield that depends on the size, surface passivation and shape of the nanocrystal. The size of a nanocrystal, as discussed above, dictates the band gap and a shift in emission spectra as the result of quantum size effects. These size dependence optical properties of semiconductor nanocrystal were discovered in 1982 and 1983 by Henglein et al. and Brus et al.
respectively. In both studies, the optical spectrum shows that the colour of nanocrystals correlates strongly with their size. Surface modification for increased photostability and quantum yield can be achieved by effective ligand coverage or by overgrowth with a shell of a second semiconductor having larger band gap which passivates non-radiative recombination or surface trap sites. The shape of nanocrystal affects the electronic structure and distribution of electrons within the nanocrystals. Growth of nanocrystals from nanoparticles confined in all three dimensions (0D) to 2D nanorods (1D) causes a shift in emission spectra and a change in Stokes shift. Growing particle into 1D (nanorods) adds extra length dependent properties such as dipole moment, conductivity and linearly polarized emission along the c-axis whereas the diameter dependent properties such as band gap can be largely preserved.

1.4 Synthesis and Shape Control of Colloidal Nanocrystals

The solution-based colloidal synthesis of inorganic semiconductor nanocrystals has been extensively studied for over the last two decades to produce a variety of nanocrystalline materials with excellent control over their size, shape and elemental composition. Typically, colloidal nanocrystals are synthesized via the thermal decomposition of molecular precursors, that is, inorganic salts or organometallic compounds at high temperature in the presence of stabilizing agents (surfactant or ligand). The colloidal synthesis involves several consecutive stages which start with burst nucleation from initially homogeneous solution followed by growth of the nuclei and subsequent isolation of particles reaching the desired size from the reaction mixture. The main reaction parameters are the temperature, monomer concentration, growth time and the choice of the inorganic precursors and surfactants, which can be used to tune the kinetics of nucleation and growth of the nanocrystals. Typical surfactants/ligands are long chain organic molecules with varying
functional groups such as amines, phosphonic acids etc. (list in Table 1.1) which serve the dual role of influencing the growth kinetics and also stabilising the particles in solution (organic or aqueous). In addition, the ligands also influence the surface charge on the nanocrystal which ensures colloid stability by steric hindrance and influences their ability to adhere to a substrate. 

Judicious selection of ligands for a particular synthesis is necessary and it involves understanding of the ligand and their strong or weak interaction with cation, anion and crystal facets which influence the size, shape and structure of nanocrystal. The key step for narrowing the size distribution during nanocrystal growth is the temporal separation of nucleation and growth stages which can be achieved either by a hot-injection technique or by steady heating of the reaction mixture. In the hot-injection method, the precursors are rapidly injected into a hot solvent, giving “burst nucleation” with a subsequent temperature drop allowing the growth at a lower temperature. Using these approaches, all the nanocrystals to be formed in the reaction have a single nucleation event, leading to equal growth which rapidly consumes the available monomer, allowing the preparation of highly uniform nanocrystals. It is important to prevent additional nucleation events during the subsequent growth process as this will broaden the size distribution. Also, if the growth of nanocrystals continues in the solution, secondary growth by Ostwald ripening can occur, where larger particles grow at the expense of smaller ones which eventually leads to saturation of the system. As a result, there is an increase of average particle size with growth time. The separation of nucleation and growth stages is adapted from La Mer and Dinegar model as shown in Figure 1.3.
<table>
<thead>
<tr>
<th>Ligands/Surfactant</th>
<th>Alkyl chain length (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Phosphonic Acid</strong></td>
<td></td>
</tr>
<tr>
<td>n-octadecylphosphonic acid (ODPA)</td>
<td>18</td>
</tr>
<tr>
<td>n-tetradecylphosphonic acid (TDPA)</td>
<td>14</td>
</tr>
<tr>
<td>n-hexadecylyphosphonic acid (HDPA)</td>
<td>16</td>
</tr>
<tr>
<td>n-dodecylphosphonic acid (DDPA)</td>
<td>12</td>
</tr>
<tr>
<td>n-decylphosphonic acid (DPA)</td>
<td>10</td>
</tr>
<tr>
<td>n-octylphosphonic acid (OPA)</td>
<td>8</td>
</tr>
<tr>
<td>n-hexylphosphonic acid (HPA)</td>
<td>6</td>
</tr>
<tr>
<td><strong>Thiols</strong></td>
<td></td>
</tr>
<tr>
<td>n-dodecanethiol (DDT)</td>
<td>12</td>
</tr>
<tr>
<td>1-octadecanethiol (ODDT)</td>
<td>18</td>
</tr>
<tr>
<td>tert-dodecylymercaptane (t-DDT)</td>
<td>12</td>
</tr>
<tr>
<td>n-hexadecanethiol (HDDT)</td>
<td>16</td>
</tr>
<tr>
<td><strong>Amines</strong></td>
<td></td>
</tr>
<tr>
<td>Dodecylamine (DDA)</td>
<td>12</td>
</tr>
<tr>
<td>1-hexadecylamine (HDA)</td>
<td>16</td>
</tr>
<tr>
<td>Oleylamine (OAm)</td>
<td>18</td>
</tr>
<tr>
<td>Octylamine</td>
<td>8</td>
</tr>
<tr>
<td>Hexylamine</td>
<td>6</td>
</tr>
<tr>
<td><strong>Phosphine/oxide</strong></td>
<td></td>
</tr>
<tr>
<td>Trioctylphosphine (TOP)</td>
<td>24</td>
</tr>
<tr>
<td>Tributylphosphine (TBP)</td>
<td>12</td>
</tr>
<tr>
<td>Trioctylphosphine oxide (TOPO)</td>
<td>24</td>
</tr>
<tr>
<td><strong>Others</strong></td>
<td></td>
</tr>
<tr>
<td>Oleic acid (OA)</td>
<td>18</td>
</tr>
<tr>
<td>3-mercaptopropionic acid (MPA)</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 1.1: List contains different type of ligands that are mostly used in the colloidal synthesis of nanocrystals.
Figure 1.3: Schematic representation showing the different stages of nucleation and growth for the preparation of monodisperse nanocrystals as per La Mer and Dinegar model.\textsuperscript{6}

With advancement in colloidal synthesis, nanocrystals with different shapes such as rods, tetrapods, wires, cubes, disks, arrows, pyramids and octopods can be produced in high quantities through judicious control and choice of the growth conditions.\textsuperscript{36-48} These shapes of nanocrystals are possible to envisage by considering the symmetry of the underlying crystal lattice. For example, lead sulphide (PbS) nanocrystal can be synthesised in the form of spheres, cubes, octahedrons as it crystallizes in the cubic rock-salt phase.\textsuperscript{28, 46} The colloidal synthesis provides freedom to modulate the shape of nanocrystals by selective adhesion of surfactant molecules to different crystal facets allowing their growth kinetics to be tuned.\textsuperscript{42, 44} The surfactant molecules that bind strongly to particular facets will suppress their growth by preventing monomer addition to these surfaces. The shape control mechanism is very well
studied for the binary semiconductor nanocrystal (II-VI) synthesis. Typically cadmium selenide (CdSe) nanorods are synthesised by hot injection method in which a metal precursor such as Cadmium oxide (CdO) and surfactants/solvents (TOPO and TDPA) are put initially in the reaction flask and heated at high temperature (~310 degree Celsius) under inert atmosphere to form an intermediate cadmium-phosphonate complex. At that temperature, the injection of anionic precursor such as (Se+TOP) in the reaction flask gives a burst nucleation which is followed by growth. CdSe possesses a hexagonal wurtzite crystal structure. As a wurtzite crystal is inherently anisotropic, it is possible to extend growth along the c-axis to form nanorods. This was achieved by using mixture of surfactants (TOPO/HPA) to provide the difference in growth rate in different crystallographic directions. A study by Manna et al. shows the effect of HPA and its concentration variation in the reaction. In subsequent work, the controlled transformation of nanocrystals from spherical to elongated shape (rod, arrow and tree) has been highlighted with the increase in concentration of HPA as shown in Figure 1.4 a-c. In their further studies, they have shown that the more complex tetrapod shaped CdTe nanocrystal can be synthesised by make use of the energy difference between the wurtzite and the zinc-blende structures. This energy difference range suggests that one structure is formed during nucleation at high temperature and the other during growth at lower temperature. The tetrapod shape arises from a zinc-blende core and 4 equivalent length wurtzite-phase arms nucleating from the (111) facets of this core (Figure 1.4 d). The abilities to control systematically and precisely the crystal phase and branching can be used to grow a rich variety of nanoscale building blocks.
Figure 1.4: HRTEM and LRTEM images of a spherical shaped (a) rod shaped (b) arrow and tree-shaped (c) and tetrapod shaped nanocrystals.

1.5 Synthesis of Compound Semiconductor Nanocrystal

Extension of colloidal nanocrystal synthesis from binary to ternary and quaternary materials is very interesting as it greatly extends the application set in addition to allowing for flexibility in tuning properties not just by size but also by varying the relative composition of constituent elements. The most attractive materials incorporate elements that are non-toxic
and of high elemental abundance in ternary (I-III-VI$_2$) and quaternary I$_2$-II-IV-VI$_4$
compounds.\textsuperscript{49-51} For example, copper indium (di) selenide/sulphide (CIS), copper indium
gallium (di) selenide/sulphide (CIGS), copper zinc tin sulphide/ selenide (CZTS) and copper
zinc/tin germanium selenide \textit{etc}.\textsuperscript{50,51} All these compound semiconductor materials are direct
band gap materials (0.9 -2.4 eV), possessing high radiation stabilities and high absorption
coefficient in the range of $\sim 10^5$ cm$^{-1}$.\textsuperscript{49-51} These materials are already widely produced in thin
film form and are very promising for photovoltaic applications.\textsuperscript{51} The current challenge limits
large scale application is their high production costs by vacuum processes. Solution synthesis
of these ternary and quaternary materials in nanocrystal form opens a new route towards low-
cost fabrication methods.\textsuperscript{49, 52-80} The colloidal solution “ink” can be easily coated to any
substrate using spin coating, printing, spraying \textit{etc}.\textsuperscript{49,53,55} A further advantage is that in
nanocrystals the stoichiometry is locked in in each crystal form and the presence of
secondary phases as an impurity (common in vacuum deposited film)\textsuperscript{51,83-86} can be eliminated
greatly improving the device properties. Several synthetic routes have been explored to
generate these material at nanometer scale including colloidal methods (hot-injection or no-
injection), chemical transformation, hydrothermal techniques and thermal decomposition of
suitable precursor.\textsuperscript{52-82} In all these approaches, the colloidal route is the most studied and
successful in controlling the size, shape, composition and crystal structure.

Forming these multicomponent materials by colloidal routes is not trivial due to the
complexity of the constituent elements and the key to impurity free synthesis with crystal
structure control is balancing the reactivity of constituent precursors by their ligands, reaction
temperature and solvent composition. Many of the studies show that the hard-soft-acid-base
(HSAB) theory can be utilised in selection of the precursors so that their relative reactivity
can be tailored precisely.\textsuperscript{58, 61, 64, 76, 82} According to HSAB theory, the tendency to donate and
accept an electron can be used to classify these elemental ions as an acid or base. These acid
and bases are further classified as hard and soft according to their atomic/ionic radius, polarizability, oxidation states and electronegativity. For example, in case of CuInS$_2$ nanocrystals synthesized in the presence of thiols, to slow down the reactivity of Copper ion (Cu$^+$) in the reaction, copper iodide (CuI) is used in place of copper acetate (CuAC). Cu$^+$ ion is a soft acid and I$^-$ is a soft base in comparison to Ac$^-$ ion which is a hard base. Thus, Cu$^+$ ion react slowly with thiols (soft base, I$^-$ > thiols) which suppress the copper sulphide growth and allow CuInS$_2$ nanocrystal growth.$^{58}$ By this approach, not only is the purity of single phase material increased but also the new crystal phase can be prepared which is generally not thermodynamically stable in the bulk phase, for example wurtzite and zinc blend structures of ternary and quaternary copper chalcogenide are not stable in the bulk phases.$^{58, 61, 62-64, 68, 76, 78, 82}$

As in colloidal synthesis, the presence of capping ligands is known to strongly influence the crystallographic phase, morphology, and growth direction of the nanocrystals.$^{38, 42, 44, 58}$ Thus, proper selection of the capping ligands can be used to induce the stabilities of these metastable phases (wurtzite & zinc blend) but also it is possible to prepare their bulk phase (chalcopyrite or kesterite) at the nanometer size regime.$^{52-82}$ Like in II-VI nanocrystal formation, the combination of capping ligands shows similar control over the growth direction and crystal phase of these multicomponent nanocrystals.$^{44}$ For example in the case of CZTS nanocrystal, the use of only DDT leads to pseudo-spherical nanocrystal while a combination with t-DDT leads to the nanorod growth in a (002) direction. There are other factors like reaction temperature, solvents and injection temperature which have an influence on the nanocrystals.$^{63}$ This has been discussed in detail in chapter 2. Recently Agrawal and co-workers used these compound semiconductor (ternary and quaternary) nanocrystals as absorber layers by using simple solution processes and then converted the nanocrystals to thin film form by selenization.$^{52, 53, 56}$ The film showed a conversion efficiency of 7.2%.$^{53}$ The
other important properties of these multicomponent copper chalcogenide such as CuZnSnSe, CuZnGeSe, CuCdSnSe and CuZnSnS as a thermoelectric material has been exploited by Cabot and co-workers, who showed that these nanocrystals have a higher thermoelectric merit then their bulk analogous.\textsuperscript{60,77-79} Therefore, colloidal synthesis provides the degree of freedom to substitute the various elements (Cd, Zn, Sn, In, Ga, Ge, Si, Co, Mn etc) in multicomponent copper chalcogenides to further explore their properties for magnetic, thermoelectric, and solar cell application.

Another simple method to prepare these nanocrystals is by chemical transformation of preformed nanocrystals by selective cation exchange protocol.\textsuperscript{87-98} In recent years, cation exchange has become a powerful technique for generating binary copper/silver chalcogenides from cadmium chalcogenides by replacing the cations within the nanocrystal lattice with different metal ion (Cu\textsuperscript{2+}/Ag\textsuperscript{2+}).\textsuperscript{87, 88, 93, 94} For example, the addition of Cu\textsuperscript{2+} cation to CdS leads to their complete conversion to the Cu\textsubscript{2}S or Cu\textsubscript{7}S\textsubscript{4}.\textsuperscript{87, 93-95} The chemical transformation of the nanocrystal occurs via diffusion or exchange of atoms in the lattice that is only kinetically feasible at the nanoscale. The diffusion or exchange of atoms can be made possible by using a coordinating molecule (methanol, TOP, TBP etc) that preferentially binds the cations (Cd\textsuperscript{2+}) within the nanocrystal lattice over the Cu\textsuperscript{2+}/Ag\textsuperscript{2+}. Depending upon the mobilities of cations within the crystal lattices, complete cation exchange can either occur rapidly in seconds at room temperature or can require high temperatures. For example, in case of cation exchange from CdS to Cu\textsubscript{2}S nanocrystals, the initial yellow colour of CdS nanocrystals changes within one second to brown which indicates the complete exchange of Cd\textsuperscript{2+} to Cu\textsuperscript{2+} ion. Partial exchange in nanocrystals is also possible by controlling the concentration of substitutional cations in solution. This process has been already shown in the exchange of different chalcogenides with various cations (Zn, Sn, Hg, Pb, Sb, and Bi).\textsuperscript{89-92, 95-98} The other important feature of this process is that it allows the shape of nanocrystals to be conserved
once it’s above the critical size threshold. The critical size threshold means that there is a certain size limit (in case of CdSe ~4 nm) above which the rigidity of anion sublattice in a structure is preserved, which allow the replacement of cation while retaining the initial shape of nanocrystal during the cation exchange. If the size of a nanocrystal is below the threshold size, the anion sublattice does not stay intact during exchange and nanocrystal transform toward equilibrium shape with lowest energy (from rod to spherical). As the cation exchange happens so fast and is feasible at room temperature, it is possible to do partial or fully cation exchange of existing mono or multi-layer nanorod assemblies without disturbing the assembly through simple solution or spin exchange method (Figure 1.5). Also this process is fully reversible to get back to the starting material (e.g. CdS-Cu2S-CdS). Recently Trizio et al. have shown that the chemical transformation is also feasible in ternary CuInS\textsubscript{2} nanocrystal to form quaternary Cu-In-Zn-S nanocrystal by partial exchange of copper with zinc cations with a precise control on their chemical composition and crystal phase.
Figure 1.5: (a) & (b) HRTEM images show before and after cation exchange of vertically aligned monolayers of CdS nanorods to Cu$_7$S$_4$ nanorods and (c) Partially exchanged multilayer vertical assembly using spin exchange process. The yellow colour of CdS can be seen clearly in the mirror while the brown colour of Cu$_7$S$_4$ can be seen in the foreground (Figure is modified with respect to the published).\textsuperscript{94}

1.6 Assembly of Nanocrystals

The propensity of uniform nanoparticles/nanocrystals to self-assemble into well-organized close-packed structures is of considerable interest on both a fundamental and practical level. In these close-packed structures,\textsuperscript{99,100} it is possible to harness their individual as well as
collective properties towards applications in nano-electronics, bio-labelling, nano-magnetics, fuels cells and photovoltaics. Assembly of spherical nanocrystals has been extensively studied both experimentally and theoretically. The most widely adopted approach to form organized superstructures of nanocrystal is by self-assembly during controlled solvent evaporation. In this process, the nanocrystals are dispersed in an appropriate carrier solvent (mostly organic such as toluene, hexane etc.) followed by solvent evaporation. During solvent drying, the local concentration gradient of nanocrystals (underneath the liquid surface) increases which reduces the distance between nanocrystals. This initiates various attractive (dipole-dipole) and repulsion interactions (Columbic) which ultimately stabilise or force the nanocrystals into a close packed 2D structure at the surface. These structures may be further assisted by surface tension which helps in holding the assembly at the surface. There are other factors which cannot be ruled out such as the rate of solvent evaporation, solvent dielectric, nanocrystal charge, dispersibility of nanocrystal etc. which also influence the final structure of the assembly. Consequently, new materials with extraordinary properties can be designed with nanocrystal size, elemental composition (metal, semiconductor), hetero particular distribution and inter-particle spacing as control factors. The parallels between the repeat order of spherical nanocrystals to that typical of atoms in crystalline solids gives a rich template of possible superstructures based on interstitial close packing which leads to more complex binary, ternary and quaternary nanocrystal superlattices with different type of crystal packing ranging from AlB₂, CsCl, AB, AB₂, AB₃, AB₄, AB₅, CuAu, MgZn₂, etc. In colloidal nanocrystals, the ability to control shape in addition to size adds even greater complexity to possible superstructure formation.

Assembly of elongated particles (eg. nanorods) into organized superstructures is inherently more difficult to achieve due to their anisotropy. To date, a range of
approaches have been developed which utilise physical properties such as charge and dipole or the presence or absence of external forces to enable assembly.\textsuperscript{31,132-159} In these processes nanorods spontaneously organize into ordered arrays due to either direct interactions between the nanocrystals through inter-particle forces or indirect interaction through their environment, mainly solvent and capping ligands. There are many different ways in which self-assembly plays a major role in organizing nanorods into superstructures. Self-assembly of nanorods can be divided into four categories, namely, (i) drying or evaporation-mediated assembly; (ii) assembly occurring in solution; (iii) assembly occurring at liquid-liquid and liquid-air interfaces; (iv) assembly assisted by external fields.

**Drying or Evaporation Mediated Assembly**

Assembly of nanorods by simple drying or solvent evaporation has been recognized as an extremely simple route to form close-packed structures of nanorods of various materials from metal to semiconductor.\textsuperscript{133-140} In this approach, a drop of nanorod dispersion is cast on the substrate and the solvent is allowed to completely evaporate. To understand the assembly process requires the consideration of various attractive and repulsive forces occurring between nanorods such as dipole-dipole interaction, electrostatic attraction and repulsion, depletion attraction, steric forces and also the solvent evaporation dynamics. The various attractive forces cause the nanorods to come close to each other while repulsive forces assist to stabilize nanorods to maintain the certain distance and direct the nanorods to nucleate the ordered phase.\textsuperscript{109, 137} Depending upon the initial concentration of the nanorod solution, parallel and perpendicular alignment up to micron and centimetre size areas is possible.\textsuperscript{134-139} Baker \textit{et al.} has explored the use of excess surfactant in the nanorod dispersion which leads to micron size monolayer vertical assemblies of CdS nanorod.\textsuperscript{135} The excess surfactant in the nanorod solution induces depletion-attraction interactions between the nanorods which helps
in nucleating the nanorod assemblies. Zanella et al. have further extended the size and number of layers in the assembly by slowing down the rate of solvent evaporation, using high boiling point solvent (ortho-dichlorobenzene or xylene) with saturated solvent environment (Figure 1.6) on CdSe/CdS nanorod assembly.\textsuperscript{136} This facile approach leads to multilayer assembly over device scale areas and is independent of the substrate. There are a few drawbacks to this approach as there is no precise control over the number of layers deposited and the assembly takes a long time.

![Figure 1.6](image)

**Figure 1.6:** (a) Schematic shows the set up for vertical nanorod assembly by slow evaporation of solvent (b) SEM images shows the multilayer assembly obtained by this process (*Figure is modified with respect to the published*).\textsuperscript{136}

The other viable route which allows control over nanorod assembly during solvent drying is the use of external directing agents such as HOPG or block-copolymers.\textsuperscript{141, 142} The surface roughness of HOPG is used to create narrow capillary forces to trap the nanorods with further assistance by evaporation of the solvent, leading to vertically alignment of the nanorods. Figure 1.7 shows the schematic representation of the process. The assembly is independent of substrate and achieved over micron range.
Assembly Occurring in Solution

To assemble nanorods in solution (defined here as assembly that occurs within the solvent without the requirement for evaporation) is also possible by exploiting the various types of interactions between the nanorods such as van der Waals, dipole-dipole and depletion attraction forces by either reducing the solubility of ligands or destabilization the nanorod solution. Here instead of forming at a substrate, the rods corral together typically in discs and then drop to the bottom of the solution under gravity sedimentation. Talapin et al. showed the first report to induce the organization of nanorods in solution into highly luminescent 3D superlattices or nanorod solids. The assembly was triggered by the slow destabilization of a nanorod solution upon allowing the diffusion of a non-solvent (methanol) into the nanorod dispersion. These nanorod solids settle down in bottom of a vial/tube over a period of time and can be transferred to any substrate. The processes involved in super-crystallization of nanorods in solution can be rationalised by considering the entropy driven and electrostatic interaction process. The entropy of the system increases when solute molecules are eliminated from between the nanorods. Manna and co-workers later utilized the depletion forces to assemble CdSe/CdS nanorods into close packed vertically aligned multilayer arrays.
In this approach, assembly was triggered by adding various additives to a stable colloidal solution of nanorods. These additives are generally long-alkyl-chain fatty acids and amines (oleic acid, hexadecylamine) or polymers (polystyrene, poly(ethylene glycol) methacrylate) which do not interact with the nanorods. The size of additives should be larger than the separation between the nanorods to induce the depletion interactions. An osmotic pressure is evolved between the nanorods due to the exclusion of the additive from the space between the nanorods which results in a local concentration gradient, and hence starts the nucleation of nanorod assembly in solution to form 2D sheets as shown in Figure 1.8. This nucleation or phase transition in nanorod solutions can be governed by the strength of depletion interaction, which depends upon size of the additive and its concentration in solution. These 2D sheets are comprised of nanorods preferentially packed in side by side fashion.
Figure 1.8: Schematic representation shows nanorod assembly driven by depletion attraction.\textsuperscript{144}

Assembly occurring at liquid-liquid and liquid-air interfaces

The organization of nanorods into ordered structures has been achieved at various interface such as liquid-liquid and liquid-air interface to give a rich template for nanorod assembly. Interfacial assembly is driven by the total reduction of interfacial free energy and is further facilitated by interface mediated capillary forces of varying origin. This process uses the trapping of nanocrystals at the interface in place of gravity sedimentation and is based upon the Pickering-Ramsden emulsions phenomenon.\textsuperscript{160-163} By carefully controlling the aspect
ratio, concentration, solvent nature, surface properties and solvent evaporation rates, different type of nanorod assemblies from 1D to 2D and 3D structures are possible. The mechanism behind the assembly of the nanorods at the liquid-liquid or liquid-air interface differs significantly from that of spherical nanocrystals where the close-packed assembly is generally preferred due to the inter-particle interactions. In the case of nanorods, the anisotropy gives rise to shape and spatially dependent interface mediated capillary forces due to undulation of the contact line at the interface. The assembly driven by these interactions in the case of nanorods leads to either end to end or side by side alignment. Kim et al. was first to show the use of liquid-air interface for assembling highly anisotropic 1D nanostructure such nanorods (BaCrO$_4$) and nanowires into isotropic, nematic or smectic liquid crystal phase by using Langmuir-Blodget (LB) technique. In LB, pressure induced isotropic-nematic-smectic phase transitions and subsequent transformation from monolayer to multilayer has been shown. However, the precise control over orientation from parallel (1D) to perpendicular (2D/3D) of nanorods over large areas is yet to be achieved. Later, Murray and co-workers used the simple protocol to explore the self-assembly of nanocrystals (spherical or nanorods) at a liquid-air and liquid-liquid interface by simply drop casting the nanocrystal dispersion on an immiscible subphase and allowing the solvent to evaporate. Assembly of nanorods using this approach has reached a point where control over orientation from 1D to 2D has been shown. In this approach, a certain concentration of nanocrystals (spherical or nanorods) dispersed in solvent (hexane, toluene etc.) was drop-cast onto an immiscible liquid surface such as ethylene glycol, diethylene glycol and acetonitrile in a Teflon well and the solvent was allowed to evaporate slowly. This resulted in the nanocrystal forming a solid film of centimetre scale suspended on the subphase surface. This solid floating film of nanocrystals could be easily transferred onto any surface such as a TEM grid, glass, silicon, indium tin oxide (ITO) etc. as shown in Figure 1.9.
Figure 1.9: (a) A Schematic representation shows the growth and transfer processes of nanocrystal assembly at liquid-air interface. (b) LRSEM image of binary nanocrystal self-assembled membranes from 15-nm Fe₃O₄ and 6-nm FePt nanocrystals obtained at liquid-air interface with inset HRTEM image shows clearly two types of nanocrystal self-assembled in AlB₂-type and SAED pattern. (c) & (d) LRTEM images show parallel and vertical assembly of NaYF₄ nanorod obtained by same approach (*Figure is modified with respect to the published*).
Assembly assisted by external fields or substrates

One of the direct strategies to assemble nanorods is the use of external field to control precisely the orientation of nanorods. The presence of a net charge on colloidal nanocrystals gives a viable parameter that can be influenced externally by using an electric fields to achieve their controlled deposition. Like the other assembly approaches, the initial studies on directed assembly in the presence of electric field has been explored for spherical nanocrystals and pioneered by Herman and co-workers. This approach has been optimised to point where not just control over the number of layers and close packed order but localization of spherical nanocrystal assemblies to discrete lithographic trenches is routinely achieved. However, the nanocrystal shape has an influence on their spatial organization under an external electric field. In the case of nanorods, the non-centrosymmetric wurtzite lattice gives a permanent dipole moment which can be further used to control both translation and orientational order. In the very first report of nanorods assembled in the presence of an electric field, a toluene solution of nanorods was drop-cast on gold coated copper electrode and solvent was allowed to evaporate in the presence of an applied electric field. Nanorods have a dipole moment which allows them to orientate parallel to an electric field which if further assisted by either solvent evaporation or polymer phase separation, allows the nanorods to close pack in vertical arrays. Figure 1.10a shows the schematic set-up of this process. The vertical nanorod arrays formed using this approach are typically of \( \sim \mu m^2 \) areas in size. This process has been further extended to lateral alignment of nanorods using lithographically fabricated interdigitated electrodes having micrometre spacing between the electrodes. The combined field with evaporation or polymer phase separation approaches leads to assemblies that have been primarily of the order of a few micron limiting their applicability for real device applications. Ahmed *et al.*
extended this assembly protocol to centimetre scale where each nanorod are vertically aligned and closed packed using an electrophoretic deposition approach. In this approach, a direct current (dc) voltage was applied between two copper electrodes having ~2 cm spacing within a nanorod solution. A conductive substrate was clamped to one of the electrode depending upon the net charge on nanorod. Nanorods have a dipole moment and net charge, the former helps them to orient parallel to electric field with the latter causing them to migrate towards electrode and deposit on the substrate as shown in Figure 1.10b. Here the packing of the rods at the substrate is caused by the field driven forces of electrophoresis such that rod assembly occurs without the requirement of evaporation or external additives. The various properties and applications associated with these assembled structure of nanorod is discussed in later section.

**Figure 1.10:** (a) Schematic of electrode and the process involved for nanorod assembly in the presence of dc electric field. (b) Schematic representation shows the EPD setup and the centimetre scale assembly of CdS nanorod on ITO.
1.7 Properties of Assembled Nanorods

In the case of semiconductor nanorods, their collective properties arise mainly due to resonance energy transfer as a result of dipole-dipole interaction between nanorods in the assembled structure.\textsuperscript{31} A theoretical study done by Schrier \textit{et al.} using a semi-empirical pseudopotential method shows that the shape of nanocrystals (spherical and rod) and their respective orientation (parallel or vertical in case of rod) have significant effect on their resonant energy transfer.\textsuperscript{172} These properties not only depend upon the centre to centre distance between nanorods but also on the orientation of the nanorods. It was also highlighted that the coupling between nanorods aligned vertically was significantly higher than those parallel aligned, which is important for nanorod-based devices where directional properties of nanorods can be further exploited in a fruitful manner.\textsuperscript{31, 132, 172} Also, Huynh \textit{et al.} and Gur \textit{et al.} proposed a device structure in their studies on nanorod-hybrid and all-inorganic nanorod based solar cell.\textsuperscript{173, 174} It was emphasised in those studies that vertically aligned semiconductor nanorods will give direct charge pathways towards electrode and minimize charge recombination, compared to the randomly oriented nanorods.

Photoluminescence (PL) studies on CdSe/CdS nanorod arrays with different orientation such as parallel, vertical and random with respect to the substrate are shown in Figure 1.11.\textsuperscript{151} The shift in the PL emission is directly correlated with the orientation of nanorods on the substrate. This energy shift results from screening of an internal (piezo) electric field present in the individual nanorods due to the photogenerated charge distributions in neighbouring nanorods. This charge distribution was more efficient in ordered assemblies then disordered aggregates.

The ability to assemble nanorods into close-packed ordered arrays on centimetre length scale makes them an interesting material for potential applications in light emitting diodes
and bio-labelling.\textsuperscript{31, 175-179} For example; Rizzo et al. used parallel aligned nanorods to fabricate a polarized light emitting diode while Sanyal \textit{et al.} used side by side assembled nanorods as a biomarker in aqueous medium.\textsuperscript{176,179} Finally, semiconductor nanorods have demonstrated extremely promising properties both at an individual level and in the form of large assemblies. This provides further motivation for future work in the area of nanorod assembly.

\textbf{Figure 1.11:} PL spectrum from parallel vertically aligned and randomly oriented nanorods with relative Gaussian best fit curves (green lines). The upper panel shows corresponding TEM, PL and laser backscattering images of regions consisting of disordered, vertically, and parallel aligned CdSe/CdS nanorod.\textsuperscript{151}
1.8 References


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Chapter 2: Colloidal Synthesis of Wurtzite Cu$_2$ZnSnS$_4$ Nanorods and Their Perpendicular Assembly

2.1 Abstract

The quaternary copper chalcogenide Cu$_2$ZnSnS$_4$ is an important emerging material for the development of low-cost and sustainable solar cells. A facile solution synthesis of stoichiometric Cu$_2$ZnSnS$_4$ in size-controlled nanorod form (11 nm × 35 nm) has been developed. The monodisperse nanorods have a band gap of 1.43 eV and can be assembled into perpendicularly aligned arrays by controlled evaporation from solution.

2.2 Introduction

Colloidal semiconductor nanocrystals are a remarkable material set that can be synthesized and processed as a “chemical” in high yield while exhibiting optical and electronic properties that are size-dependent.\textsuperscript{1, 2} Applications ranging from biolabeling to photocatalysis and photovoltaics that exploit either the discrete or collective properties of these size-controlled crystals have emerged.\textsuperscript{3–7} The synthesis of the archetypal binary (II–VI) nanocrystals has progressed to the point where precise control over their size, shape, composition, and crystal phase has become routine, thereby rapidly accelerating the advances that utilize these as building blocks.\textsuperscript{2,8–10} Extension of colloidal nanocrystal synthesis to ternary and quaternary semiconductors has the capacity to expand this research platform greatly.\textsuperscript{11–30}

In particular, copper-based ternary and quaternary semiconductors such as CuInS$_2$ (CIS), CuIn$_x$Ga$_{1−x}$Se$_2$ (CIGS), and Cu$_2$ZnSnS$_4$ (CZTS) are of interest because of their high absorption coefficients, low toxicities, and band gaps suitable for solar energy conversion.\textsuperscript{11–33} Advances in the colloidal synthesis and shape control of CIS and CIGS nanocrystals have been demonstrated, although similar reports for CZTS remain elusive.\textsuperscript{12–14} CZTS has been
flagged as the material most likely to allow unrestricted photovoltaic application on a global scale, given the relatively abundant nature of Zn and Sn in comparison with In and Ga and the promising efficiencies of 9.7%.\textsuperscript{31-34} Generating CZTS in nanocrystal form allows absorber layer production by simple solution processes (spin-casting, spraying, or printing methods), dramatically offsetting the cost of expensive vacuum processes.\textsuperscript{32-36} While synthesis of zero-dimensional (0D) CZTS nanocrystals in the tetragonal crystal structure has been achieved,\textsuperscript{21-25} their formation in the more attractive rod geometry remains elusive. In nanorods, maximization of total absorption and directional charge transfer is possible by controlling the length while retaining the diameter dependent properties such as band gap. Moreover, control of orientation and positioning such that each nanorod is vertically aligned and close-packed allows their collective properties to be harnessed at the device scale.\textsuperscript{37-47}

Herein we describe a colloidal synthesis of monodispersed stoichiometric CZTS nanorods in high yield. The quaternary semiconductor nanorods have the wurtzite crystal structure with elongation occurring along the [002] direction and exhibit a band gap of 1.43 eV. This crystal phase is not just attractive for shape control but is also known to allow wide-range tuning of the band gap as a result of the random distribution of In/Sn and Ga/Zn ions in the crystal structure.\textsuperscript{15, 16, 26} We further demonstrate the subsequent assembly of the rods into superstructures with each rod close-packed and oriented orthogonal to the substrate. The rod geometry, hierarchical assembly, and optimal crystal structure make this route of significant interest for low-cost photovoltaic devices.

2.3 Experimental

Chemicals

Copper (II) acetylacetonate (Cu(acac)$_2$; >99.99%), Tin(IV) acetate (Sn(OAc)$_4$, >99.99%), Zinc acetate (Zn(OAc)$_2$, >99.99%) Trioctylphosphine oxide (TOPO, 99%), 1-octadecene
(ODE, 90% tech), 1-dodecanethiol (1-DDT, 98%), tert-Dodecyl Mercaptan (t-DDT) were purchased from Aldrich. All chemicals were used as received without any further purification.

**Synthesis of Cu$_2$ZnSnS$_4$ Nanorods**

In a typical synthesis, copper(II) acetylacetonate (0.261 g, 1mmol), zinc acetate (0.091 g, 0.5mmol), tin(IV) acetate (0.177 g, 0.5 mmol), and trioctylphosphine oxide (1.353 g, 3.5mmol) were mixed with 10 mL of 1-octadecene in a three-neck round bottom flask and evacuated at room temperature for 30−45 min. The solution was then heated to 240−260 °C under an argon atmosphere. At 150−160 °C, a mixture of 0.25 mL of 1-dodecanethiol (1-DDT) and 1.75 mL of tert-dodecyl mercaptan (t-DDT) was quickly injected into the flask, resulting in an immediate color change from dark-green to wine-red and then finally to brown. After injection, the reaction was allowed to proceed for 15−30 min with continuous stirring. Nanorod growth was terminated by removal of the heating mantle, and at 80 °C, 2−4 mL of anhydrous toluene was added to the mixture to quench the reaction. The nanorods were then washed in 1:1 toluene/ethanol and centrifuged at 4000 rpm for 10 min to yield a brownish centrifuged product.

**Synthesis of wurtzite CZTS nanocrystal in presence of 1-DDT**

In a three-neck flask, copper(II) acetylacetonate (0.261 g, 1mmol), Zinc acetate (0.091 g, 0.5mmol), Tin(IV) acetate (0.177 g, 0.5mmol) and TOPO (1.353 g, 3.5mmol) were mixed with 10 mL of 1-octadecene. The contents of the flask were evacuated at room temperature for 30-45 minute to eliminate adventitious water and dissolved oxygen. The reaction mixture was then heated to 250 °C - 260 °C under argon flow and 2 ml of 1-DDT was rapidly injected into the system at 150-160 °C with continuous stirring. After injection, the solution colour
changed immediately from dark green to wine red and then finally to brown. The nanocrystals were allowed to grow for 15-30 minutes to reach the desired size, with nanocrystal growth terminated by removal of the heating mantle. After cooling to 80 °C, 2-3 mL of toluene was added to quench the reaction. The nanocrystal were washed 2-3 times in a 1:1 ratio of toluene to ethanol and centrifuged at 3000 rpm for 5 mins to yield a brownish centrifuged product. After each centrifugation, the supernatant was removed and the precipitated nanocrystals were redispersed in fresh solvents.

**Perpendicular Assembly of CZTS Nanorods**

To find the optimum concentration of CZTS nanorod for their perpendicular assembly was investigated by dropcasting solutions of various concentrations on to carbon supported Cu-TEM grids and the solvent was allowed to evaporate slowly. All experiment was performed in a similar environment (glove box) giving a constant evaporation rate. The strict concentration dependence of the nanorod solution is necessary for perpendicular nanorod assembly where outside of certain window, nanorods deposit randomly on the substrate. The optimum concentration was found to \((10^{-5} \text{ mol L}^{-1})\), resulting in the formation of 3D assemblies of CZTS nanorods.

**Transmission and scanning electron microscopy**

The morphology of CZTS nanorods and their vertical assemblies on Carbon supported TEM grids was characterized by transmission electron microscopy (TEM) and angular dark-field scanning transmission electron microscopy using a JEOL JEM-2011F operating at an accelerating voltage of 200 kV. An Energy dispersive spectroscopy (EDS) of CZTS nanorod on a silicon substrate was performed using a Hitachi SU-70 equipped with EDS detector.
X-Ray diffraction analysis

X-Ray diffractograms of drop-cast films of CZTS nanorods on a glass substrate were carried out on a PANalytical X'Pert MPD Pro using Cu Kα radiation with a 1-D X'Celerator strip detector.

X-Ray photoelectron spectroscopy

XPS measurement of CZTS nanorods were carried out using a Kratos Axis 165 spectrometer. High resolution spectra were taken using monochromated Al Kα radiation of energy of 1486.6 eV at fixed pass energy of 20 eV. For peak synthesis, a mixed Gaussian-Lorenzian function with a Shirley type background subtraction was used. Samples were flooded with low energy electrons for efficient charge neutralisation. Binding energies (BE) were determined using C 1s at 284.8 eV as charge reference.

Raman spectroscopy

Raman spectra of CZTS nanocrystals were collected from a Dilor XY Labram spectrometer equipped with an Olympus BX40 confocal microscope under ambient conditions by using a ArHe green laser.

UV-vis absorption spectra

UV-vis spectroscopy of CZTS nanorod solutions were carried out on a PerkinElmer's LAMBDA 35 UV-vis spectrophotometer operated at a resolution of 1 nm.
**Zeta-Potential Measurement**

Zeta-potential (ζ) was measured using Zeta PALS (Zeta Potential Analyzer, Brookhaven Instruments Corporation, US) using low and high electric-field, $E = 137 \text{ Vcm}^{-1}$ and $274 \text{ V cm}^{-1}$, across the palladium electrodes and measured zeta-potential values was constant from two fields which was averaged from 10 repeated experiments.

**2.4 Results and Discussion**

The dark-field scanning transmission electron microscopy (DF-STEM) image in Figure 1a shows that the nanorods were formed with good monodispersity, having an average length of $35 \pm 3 \text{ nm}$ and diameter of $11 \pm 0.5 \text{ nm}$. The as-synthesized CZTS nanorods were predominantly bullet-shaped with $\sim 7\%$ polydispersity, which could be improved by size-selective precipitation. The polycrystalline selected-area electron diffraction (SAED) pattern (Figure 1a inset) is indexed with rings to (002), (101), and (102), corresponding to the wurtzite phase of CZTS. High-resolution TEM (HRTEM) images of an individual bullet-shaped nanorod (Figure 1b) showed lattice fringes with a spacing of $d = 0.32 \text{ nm}$, which corresponds to the (002) lattice plane of the wurtzite CZTS structure. This growth direction along the $c$-axis is characteristic of the wurtzite phase, and its preferred formation in this synthesis, rather than kesterite, is critical to elongation. The key for stabilizing the wurtzite phase rather than kesterite is the use of dodecanethiol in the reaction, as it acts as both a sulfur source and a ligand. Dodecanethiol has been previously reported as a strong coordinating ligand for the wurtzite copper-based chalcogenide nanocrystals CIS and CIGS, while studying the effect of thiols (1-DDT and t-DDT) on the formation of wurtzite CZTS nanocrystals, we observed that a combination of the two is necessary for the nanorods to form. In addition, single-phase CZTS nanorods were formed only when the
thiols were injected at a temperature of < 200 °C to avoid the formation of unwanted Cu₂S side products. Synthesis carried out in the presence of only 1-DDT yielded only smaller pseudospherical wurtzite CZTS nanocrystals (Figure 2). Conversely, when the concentration of 1-DDT in the reaction mixture was doubled, the shape of the CZTS nanocrystals changed

**Figure 1:** (a) Dark-field STEM (DF-STEM) image of bullet shaped CZTS nanorods with inset showing the corresponding Selected Area Diffraction Pattern (SAED). (b) HRTEM image showing the bullet shaped CZTS nanorods are elongated in [002] direction. (c) DF-STEM image of CZTS nanorods synthesized in the presence of a higher 1-DDT concentration. (d) HRTEM image of single CZTS nanorod.
Figure 2: (a) Low resolution TEM image shows the as-synthesised pseudo-spherical CZTS nanocrystal prepared by using 1-DDT only. (b) HRTEM image shows the nanocrystal have good crystallinity of the nanocrystal. (c) XRD pattern of as-synthesized pseudo-spherical CZTS nanocrystal prepared in presence of only 1-DDT.
from bullet-shaped to more conventional rod-shaped (Figure 1c). This suggests that 1-DDT binds more strongly to facets other than (002), allowing anisotropic growth in this direction. The HRTEM image of an individual rod-shaped CZTS nanorod (Figure 1d) shows clear lattice fringes with \( d = 0.32 \) nm, corresponding to the (002) lattice planes of the wurtzite structure.

X-ray diffraction (XRD) was employed as a bulk analysis technique to ensure compositional homogeneity across the nanorod samples. A resultant XRD diffractogram (Figure 3a) shows major reflections at \( 2\theta \) values corresponding to the (100), (002), (101), (102), (110), (103), and (112) planes of a hexagonal structure and matching well with those of the previously reported CZTS wurtzite structure.\(^{26}\) This structure can be derived from wurtzite ZnS by substitution of Zn with Cu and Sn atoms.\(^{26}\) In particular, the XRD pattern of wurtzite CZTS matches the combined reflections from hexagonal ZnS and monoclinic \( \text{Cu}_2\text{SnS}_3 \), as shown in Figure 3a. The single Raman peak at 333 cm\(^{-1}\) is close to the value reported for bulk CZTS (Figure 3b).\(^{48}\) The noted broadening of the Raman peak has been seen previously for nanocrystals and is due to the phonon confinement within the nanocrystal.\(^{49}\) It is noticeable that there are no additional peaks for other phases such as ZnS, SnS, and \( \text{Cu}_2\text{S} \), which confirms the single phase of the CZTS nanorods.

X-ray photoelectron spectroscopy (XPS) was performed to investigate the chemistry of the CZTS nanorods. A survey spectrum of the synthesized nanorods identified the presence of Cu, Zn, Sn, S, O and C (Figure 4). High-resolution spectra of Zn 2p, Cu 2p, Sn 3d, and S 2p were measured to determine the oxidation states of the constituent elements (Figure 5). The narrow doublet peaks in the Cu 2p spectrum appear at 932.1 eV (2p\(_{3/2}\)) and 951.9 eV (2p\(_{1/2}\)); the peak separation of 19.8 eV is indicative of Cu(I).\(^{50,11}\) The peaks of Zn 2p appear at binding energies of 1021.6 and 1044.7 eV, which can be assigned to Zn(II) with a peak splitting of 23.1 eV.\(^{10}\) The Sn (IV) state was confirmed by peaks located at 486.4 and
Figure 3: (a) XRD pattern of as-synthesized wurtzite CZTS nanorods. For reference, the XRD pattern of wurtzite ZnS (PCPDF no. 98-001-7525) and monoclinic Cu2SnS3 (PCPDF no. 98-005-8919) are also shown. (b) Raman spectra of CZTS nanorods.

494.8 eV with its characteristic peak separation of 8.4 eV.\textsuperscript{50,51} The sulphur spectrum can be assigned to the presence of sulfides at binding energies of 161.7 and 162.9 eV with a doublet separation of 1.2 eV.\textsuperscript{50,51} Also, to investigate the quantitative analysis of all four elements in the nanorods, a scanning electron microscope equipped with an energy-dispersive X-ray spectroscopy (EDS) detector was used to find the Cu:Zn:Sn:S stoichiometric ratio, which was close to 2:1:1:4 (Figure 6), corresponding well with the elemental ratio of CZTS.

The as-synthesized CZTS nanorods have high uniformity across the length and diameter, which is a prerequisite for self-assembly. We have recently shown with wurtzite (II–VI) nanorods that the simplest method to achieve perpendicular assembly is to create conditions under which the rods preorganize in solution. At an optimal concentration, the inter-nanorod distance in solution is sufficient to allow attractive interparticle interactions such as dipole–dipole to overcome the Coulombic repulsion, resulting in nucleation and growth of 2D-assembled sheets.\textsuperscript{42–43} The CZTS rods have a $\zeta$ potential of $5 \pm 2$ mV and a permanent dipole along the [002] direction. Therefore, simply modulating the nanorod
concentration over a range allows the isolation of the critical concentration for preferential assembly (Figure 7). The top-down DF-STEM image in Figure 8a shows a 3D superstructure of CZTS nanorods. Figure 8b shows a TEM image of a monolayer of vertically oriented CZTS nanorods in which the perfect close-packed hexagonal ordering can be seen. The inset top-down HRTEM image of a single nanorod shows the spacing of the lattice fringes to be $d = 0.32$ nm, which matches the (002) plane of the wurtzite structure of CZTS nanorods. When the rate of evaporation of the solvent is controlled, the 2D sheets can be deposited sequentially to form 3D multilayer arrays, as shown in Figure 8c, d. Assemblies up to micrometer-sized areas can also be obtained by this approach (Figure 9). The direct optical band gap of CZTS nanorods was calculated from the UV-vis spectrum (Figure 10) to be 1.43 eV by extrapolation of the linear region of a plot of $(\alpha h\nu)^2$ versus energy, where $\alpha$ represents the absorption coefficient and $h\nu$ is the photon energy.\textsuperscript{26}

![Figure 4: XPS survey spectrum of the CZTS nanorods.](image-url)
Figure 5: High-resolution XPS analysis of CZTS nanorods
Figure 6: EDS of the CZTS nanorods. The relative elemental ratios for Cu:Zn:Sn:S were close to 2:1:1:4 stoichiometry. We also noted a small relative increase in the sulphur content, which is likely due to the thiol capping ligands which passivate the nanorod surface. The Si, C, and O signals resulted from the silicon substrate.

Figure 7: DF-STEM images shows the concentration effect at optimum concentration (a), low concentration (b) and high concentration (c) on the CZTS nanorods assembly. The optimum concentration was found to (10^{-5} \text{ mol L}^{-1}), resulting in the formation of 3D assemblies of CZTS nanorods.
Figure 8: (a) DF-STEM image shows 3D superstructure of CZTS nanorods. (b) Top-down HRTEM images show the closed-packed monolayer of CZTS nanorods with inset HRTEM image of single rod. (c) & (d) SEM and HRSEM images show the top-down and side view of multilayer assembly of CZTS nanorods.
Figure 9: (a) & (b) Low magnification SEM images shows micron sized multilayer 2D sheets of CZTS nanorod assembly.
Figure 10: UV-vis absorption spectra of the CZTS nanorods.

2.5 Conclusion

In conclusion, a reproducible method for solution synthesis of high-quality monodisperse wurtzite Cu$_2$ZnSnS$_4$ nanorods has been reported. The rods are defect-free single crystals with a band gap in the visible part of the electromagnetic spectrum. The constituent elements of these rods are nontoxic and highly abundant, allowing for a wide range of low-cost applications exploiting their absorption or emission properties (e.g., biolabels, fluorescent emitters, or photocatalysis). Their facile organization into close-packed and vertically oriented arrays on the substrate strengthens their potential for use as solar absorber layers, where directional orientation and length control will likely allow for enhanced efficiencies.\textsuperscript{38, 39, 52-54}

2.6 References


51. NIST-XPS database, version 3.5 (http://srdata.nist.gov/xps/).


Chapter 3: Directing Semiconductor Nanorod Assembly into 1D or 2D Supercrystals by Altering the Surface Charge

3.1 Abstract

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.

3.2 Introduction

The ordered patterns from a drying dispersion of particles offer an insight into the interplay of processes that direct self-assembly.\textsuperscript{1-3} 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 obtained.\textsuperscript{4} Of recent interest are semiconductor nanorods 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.\textsuperscript{5-8} The long axis of nanorods, however, complicates assembly from solution. Early reports countered the anisotropy restriction\textsuperscript{9} with external fields directing perpendicular orientation of the rods while drying in a droplet.\textsuperscript{10-12} Experiments without fields showed that with optimal aspect ratio and concentration, perpendicular assemblies of CdS nanorods could form.\textsuperscript{13-17} 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.\textsuperscript{18-21} 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.
3.3 Experimental

Chemicals

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. Briefly, Cadmium oxide (CdO, 0.2 g), n-tetradecylphosphonic acid (TDPA, 0.71 g), n-Hexylphosphonic acid (HPA, 0.16 g) and tri-n-octylphosphine oxide (TOPO, 3.00 g) was loaded in 25 ml three-neck flask equipped with a condenser, septum and a thermocouple adapter. The mixture is heated to 120 °C in an atmosphere of Ar/N2 and then evacuates for 1 hour (pressure range between 100 – 300 mTorr) and followed by heating at 300 °C under Ar/N2 atmosphere, during which the CdO decomposed and the colour of solution change from brown to optical clear. At this point 1.5 g of Triocylphosphine (TOP) was injected to the mixture, and the temperature was further raised to 310 °C. Next inject rapidly the pre dissolved Selenium in TOP solution (0.073 g Se + 0.416 g TOP) in the flask and the resulting nanocrystal were further allowed to grow for 5-10 min at 310 °C and then it was cooled to room temperature under Ar/N2 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 (0.0082 g/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.

**Characterization**

Transmission electron microscopy (TEM) was performed using a JEOL 2011 TEM operating at an accelerating voltage of 200 kV. Selected area electron diffraction (SAED) was also observed from the regions of perpendicularly aligned CdSe nanorods. Scanning electron microscopy (SEM) of the assembled nanorod on a Si (111) substrate was performed by a Hitachi S-4800 machine.

**3.4 Results and Discussion**

The 2D assemblies in Figure 1a occur only when the concentration of phosphonates/TOPO capped CdSe (pT–CdSe) nanorods in toluene is \(7 \times 10^{-7}\) mol L\(^{-1}\). The nanorods are packed into hexagonal 2D perpendicular arrays that extend to mm-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 (Figure 1b–d). Increasing the pyridine concentration elongates the chains and increases their relative density (Figure 1c and d). TEM (Figure 1) and STEM (Figure 2) 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
Figure 1: (a) TEM image showing closed-packed 2D superlattice of pT CdSe nanorods (b) TEM image of the self-assembled Py-CdSe nanorods shows that the vertical assembled nanorods are lying below the side by side aligned (rail-track) Py-CdSe nanorods. (c, d) Representative TEM images at a 1:1 and 3:1 volume ratio of Py- to pT-CdSe nanorods respectively.

Pyridine capped CdSe nanorods (Py–CdSe) gives ring patterned deposits (Figure. 3a, Figure 4). The rings can occur due to the random pinning of the receding solvent line depositing the dissolved material, or the formation of “breath patterns”. The anisotropy in the outward capillary flow of nanorods towards the pinned contact line to compensate the evaporating solvent creates thicker deposits in the outermost ring (track “b”, also Figure 3b). The next track “c” (Figure 3c) shows dense wire-like hierarchical structures similar to the “spaghetti-like” structures observed by Nobile et al. Furthermore, the density of the NR fringes
decreases from track “b” to “d” (Figure 3). 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 nanorods is different with the two alignments occurring independently. Understanding both alignments requires consideration of the forces acting on the nanorods in the droplet. The dipole–dipole energy between the rods can be approximated by where \( m_i \) is the dipole moment of \( \mu_i \), \( R_{ij} \) is the displacement between the dipoles i and j, \( \theta_i \) is the angle between dipole i and the displacement, and \( \phi \) is the torsion angle between the dipoles. The dipole moment for CdSe nanorods is large, with a value of 250 D (or \( 8.3 \times 10^{-28} \text{ C m} \)) in SI units for a 35 × 7 nm NR expected. Nanorods 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

\[
V(R_{ij}, \theta_i, \theta_j, \phi) = -\frac{\mu_i \mu_j}{4\pi \varepsilon_0 R_{ij}^3} \left( 2 \cos \theta_i \cos \theta_j - \sin \theta_i \sin \theta_j \cos \phi \right)
\]

between dipole i and the displacement, and \( \phi \) is the torsion angle between the dipoles. Figure 6a shows the combined energy, \( \Delta E \) versus rod displacement, \( R_{ij} \). For rods with a zeta potential, \( \zeta <~15 \text{ mV} \), 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 \( \zeta \) 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 \( \zeta =20 \text{ mV} \) and 25 mV, respectively. Once within the attractive potential, the dipoles can align and assemble. Thus, there is a critical concentration whereby assembly of nanorods with a high \( \zeta \) can align. End-to-end assembly unaided by any other factor can be overcome by the thermal
Figure 2: 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.
Figure 3: (a) TEM image showing formation of ring patterns by PyCdSe nanorods (b)-(d) Representative TEM images magnified from the corresponding tracks b-d marked in (a), respectively showing the lateral assembly of Py-CdSe nanorods.

Figure 4: The TEM image in (a) & (b) show the nature of the receding evaporation line of the drying solvent as it deposits
Figure 5: 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. (b) The Py-CdSe has, on the other hand, a charge that is measurable, having a value of 23 ± 3 mV.
Figure 6: (a) A plot of energy versus nanorod–nanorod displacement for nanorods of different zeta potential. The barrier to assembly is less than the thermal energy for lower zeta potential particles. It can be overcome thermally for all zeta potential 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. (b) A schematic of the two types of NR self-assembly in a drying droplet; Py–CdSe [(i)–(iii)] and pT–CdSe [(iv)–(vi)].
energy, and as such, side-by-side alignment is favoured. Therefore, assembly in the solution is predicted to occur for low \( \zeta \) at an optimal concentration. The experimentally determined zeta potential data (Figure 5) show pT–CdSe nanorods at \( (1 \pm 4 \text{ mV}) \) in comparison to Py–CdSe nanorods at \( (23 \pm 3 \text{ mV}) \). Consequently, there is no repulsive Coulomb barrier preventing the pT–CdSe nanorods from aligning due to the dipole–dipole force and thereby assembling in the bulk solution (Figure 6b). 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.\(^{26, 27}\) The higher \( \zeta \) 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 \( \zeta \) Py–CdSe rods will migrate to and get trapped at the liquid–air interface.\(^4\) 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.,\(^{28}\) where \( l \) and \( w \) are

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

the basal width and the length of the NR, respectively; \( \gamma_{x-y} \) is the interfacial tension between phases \( x \) and \( y \); and \( \theta \) is the contact angle between the rod surface and the toluene-air interface, given by \( \cos \theta = (\gamma_{\text{CdSe-Toluene}} - \gamma_{\text{CdSe-Air}})/(\gamma_{\text{Air-Toluene}}) \). \( \gamma = 15.0, 33.0 \) and \( 28.1 \text{ mT m}^{-1} \) for the CdSe-toluene, the CdSe-air and the toluene-air interfaces, respectively,\(^{29-31}\) this gives a potential of 450 k\( k_B T \), 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 (Figure 6b). The surface concentration will increase as droplet size reduces and can trap more rods while reducing the surface area. At critical concentration for high \( \zeta \) rods, the rods align due to the dipole–dipole attraction and form the 1D array. 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 nanorods 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.\(^1\)\(^-\)\(^4\) For nanorods which 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. Therefore, for highly ordered assemblies, a solvent with a low volatility and low dielectric permittivity is required (for different solvent data, see Figure 7).

The NR centre-to-centre distance in the 1D assembly is shorter by approximately 10% than that of the rods in the 2D assemblies, representing a reduction of ligand spacing between the rods of 32% after washing, due to the shorter-length pyridine replacing the longer chain p/TOPO. This model based on charge and dimensionality rationalises reports where slight modifications of similar systems gave differing results. Querner et al. reported no vertical assemblies—only rail-track assemblies occurred with pT–CdSe NR assembled from hexane/octane.\(^19\) However, \(\zeta\) of the pT rods in these solvents is found to exceed that of pT–
CdSe rods in our study, which implies 1D assembly should form. Similarly, in reports of orthogonal assemblies in solution of CdSe/CdS and Au–CdSe, the preassembly of the nanorods in the bulk solute is critical to vertically aligned order.\textsuperscript{12,12} In both cases the equilibrium of dispersion and aggregation was deliberately modulated; 2D monolayers and not 3D supercrystals were formed from assembling nanorods in the bulk.

\textbf{Figure 7:} TEM images shows the effect of different solvent on nanorod assembly
3.5 Conclusion

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.

3.6 References


Chapter 4: Controlled Semiconductor Nanorod Assembly from Solution: Influence of Concentration, Charge and Solvent Nature

4.1 Abstract

Spontaneous supercrystal organisation of semiconductor nanorods (CdS and CdSe) of different aspect ratios into ordered superstructures was obtained by controlled evaporation of a nanorod solution. The rods either align into two dimensional close packed perpendicular arrays or into one dimensional rail tracks depending on the total interaction energy between the rods in solution. A detailed study has identified critical factors that affect this interaction energy such as nanorod concentration, surface charge, dipole moment and solvent nature (polarity and volatility), thereby allowing a general approach to control the nature of nanorod assembly (1D or 2D). Molecular dynamics (MD) of small charged nanorods showed that opposite dipolar alignment (antiferromagnetic) was the preferred rod orientation during self-assembly.

4.2 Introduction

Colloidal semiconductor nanocrystals have attracted significant interest as building blocks for applications ranging from biomedical diagnostics to next generation electronics. Optimisations of synthetic protocols have allowed precise control over their size, shape, composition and surface chemistry. Concurrent efforts have been devoted towards understanding the organisation of these nanocrystals into superstructures extending to several centimetre length scales. While self-organization of zero-dimensional semiconductor nanocrystals is well established, organization of one-dimensional semiconductor nanocrystals (or nanorods) is more challenging due to their inherent shape anisotropy. The cylindrical shape typically results in short range ordering producing raft like assemblies parallel to the
surface. The most viable architecture for functional application of nanorod assemblies is where each rod is vertically aligned and close packed. This allows the greatest density of packing and the collective optimisation of diameter and length dependent properties such as quantum confinement and polarised light emission respectively.\textsuperscript{18, 19} In proposed photovoltaic applications, for example, the tuneable rod diameter defines the band gap whereas the nanorod length optimises total light absorption.\textsuperscript{20}

Directed assembly methods which exploit the shape dependent dipole moment in the rods has allowed vertical assemblies to be obtained when the field lines are perpendicular to the substrate.\textsuperscript{21} This route when combined with the presence of an intrinsic net charge on nanorods allows very large scale assemblies to be obtained by electrophoresis.\textsuperscript{12, 13}

The propensity of nanorods to self-organise into orthogonal close packed assemblies in the absence of external electromagnetic fields is a recent discovery. Ahmed demonstrated HOPG assisted assembly of the nanorods which formed on a substrate from a drying dispersion.\textsuperscript{22} Baker et al expanded the assembly size by adding excess surfactant to the drying dispersion resulting in a self-assembled substrate bound monolayer over large areas.\textsuperscript{23}

Assembly from a drying liquid dispersion at a substrate requires understanding of solvent-evaporation dynamics and its influence on the resultant concentration gradient of the dissolved solutes (here nanorods).\textsuperscript{24, 25} The further factors of solvent line pinning at the surface and fluid flow within the droplet demands tight control of several critical factors to achieve the desired assembly.\textsuperscript{26-28}

Pre-assembly of the nanorods into perpendicular superlattices within the liquid phase is also possible and is less complicated due to the absence of interfacial considerations. Manna and co-workers showed that the introduction of a non-solvent into a nanorod dispersion acts as a driving force for side by side rod assembly by depletion attraction in solution.\textsuperscript{29} The assembled discs settle to the substrate due to gravity sedimentation. Singh et al has shown
more recently that perpendicular assemblies can spontaneously form in solution if the net charge on the rod is optimised.\textsuperscript{30} Further, by calculating the total Coulombic energy interactions of net charge (repulsive) and dipole-dipole (attractive) the conditions for optimal assembly in solution were formulated. Importantly, this work rationalised the occurrence of both perpendicular (2D) and linear rail-track (1D) assemblies from a single droplet with the former occurring in the droplet bulk and the latter occurring from the droplet surface on drying. Isolating the importance of net charge on the rod, as a key factor in assembly, essentially created a tuneable parameter for controlling their formation that is easily applicable to a wide range of nanorods.

Here we show that CdS nanorods with different physical properties and ligand chemistry to CdSe can be easily assembled by the same charge based protocol. The total energy calculations are shown to be valid for this system with the predicted assembly patterns occurring under experimental conditions as verified by HRTEM and HRSEM. In addition, we expand on the other important factors necessary for general application of this assembly method. The existence of a critical rod concentration for assembly is necessary such that inter-rod distances are sufficiently small such that attractive interactions can dominate. The methodology to establish the optimum concentration window for assembly is detailed and the effect of concentration variations outside this is shown. Furthermore, how changes in the solvent permittivity and boiling point affects the assembly patterns are detailed extensively. The screening effect of high permittivity solvents on inter-rod interactions is shown to have a predictable effect on assembly patterns. In addition the rate of solvent evaporation, dictated by the solvent boiling point, dictates the degree of order in assembly formation. Finally, molecular dynamics (MD) simulations shows that small, positively-charged cadmium selenide nanorods in toluene led to the adoption of anti-ferromagnetic ordering of the rod dipoles, in good agreement with our experimental findings.
4.3 Experimental

Materials

Cadmium oxide (>99%), trioctylphosphine (TOP, 90%), tri-n-octylphosphine oxide (TOPO, 99%), sulfur (99.98%) and selenium (99.98%), pyridine were purchased from Aldrich. n-Octadecylphosphonic acid (ODPA), n-tetradecylphosphonic acid (TDPA) and n-hexylphosphonic acid (HPA) were obtained from PolyCarbon Industries, Inc. (PCI). All the chemicals were used as received.

Synthesis of CdSe Nanorods

CdSe nanorods were synthesised according to published procedure.\textsuperscript{20} Briefly, CdO (0.20 g.) as a cadmium precursor was dissolved in mixture of surfactants like n-tetradecylphosphonic acid (TDPA, 0.71 g), n-Hexylphosphonic acid (HPA, 0.16 g) and tri-n-octylphosphine oxide (TOPO, 3.00 g) in 25 ml three-neck flask equipped with a condenser and a thermocouple adapter. The mixture is heated to 120 °C in an atmosphere of Ar and then evacuates for 60 min and followed by heating at 300 °C under Ar atmosphere so that CdO decomposed and give optical clear solution. Once a clear solution was obtained, 1.5 g of Trioctylphosphine (TOP) was added to the mixture, and the temperature was further raised to 310 °C. Next the stock solution of Selenium (~500 µl) containing 73 mg of selenium in 416 mg of TOP was injected rapidly to the vigorously stirring Cd solution and the resulting particles were further allowed to grow for 5-10 min at 310 °C. The nanorod growth was terminated by removal of the heating mantle, and at 80 °C, 2-4 ml of anhydrous toluene was added to the mixture to quench the reaction. The nanorods were purified by dissolution in toluene and precipitation from anhydrous isopropanol. They were cleaned thrice with toluene and isopropanol mixture and redispersed in toluene for further measurements.
Synthesis of CdS Nanorods

CdS was also synthesised in a procedure similar to that of CdSe nanorods. In detail, 0.21 g 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 120 °C under Ar- gas flow at which ODPA and TOPO were dissolved (mixture becomes a brown colour). The mixture is degassed at 120 °C for 20 minutes followed by switching from gas to vacuum line with a vacuum range of 150-200 mTorr. The mixture was heated to 300 °C under Ar-gas at which CdO completely dissolved and the solution becomes clear. The mixture was cooled to 120 °C and further degassed for another 45 minutes. After this second degas, the apparatus was switched back to Ar-gas line and mixture is heated to 300 °C at which time the sulphur stock solution (~ 800 µl) containing 64 mg of sulphur in 7.64 mg TOP was rapidly injected (~1.0 s) and the nanocrystals were allowed to grow for 30 minute. The nanorod growth was terminated by removal of the heating mantle. Once the reaction mixture reached ~80 °C, the reaction was quenched via the addition of 2-3 mL of anhydrous toluene. The nanorods were purified by dissolution in toluene and precipitated from acetone. They were cleaned thrice with toluene and acetone mixture and redispersed in toluene for further measurements.

Ligand exchange of nanorods with pyridine

To prepare pyridine capped nanorods, 1 ml of nanorods solution (0.0013 g/ml) was dispersed in anhydrous pyridine (5 ml) followed by vortex for 5-10 min and then sonicated for 30 min. The solution then centrifuged at 13000 rpm for 10 min following which the filtrate was discarded and the resulting residue was redispersed in toluene for further studies.
Sample preparation

Nanorod solutions with different concentration range from $8 \times 10^{-7}$ mol L$^{-1}$ to $3.2 \times 10^{-6}$ mol L$^{-1}$ were prepared in fixed amount of toluene solution (5 ml). A drop (~ 7 µL) of nanorod solution was drop cast on carbon coated TEM grid.

Characterizations

The images of the nanorods and nanorods assemblies on Carbon supported TEM grids were characterized by transmission electron microscopy (TEM) and scanning transmission electron microscopy by using a JEOL JEM-2011F operating at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) of the nanorods assembly on a Si (111) substrate was performed by a Hitachi SU-70 machine. Zeta-potential was measured using Zeta PALS (Zeta Potential Analyzer, Brookhaven Instruments Corporation, US) using low and high electric-field, $E = 137$ Vcm$^{-1}$ and $274$ Vcm$^{-1}$, across the palladium electrodes and measured zeta-potential values was constant from two fields which was averaged from 10 repeated experiments.

Molecular Simulation Methodology

Four small, cylindrical rigid-body cadmium selenide (CdSe) nanorods of wurtzite geometry, approximately 15 Å in height and 8 Å in diameter, were constructed and placed axially oriented along the $y$-axis, with their centres-of-mass (COM) at the vertices of a square in the $x$-$y$ plane with a side-length of 25 Å. The inter-atomic energy function (Lennard-Jones) was taken from ref. 31; it is relevant to highlight the ionic nature of the CdSe rods, which consist of negatively (-1.18e) and positively (+1.18e) charged ions, respectively. Two cases of net positive surface charges of 0.2 and 0.4 e were applied to each rod, with incremental charges divided evenly over each surface atom in the rod so that the total positive surface charge was
either 0.2 or 0.4 e. The simulation box was cubic, with an approximately 60 Å side-length, to which periodic boundary conditions were applied. The OPLS\textsuperscript{32} potential was applied to the toluene solvent molecules, and either one or two chloride ions were added to render the whole system electro-neutral (with respective negative charges of 0.8 and 1.6 e for the positive charge cases of 0.2 and 0.4 e per rod). Toluene molecules were placed in the simulation box from a separate NPT liquid-phase simulation. The temperature and pressure was then allowed to relax to 298 K and 1 bar.

The particle-mesh Ewald\textsuperscript{33} method was used to treat full long-range electrostatics. A cut-off distance of 12 Å was applied to real-space Ewald interactions. An equal value was used for van der Waals interactions, using a smooth switching function applied thereto between 10 and 12 Å. A multiple time step scheme was used with 1 fs for bonded interactions and short-range non-bonded interactions, and 4 fs for reciprocal-space electrostatics evaluation, using the r-RESPA method.\textsuperscript{34} All production runs (for both rod-surface charge states) were simulated for up to 5 ns using coupling to an NPT reservoir, using the Anderson-Hoover approach with a temperature of 298 K and a pressure of 1 bar, with respective barostat and thermostat periods of 0.5 and 2 ps.\textsuperscript{35} The SHAKE\textsuperscript{36} algorithm was applied to constrain bond lengths to all hydrogen atoms. Prior to production runs, initial relaxation MD simulations of 1 ns (of liquid toluene) at 298 K and 1 bar pressure were performed without any nanorods. Subsequently, the rigid-body nanorods were inserted as described above, avoiding (van der Waals) overlap with the toluene, and fixed in place. After energetic minimisation of the toluene, the system was equilibrated to 298 K in an NVT simulation increasing the temperature by 20 K every 20 ps. NPT dynamics was then carried for 1 ns while reducing harmonic restraint forces from 1 to 0 kcal/(mol Å\textsuperscript{2}) on the rigid-body nanorods in 0.2 kcal/(mol Å\textsuperscript{2}) steps every 0.2 ns.
4.4 Results and Discussion

The extension of the successful charge based assembly from CdSe nanorods to the CdS first requires a narrow distribution in both length and diameter across the nanorod dispersion. Here a TEM image of unaligned CdS rods used in this study, Figure 1a, show they possess aspect ratios of $7 \times 30$ nm with polydispersity $< 5\%$. Although this is a comparable aspect ratio to the CdSe rods, Figure 1d, ($7 \times 35$ nm) there are several physical and structural differences that could affect their propensity for assembly. The dipole moments are significantly different at $240 \pm 15$ Debye for CdSe in comparison to $485 \pm 45$ Debye for CdS.

![Image of TEM images showing CdS and CdSe nanorods and their assemblies.](image)

**Figure 1:** (a) TEM image showing CdS nanorods. (b) TEM image showing closed-packed 2D superlattice of CdS nanorods with inset SAED pattern. (c) TEM image of the pyridine washed CdS nanorods shows 1D (rail-track) nanorods assembly. (d-f) Representative TEM images of CdSe nanorods and their 2D and 1D nanorods assembly respectively.
CdS. \textsuperscript{21, 22} As the ligand environment affects the charge, the change to octadecylphosphonic acid/TOPO for CdS in comparison to tetradecylphosphonic/TOPO is for CdSe must be accounted for. Here the similar phosphonic acid environment has only a small affects on the zeta potential resulting in a negligible change from $1 \pm 3$ mV for CdSe to $2 \pm 3$ mV for CdS. As the total energy considerations for attraction or repulsion are a function of charge and dipole moment, balancing these interactions through concentration allows pre-assembly in solution to occur. The TEM images (Figure 1b) show the resultant assemblies of CdS rods obtained at optimal conditions. Each sheet is a 2D close packed monolayer of orthogonal aligned rods which form in solution and drop to the substrate. The multilayer architectures occur when sheets overlap in the final deposit. The uniaxial alignment of the nanorods throughout the layers is further confirmed by electron diffraction inset. The slightly diffused diffraction spots correspond to (100), (110) and (001) of the wurtzite CdS and are slightly

![Figure 2: A plot of energy versus nanorod-nanorod displacement for CdS and CdSe nanorods.](image)

\textsuperscript{21, 22} As the ligand environment affects the charge, the change to octadecylphosphonic acid/TOPO for CdS in comparison to tetradecylphosphonic/TOPO is for CdSe must be accounted for. Here the similar phosphonic acid environment has only a small affects on the zeta potential resulting in a negligible change from $1 \pm 3$ mV for CdSe to $2 \pm 3$ mV for CdS. As the total energy considerations for attraction or repulsion are a function of charge and dipole moment, balancing these interactions through concentration allows pre-assembly in solution to occur. The TEM images (Figure 1b) show the resultant assemblies of CdS rods obtained at optimal conditions. Each sheet is a 2D close packed monolayer of orthogonal aligned rods which form in solution and drop to the substrate. The multilayer architectures occur when sheets overlap in the final deposit. The uniaxial alignment of the nanorods throughout the layers is further confirmed by electron diffraction inset. The slightly diffused diffraction spots correspond to (100), (110) and (001) of the wurtzite CdS and are slightly
rotated by approximately 10°, which is consistent with our previous reports. Similar behaviour is obtained with the CdSe nanorods; Figure 1e with inset diffraction patterns indexed to wurtzite CdSe. The mechanism of assembly for CdS can be rationalised when the various thermodynamic forces acting on the nanorods such as dipole-dipole interaction, coulomb repulsion and Van der Waals attraction are taken into account. The total energy calculations for CdS, Figure 2 (yellow curve), and fits a similar profile to that previously reported for CdSe Figure 2 (violet curve). As the ODPA/TOPO capped rods have a small net zeta potential, 2 ± 3 mV, the attractive forces pulling the rods together in solution dominate. The optimum concentration window facilitates the minimum inter-rod distances in solution for nucleation of this nanorod cluster to occur. Outside of this optimum concentration, nucleation does not occur and the evaporating droplet results in randomly deposited rods, with raft like order, Figure 1a. Once the nucleation of the supercrystal occurs, growth is facilitated by the dynamic attachment/detachment of rods from solution.

If the charge state of the rod is increased dramatically by pyridine washing, the repulsive forces dominate in solution and the rods remain dispersed. No assembly occurs within the droplet volume regardless of concentration. As the solvent dries, the rods migrate to the surface of the droplet eventually getting deposited at the substrate interface as the droplet diameter recedes. Here the rods are trapped on a 2D manifold (droplet surface) thereby restricting the possible type of assembly to 1D. Consequently rail track type assemblies occur due to antiferromagnetic dipolar alignment of the rods on deposition (Figure 3). In comparison, the density and length of the tracks is increased in pyridine capped CdS (Figure 1c) in comparison to pyridine capped CdSe (Figure 1f). This is expected due to higher zeta potential value for pyridine capped CdS nanorods (26 ± 3 mV) in comparison of pyridine capped CdSe (20 ± 3 mV). Increasing the average charge on nanorods increases the rate at which the rods migrate to the droplet surface thereby increasing the relative density of
Figure 3: Schematic representation shows the progression of the 1D (rail-tracks) nanorod assemblies in different stages of droplet drying.

The occurrence of both rail-track (1D) and perpendicular assembly (2D) from a single droplet is also possible with CdS by partial ligand exchange. In this case, the alkyl phosphonates capped rods assemble in 2D layers and drop to the substrate with the pyridine capped rods only assembling at the liquid contact line resulting in 1D deposits on top of the 2D in all cases (Figure 4). This finding is in excellent agreement with our previous studies of CdSe nanorods. Furthermore, this is the first report of side-by-side assembly of CdS nanorods and demonstrates the general applicability of assembly control by charge modulation.

Figure 4: STEM and TEM images clearly show that the 1D (rail-tracks) deposit on top of the 2D arrays of nanorods.
**Concentration Effect on Nanorods Assembly**

The concentration of nanorods affects the nearest neighbour distances in solution and hence dictates the occurrence or absence of spontaneous nucleation of 2D supercrystals if the nanorod charge state is favourable. Using total energy calculations, (Figure 2) we can calculate the optimum inter rod distance for assembly. However, in practise correlating this distance value to an exact concentration of nanorod dispersion is difficult. A more straightforward route is to evaluate assembly patterns over a concentration range until the desired assembly is obtained. This is demonstrated in Figure 5 where all samples were prepared by using a fixed amount of toluene and varying the concentration of CdS nanorods (see detail in the experimental section). The solutions were evaporated in a similar environment (glove box) giving a constant evaporation rate. A low concentration ($8 \times 10^{-7}$ mol L$^{-1}$) of CdS nanorods in toluene resulted in randomly distributed CdS nanorods with their c-axis parallel to the plane of the TEM grid (Figure 5a). In this case, the low concentration results in weak dipole-dipole attractions between nanorods and prevents assembling of the nanorods within the volume of the droplet prior to drying. These nanorods are deposited randomly as the droplet evaporates, resulting in their long axis parallel to the substrate with no side-by-side ordering (Schematic representation in Figure 5gI). As the concentration of nanorods is increased to $1.4 \times 10^{-6}$ mol L$^{-1}$ the emergence of small ordered areas in the centre of the grid encompassed by randomly distributed nanorods (Figure 5b and 5gII) is apparent. The progression of apparent order in this aggregate from smectic at the edges to columnar at the centre occurs when the evaporating droplet gradually constricts the confined rods. A further increase in the nanorod concentration to $2.1 \times 10^{-6}$ mol L$^{-1}$, results in a dramatic change in the assembly type. Here both vertically oriented hexagonal 2D (Figure 5c) arrays and multilayer 3D superstructure arrays occur. Here the vertical alignment of the rods in the layers is resolute with no progression of order from edge to centre. The complete
perpendicular ordering strongly suggests the pre-assembly of rods in solution and their deposition on a surface as opposed to residual deposition from a completely evaporated droplet, which would typically have disorder at the edges. The strict concentration dependence of the starting solution is typical for crystallisation where outside of a certain window; nuclei are kinetically unstable to disassociation. The nuclei grow into ever-larger supercrystals as nanorods add in a periodic and defined manner, with the reducing droplet volume replenishing the concentration of free nanorods (Figure 5gIII). As these supercrystal sheets grow, they gradually sink due to gravity supercrystal sheets grow, they gradually sink due to gravity sedimentation such that the dwell time in the 3D volume of the droplet is the likely factor which restricts the sheet size. Assemblies up to micron-sized areas are possible (Figure 6) and are remarkably consistent across multiple experiments. The HRTEM image inset shows the consistency of nanorod diameter and inter-nanorod repeat distance (< 3 nm) in the assembly. However, a further increase in the concentration of nanorods to $3.2 \times 10^{-6}$ mol L$^{-1}$ results in a complete loss of long range order (Figure 5d) demonstrating the effective concentration window for perpendicular assembly.

As the sheets are depositing from a three-dimensional volume onto a 2D surface, multilayer formation resulting from stacking of the sheets is expected. This is clearly evident in Figure 5e and 5f where the monolayer and multilayer can be identified. The occurrence of these multilayers is further evidence for the preformation of perpendicular oriented nanorod assemblies in sheets prior to deposition on a surface. As the optimal concentration for assembly is essentially a distance dependence at which the attractive forces in solution outweigh the repulsive forces, different optimal concentrations will manifest for other rods such as CdSe (Figure 7). This is the first report of vertical assembly of CdSe nanorods over large areas without the use of any external directing agents and effectively shows the generality of this technique for achieving perpendicular assembly.
**Figure 5:** TEM image of CdS nanorods with concentration. (a) $8 \times 10^{-7}$ mol L$^{-1}$ (b) $1.4 \times 10^{-6}$ mol L$^{-1}$ (c) $2.1 \times 10^{-6}$ mol L$^{-1}$ and (d) $3.2 \times 10^{-6}$ mol L$^{-1}$. The optimum concentration was found to be $2.1 \times 10^{-6}$ mol L$^{-1}$ where closed-packed 2D superlattice of CdS nanorods with inset HRTEM image in Figure(c) shows the monodispersity of nanorods. (e)-(f) HRSEM images showing monolayer and multilayer, vertically oriented CdS nanorods. (g) Schematic representation shows the progression of the nanorod assembly in different stages of droplet drying for different concentration, the nucleation of the assemblies in the droplet for optimum concentration and further growth process of nanorod assembly is shown in gIII.
Figure 6: (a-b) Low and higher magnification TEM images shows micron sized areas of vertically aligned CdS nanorods. (c) Low magnification SEM images shows micron sized multilayer 2D sheets of nanorod assembly. (d) Higher magnification SEM image of one of 2D sheet shows nanorods are vertically oriented to the substrate.
Figure 7: (a) STEM image shows randomly deposited CdSe nanorods. (b-c) TEM, STEM images showing the vertically aligned CdSe nanorods. (d-f) SEM images of multilayer, vertically aligned CdSe nanorods over micron sized area. The optimum concentration was found to be $7.8 \times 10^{-7}$ molL$^{-1}$.

Influence of Solvent Nature

The choice of solvent is also important in these experiments, as it is the medium within which all forces have to balance each other to attain the stable state. For the assembly of nanorods from a drying solvent droplet, the solubility, volatility and dielectric permittivity of the solvent determine the nature of the assemblies as much as the nanorod properties themselves.

Solubility – the ability to effectively disperse the nanorods in the first instance – restricts our choice of solvent. Toluene, cyclohexane, benzene and chloroform have all been reported as good solvents for nanorods covered with hydrophobic ligands (phosphonates, TOPO, oleic acid etc.). Conversely, dichloromethane and methanol are poor solvents for these nanorods. In this case, drying leads to a random agglomeration of the nanorods, as would be expected from a poorly-solvated material (Figure 8a). This would also be seen if the diffusion
coefficient of the nanoparticles on the substrate is lower than the dewetting front velocity. In such a case there is not enough time for well-ordered assemblies to form before the evaporation of the solvent for the two remaining properties – volatility and permittivity – useful information can be extracted from the nature of the assemblies obtained from them. It is important, however, that when comparing the effect of differing volatilities, the dielectric constants of the two solvent must be almost equal and vice versa.

The dielectric constant has a direct bearing on the solubility, given that the electrostatic interaction is scaled by the dielectric constant. The ligands on the nanorod surface are non-polar and as a general rule will not dissolve in a highly polar solvent with a relative permittivity greater than \( \varepsilon_r \approx 10 \) - 15, such as water. For a solvent with a permittivity that is below this threshold but still relatively high (\( \varepsilon_r \approx 4 \) – 10), the strength of both the dipole-dipole and the Coulomb interaction will be screened to a greater extent. As a result, the electrostatic forces driving the assembly are reduced, and assembly in chloroform (\( \varepsilon_r = 5 \)) is not seen (Figure 8b).

The volatility of the solvent determines the drying rate of the droplet. A volatile solvent droplet may dry too fast for assembly to occur. The effect of volatility can be investigated by comparing nanorod patterns formed from toluene and cyclohexane evaporation. Both of these solvents have a similar dielectric constant and are both good solvents for the nanorods, but cyclohexane has a lower boiling point. The one-dimensional patterns formed after pyridine washing are much shorter in the cyclohexane, and the two-dimensional assemblies from partially washed or un-washed nanorods have smaller domain sizes as seen in (Figure 8c).

Regardless of solvent nature, the surrounding environment, and thus the rate of evaporation, also has an impact on the degree of nanorods assembly. To study this effect, the toluene solution of nanorods with optimum concentration was investigated at varying drying times in a closed environment (glove box). When the drop takes the maximum time to dry (7-
Figure 8: (a-b) TEM image showing agglomeration and random deposition of nanorods when drop cast from nanorods solution in dichloromethane and chloroform respectively. (c) TEM image showing the shorter domain of 2D and 1D nanorod assembly when drop cast from nanorods solution in cyclohexane.

Figure 9: TEM images show the effect of rate of evaporation of solvent in both type of assembly (2D and 1D). When the solvent drop took the maximum time to evaporate (7-8 min), large area of 2D and 1D nanorod assemblies were obtained as shown in a and c as compared to 3-4 min evaporation time (b, d).
8 minutes), a large hexagonally close packed nanorod assembly was obtained but as the evaporation rate increased (3-4 minutes) the assembly size decreases. This clear progression in the 2D nanorod domain size is shown in Figure 9a-9b. This indicates that the rate of evaporation affects the crystallization process with longer interaction times for dipole–dipole attraction leading to the energetic favouring of large scale assembly. Interestingly, the 1D nanorod assemblies also shows similar behaviour under these conditions where the length of the rail track decreases as the evaporation rate increases (Figure 9c-9d). Therefore in considering the optimum solvent for nanorod assembly, the volatility in addition to dielectric constant and polarity are important considerations. A solvent with a low dielectric permittivity and a low volatility (such as toluene) is therefore the ideal solvent for facilitating assembly.

**Molecular Simulation Insights into Self-Assembly**

In Figure 10a, orientation angles are depicted of each the four +0.2 e-charged nanorods’ axes (and dipoles) vis-à-vis the –z-direction, determined from the MD simulations. Initially, the rods are at right angles to the –z-direction (approximately 90°), and then two of each align in opposite directions, corresponding to an anti-ferromagnetic configuration. This finding is in broad agreement with those of Titov, for which opposite alignments were found to be energetically preferred. Larger surface charges on the rods were found to lead to more rapid anti-ferromagnetic alignment, due to a larger dipole moment. The agglomeration of the rods is highlighted in Figure 101b, where the average of the six inter-rod centre-of-mass spacing are shown as a function of time for the +0.2 and +0.4 e-charged rods. As one might expect, the repulsive electrostatic interactions between the rods leads to a greater separation for the larger charge case (for which the dipoles are in opposite directions, Figure 10a). Therefore, MD simulation has confirmed the adoption of an anti-ferromagnetic configuration due to the
minimisation of dipolar energy, while the effect of more repulsive surface charge is evidenced clearly in the slower agglomeration and lesser extent of self-assembly. These findings are in broad agreement with our experimental results, and provide insight to the picture of the physical agglomeration mechanism being dominated by dipolar energy minimisation, the kinetics of which is highly sensitive to surface charge.

**Figure 10:** (a) Orientation angles of each of the four +0.2 e-charged nanorods’ axes (and dipoles) vis-à-vis the –z-direction. Initially, the rods are at right angles to the –z-direction (approximately 90°), and then align with two of each in opposite directions (antiferromagnetic state). (b) Average of the six inter-rod centre-of-mass spacings as a function of time for the +0.2 and +0.4 e-charged rod.
4.5 Conclusions

In summary, we have discussed the important factors for the self-assembly from solution of 1D, 2D and 3D superstructures of CdS and CdSe nanorods. In addition to net charge and dipole, the role of critical rod concentration, surface charge and solvent nature on assembly formation is outlined. Optimising these factors allows multilayer perpendicular assemblies to be formed with excellent reproducibility. This approach negates the need for external additives such as non-solvents or excess surfactants that can contaminate the final assembly. This study is generally applicable and allows for a complete protocol to control the nature of nanorod self-assembly from solution regardless of elemental composition.

4.6 References


Chapter 5: An Insight into the 3D Architecture and Quasicrystal Symmetry of Multilayer Nanorod Assemblies from Moiré Interference Patterns

5.1 Abstract

Vertical nanorod assembly over three dimensions is shown to result in the formation of Moiré interference patterns arising from rotational offsets between respective monolayer sheets. Six distinct patterns are observed in HRTEM and angular dark-field STEM (DF-STEM) images, allowing the exact angle of rotation to be determined from their respective size and repeat order. At large rotation angles approaching 30°, the aperiodicity in the structure of the nanorod supercrystals becomes apparent resulting in 12 fold ordering characteristic of quasicrystal. The rotational offsets are further elucidated from Fourier transform and Small Angle Electron Diffraction allowing interpretation of several multilayers when combined with DF-STEM and SEM. Pattern formation owing to angular rotation is differentiated from those occurring from a lateral shift, providing an important insight into the complex multi-layered structures in assembled rods that may have an impact on their collective electronic or photonic properties. We also show how random tetrapods when present at low concentrations in colloidal nanorod solutions act as termination points for 2D sheet crystallization, impacting on the size and shape of the resultant assemblies. The occurrence of Moiré patterns in rod assemblies demonstrates the extraordinary order achievable in their assembly and offers a non-destructive technique to precisely map the placement of each nanorod in this important nano-architecture.

5.2 Introduction

Moiré interference patterns occur when two lattices overlap with a rotational misorientation and are independent of length scale once the effect is observable to the eye. These patterns,
initially only of aesthetic interest, are now finding important applications for characterising the three dimensional architecture of layered nanomaterials.\textsuperscript{2-3} As these materials can be imaged in transmission mode (TEM, STEM, or STM), sequential layers that have an angular offset generate Moiré patterns in the upscaled images allowing 3 dimensional structural determination in both crystalline (e.g. Anodic Alumina)\textsuperscript{4} and non-crystalline materials (e.g. self-patterned block copolymers).\textsuperscript{5} In samples of the important electronic material graphene, Moiré patterns allow non-destructive characterisation of whether the desired monolayer or multilayer is present.\textsuperscript{6-8} Equally, Moiré patterns in folded biological cell membranes allow the structural biology arising from lipid packing to be elucidated.\textsuperscript{9} The pattern formation is not only a powerful tool for the three dimensional characterisation of layered materials with nanoscale order but is expected to find application in complex lithographic patterning.\textsuperscript{4}

Moiré patterns have particular importance in the area of nanocrystal assembly as the interparticle length scales (1-10 nm) allow manifestation of interference patterns that allow detailed interpretation of the three dimensional structure.\textsuperscript{10-19} As new materials with extraordinary properties are designed with nanocrystal size, elemental composition (metal, semiconductor), hetero particular distribution and interparticle spacing as control factors, techniques that reveal the precise three dimensional architecture are of critical importance.\textsuperscript{10-23} As spherical nanocrystals arrange in expected packing parameters as a function of radius, Moiré patterns have been observed and used to elucidate the simplest AB binary superlattice through to structures with forbidden symmetry (quasicrystals).\textsuperscript{10-15} In colloidal nanocrystals, the further ability to control shape \textsuperscript{24-26} adds even greater complexity to possible superstructure formation.\textsuperscript{27} Recent advances in nanorod assembly, using self or directed methodologies, have allowed large scale architectures to be formed where each rod is vertically aligned and close packed.\textsuperscript{27-40} In this geometry, the collective absorption or luminescence of the oriented rods can be optimised by tuning the length while retaining size
defined properties dependent on the diameter such as band gap. These superstructures have outstanding promise with emergent applications impacting on energy conversion (photovoltaics and photocatalysis), electronics (semiconductor patterning) and photonics (sub-diffraction wave guides) in development. The principle challenge being addressed is extending the assembly size to meaningful scales where the nature of assembly (either 1D or 2D) and number of assembled layers can be controlled. The subsequent and equally important challenge will be in characterising these 3D architectures such that the precise position and placement of each nanorod building block is known.

Here we report the formation of an array of complex Moiré interference patterns from self-assembled nanorods demonstrating the extraordinary order attainable with these materials. The Moiré patterns are uniquely characterized by angular dark-field STEM (DF-STEM) and referenced against SAED, HRTEM and HRSEM for comparison. Six distinct patterns are observed and are indexed to an angular rotation between underlying sheets allowing the three dimensional architecture to be accurately determined. The interpretation of additional lateral stacking faults and defects owing to random tetrapod distribution offer a critical depth of understanding necessary for next generation applications incorporating orthogonal rod assembly.

5.3 Experiential

Materials

Cadmium oxide (>99%), trioctylphosphine (TOP, 90%), tri-n-octylphosphine oxide (TOPO, 99%), sulfur (99.98%) were purchased from Aldrich. n-Octadecylphosphonic acid (ODPA), were obtained from PolyCarbon Industries, Inc. (PCI). All the chemicals were used as received.
Synthesis of CdS nanorods

In a typical synthesis, 0.20 g of CdO, 1.07 g of ODPA and 2.74 g of TOPO were loaded into a 25 ml three-neck round bottom flask, fitted with a reflux condenser and a rubber septum. The mixture in the flask was heated to 100 °C under Argon gas until the reactants dissolve. The flask is then evacuated at 100 °C for one hour to remove any excess moisture. The mixture is then heated to 300 °C under Ar-gas where the CdO completely dissolves and the solution becomes optically clear. The mixture is cooled to 100 °C and further degassed for another 30 minutes. After this second degas, the apparatus is switched back to the argon line and the mixture was heated to 300 °C. 0.8 g of sulfur stock solution (0.65 g of sulfur powder dissolved in 8.25 g of TOP) was injected into the flask. After injection, nanocrystals grew at 300 °C for 30 minutes to reach desired size. The nanorods were washed 3-5 times to remove an excess surfactant by dispersing them in a 1:1 ratio of acetone to toluene. The solution was then centrifuged at 3000 rpm for 3 min and the sediment was decanted from the supernatant. After all washing the stock solution of CdS nanorod in toluene was stored in a nitrogen-filled glove box.

Formation of vertically aligned close-packed CdS nanorod superstructures

The nanorod solutions are subjected to repeat (2-3 times) size selective centrifugation (toluene only) (1000-2000 rpm/3 min) prior to assembly. This allows focusing of the rod size dispersity and allows removal of the majority of tetrapods. The optimum concentration for vertical assembly was determined by drop-casting 7 µl solutions (Eppendorf Pipette) of concentrations varying from 9 ×10^{-7} mol L^{-1} to 1 ×10^{-6} mol L^{-1} onto a carbon supported Cu-TEM grids. The solvent was allowed to evaporate slowly in an argon glove box, with 0% relative humidity, giving a constant evaporation rate (Typically 7-10 mins total). Rapid
evaporation rates of 2-3 min resulted in no observable vertical alignment with slower rates not changing the degree of alignment but increasing the number of assembled layers depositing on top of each other. The optimum concentration for perfect vertical assembly was found to be $2.1 \times 10^{-6}$ mol L$^{-1}$. This is the typical process used for the nanorod assembly formation shown in Figures 1-4. To study the effect of tetrapod (Figure 5), as-synthesised nanorod solution containing tetrapods were used without size selective centrifugation.

**Characterization**

For STEM and TEM analysis, a toluene solution with optimum nanorod concentration was deposited on Carbon supported TEM grids. STEM and TEM images and Small Angle Electron Diffraction were obtained using a JEOL JEM-2100F operating at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) of the nanorods assembly on a Si (111) substrate was performed by a Hitachi SU-70.

### 5.4 Results and Discussion

Colloidal II-VI nanorods have a permanent dipole moment and a net charge that varies: primarily as a function of ligand.$^{45,46}$ We have recently shown that the simplest method to achieve perpendicular assembly in solution is to direct the total energy considerations such that attractive interactions (dipole-dipole) slightly outweigh repulsive interactions (coulombic) to allow supercrystallisation.$^{34,35}$ Nucleation of assembly thereby has a distance, hence concentration dependence that suboptimal will result in random rod alignment as highlighted in Figure 1a and when optimised allows formation of a perfect 2D supercrystal layer (Figure 2) that forms on the surface after sedimentation from solution. Apart from a prerequisite tight size distribution in both length and diameter of the rods, here (7 × 30 nm), this method of assembly requires no external directing agents or addition of additives.
resulting in a defect free assembly with minimal contamination from excess organics (Figure 1b). The 2D sheets can be deposited sequentially forming multilayer arrays as shown in SEM image Figure 1c, when the rate of evaporation of the solvent is controlled. The rods at the edges of each layer are perfectly orthogonal confirming that each layer forms as a preassembled sheet in solution. Imaging these multilayer assemblies in transmission mode (TEM, STEM) results in characteristic Moiré interference patterns, Figure 1d and Figure 3, that vary depending on the number of monolayers.

**Figure 1:** (a) TEM image shows randomly lying CdS nanorods (7× 30 nm). (b) HRTEM showing top down image of vertically oriented close-packed CdS nanorods. (c) SEM image showing the multilayer, vertical assembly of nanorod superstructures. (d) TEM image shows different Moiré pattern revealed in CdS nanorod superstructures.
Figure 2: (a) Low magnification TEM image shows monolayer of vertically aligned close-packed CdS nanorods. Higher magnification DF-STEM image reveal defect-free 2D sheet of CdS nanorods.
**Figure 3:** Low magnification DF-STEM image showing the multilayer, vertical assembly of CdS nanorod superstructures over micron sized area and different Moiré pattern revealed in these superstructures.

Scanning Transmission electron Microscopy (STEM) removes the diffraction contrast commonly seen in the TEM images leaving only the mass thickness contrast. As the rods have a larger mass than the carbon support film, and are of similar mass and thickness, the only contrast differences in DF-STEM results from overlapped layers. Figure 4 shows the range of different Moiré patterns seen in the DF-STEM images of multi-layered CdS hexagonal sheets. Each image consists of a first (base) layer and a second layer with the
difference between each image occurring due to a rotational offset between each layer (the interference pattern reveals itself initially as a repeating hexagonal motif the size of which correlates with a specific angle of rotation between underlying sheets (Figure 5). This is highlighted with 5° rotation (Figure 4a) resulting in a centre-to-centre distance of 116 nm sequentially reducing with the larger angular rotations of 9°, 13° and 17° in Figure 4b-d respectively. The inverse relationship between angle of rotation and size of motif is expected as lines or patterns only appear when the cumulative effect of the rotational offset is sufficient to reveal a distinct image of a row of rods in an underlying layer. The measured motif repeat (D_{motif}) distance for each rotation angle, \( \alpha \) is in good agreement with the theoretical value D_{tm} obtained from the rotational Moiré equation (Table 1.0).

Rotational Moiré patterns from offsets as small as 1° are observable as the repeat motifs are in the sub-micron range (570 nm) and are hence smaller than the typical assembly dimensions (additional DF-STEM images of Moiré pattern observed for other misorientation angles are shown in Figure 6).

As the rotation angles increase to >17°, the size of the motif decreases and the aperiodic symmetry of the motifs is revealed. When the misorientation angle approaches close to 30°, pattern symmetry resembles the traditional 12-fold ordering seen in quasicrystals. Here the quasicrystal in nanorod superstructures lacks translational symmetry but possess rotational symmetry originating from the directionality of the nanorod superstructure. This resemblance to quasicrystals occurs as when one ordered sheet settles randomly on top of another ordered sheet, the resulting Moiré pattern cannot be entirely disordered and should instead be aperiodic. If one or both sheets have a small amount of disorder, then this aperiodic structure is less well formed. The hexagonal symmetry in the nanorods means that each 30° rotation is equivalent to 0° rotation such that 45° corresponds to a 15° Moiré pattern. The importance of the uniform size and shape of the rods becomes
Figure 4: (a-e) DF-STEM images and the corresponding FFT and SAED patterns (inset) of Moiré patterns arising from the stacking of two sheets of vertically oriented CdS nanorod superlattice films. Misorientation angle: (a) ~ 5°, (b) ~9°, (c) ~13°, (d) ~17°, (e) ~ 26°. (f) DF-STEM image with inset SAED pattern shows 12-fold quasicrystalline-like Moiré pattern revealed when the misorientation angle between two CdS nanorod layers is close to 30°.
Figure 5: Schematic representation of Moiré pattern formed by superposition of two hexagon patterns (layer 1 & 2) with 9° rotation angle.

Table 1.0:

Rotational moiré equation (1)

\[ D_{rm} = \frac{d}{2 \sin \left( \frac{\alpha}{2} \right)} \]

Where d is the d-spacing of the supercell (d = 10 nm) and alpha is the rotation angle.

<table>
<thead>
<tr>
<th>Degree rotation</th>
<th>( D_{\text{motif}} ) (nm)</th>
<th>( D_{rm} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>116</td>
<td>114.6279281</td>
</tr>
<tr>
<td>9</td>
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<td>22.22705741</td>
</tr>
<tr>
<td>29</td>
<td>19</td>
<td>19.96964581</td>
</tr>
</tbody>
</table>
Figure 6: (a-d) DF-STEM images of Moiré patterns revealed with misorientation angle of (a) ~ 3°, (b) ~7°, (c) ~19°, (d) ~22° respectively.
**Figure 7**: Moiré pattern revealed in “rice shaped” CdSe nanorods. As these nanorods assembly have pinholes which ultimately leads to disrupt the aperiodicity and no long range ordering can be seen in the above DF-STEM image.

apparent in these patterns when perfect columnar CdS rods are compared to ‘rice shaped’ CdSe rods a 10% pinhole vacancy causes the aperiodicity to be disrupted and no long range ordering can be seen in Figure 7.

The Fast Fourier Transforms (FFTs) and Small Angle Electron Diffraction (SAED) are a result of the individual hexagonal diffraction of each overlapping layer (Given as A and B).
A large camera length (200 cm) was used for the SAED to get information only from the hexagonal ordering and not the crystal structure. By measuring the angle between the spots from two patterns results in the calculation of the misorientation angle. The low angle spots up to 10 degrees manifests as a broadening in the low index peaks and separate spots for the two layers only become apparent in the second or third rings. As a result FFTs are normally best used for the low angles due to the intensities and proximity of the two spots (Figure 4a and b insets). The separate spots for A and B layers can be more clearly seen in Figure 4c and d where the misorientation angle is increased. As the angles increase, the two spots diverge further tending towards 12-fold quasicrystal as the rotation approaches 30 degrees.

Interestingly, the diffraction patterns and FFTs are not purely two separate diffraction patterns overlapped, like that commonly seen for twin defects. Instead, there is the presence of satellite spots coming from the Moiré superstructure from the overlapped layers. This is due to the multiplication of intensities, leading to the convolution of diffraction patterns in which the frequency vectors being added vectorially, whilst the corresponding impulse amplitudes are multiplied.\(^1\)\(^5\) As a result, these satellite spots cannot be indexed using the standard miller indexing (hkl) and as a result need a minimum of 2 extra vectors added. This indexing and explanation is given in the Figure 8. Figure 4f and inset SAED image clearly shown this unique symmetry found in the nanorods superlattice and is in good agreement with the previous report \(^5\),\(^10\),\(^12\) (Larger images of SAED for all rotation angle can be seen in Figure 9).
**Figure 8:** Example of indexing the SAED pattern from a Moiré pattern with 26° rotation. In order to index all the satellite spots in the pattern, the standard miller indices (hkl) are not suitable alone. Two modulation vectors are required to index the satellite spots, indicated as q1 and q2, and to fully index the pattern in the form (hklmn). The image on the right indicates the hklmn indices for the Moiré diffraction/FFT patterns. All of the rotational Moiré patterns, Figure 9, can be indexed in a similar fashion.
Figure 9: Fast Fourier Transforms (FFTs) and Small Angle Electron Diffraction (SAED) for all six different Moiré pattern arising upon the stacking of two CdS nanorod assembled sheets.
Moiré patterns formed when more than 2 sheets overlaps are more complex due to the sum of the rotation differences between the layers, although indexing is possible. Figure 10 shows an example of this multilayer, with the three sheets easily identifiable in the DF-STEM image. M1,2 and M1,3 are first order Moiré patterns, with 9° and 26° misorientation respectively, and M1,2,3 is the second order Moiré pattern which is made up from all 3 layers. As above, the misorientation angle can be calculated from the first order Moiré patterns (M1,2 and M1,3) from either the size of the hexagonal motifs or from FFT. M1,2,3 as a second order Moiré pattern, however, cannot be determined from the image alone therefore FFT, or SAED, needs to be employed.

![Figure 10: First order (M1,2 & M1,3) and second order Moiré pattern (M1,2,3) can be seen in the DF-STEM image and FFT pattern of respective area.](image-url)
Figure 11: DF-STEM image shows CdS superlattice consisting of three layers. (b) High-resolution DF-STEM image of the region indicated as 3 showing a complex Moiré pattern due to the relative rotations of the three layers. (c) FFT of region indicated as 2 shows two hexagonal spot with misorientation angle of 24°. (d) FFT of region indicated as 3 showing three sets of hexagonal spots corresponding to three different CdS layer with misorientation angle with respect to each other is measured as 8°, 24° and 16°.

An FFT on each region M1,2 and M1,3 reveals two misoriented hexagonal patterns corresponding to rotational misorientations of 9° and 26° respectively as expected. Three misoriented hexagonal patterns can be identified from the FFT M1,2,3 correlating with the
number of layers. Comparison of this patterns with the corresponding FFT’s of M1,2 and M1,3 allows the degree of misorientation between the hidden layers M 2,3 to be identified as 17° (additional DF-STEM images of Moiré pattern in multilayer nanorod superlattice and FFTs are in Figure 11).

Absence of Moiré patterns occur when there is either no rotation or the offset is at exact multiples of 30° (Figure 12 (a)). However different pattern formation occurs in Figure 12 (b) where there is no rotational offset but a lateral shift occurs. The hexagonal structure of the layers can still be seen to be intact, (FFT inset of Figure 12 (b) with no first order Moiré patterns present. Figure 12 (c) is a higher resolution image of Figure 12 (b), the yellow indicates the first layer and the green the second layer. This shift of ~1/3 of the unit cell can easily be seen due to the visibility of the space between the rods forming a hexagonal pattern. Other fractional shifts are of course possible and are quite often difficult to distinguish from tilted hexagonal sheets (Figure 13).

A noticeable feature of the 2D monolayer sheets of CdS nanorods is their termination with apparently random angular edges. Closer examination Figure 14 (a, b) reveals the presence of tetrahedral shaped nanocrystals (tetrapods) that act to terminate the growth of the supercrystal. Tetrapods form as percentage of each colloidal synthesis due to nucleation of some crystals in the zinc-blende instead of wurtzite phase, and while they can be reduced through growth control their complete elimination is difficult to achieve.24 The 4 equivalent length arms are typically of the same dimensions of the colloidal rods and as such one arm of the tetrapod can join the super-crystallisation with the other 3 arms acting as a barrier to further addition. Straighter edges of the sheets, such as that from the highlighted region of Figure 14 (c), reveal multiple tetrapods present in a small area. In multilayers, tetrapods are difficult to distinguish in TEM (Figure 14c) but can be more clearly observed in HRSEM (Figure 14d).
Figure 12: (a) TEM image show no Moiré pattern generates when two 2D sheets overlap perfectly (0° misorientation angle). (b,c) TEM and HRTEM images clearly indicate the lateral shifts between two 2D sheets respectively. The inset FFT in (b) shows only one hexagonal pattern.

Figure 13: Schematic representation of lateral shift formed by superposition of two hexagon patterns with ~ ¼ lateral shift.
Figure 14: (a-c) DF-STEM and TEM show the presence of single and multiple tetrapods in nanorod assembly. (d) SEM image revealed the tetrapod presence in the second and third layer of CdS nanorod superstructures.

5.5 Conclusions

The occurrence of Moiré Patterns in assembled sheets of vertically aligned semiconductor nanorods not only demonstrates the extraordinary order attainable in their assembly but allows the three dimensional architecture to be elucidated with precision. The use of STEM as a characterisation tool for Moiré patterns in nanorod assembly allows detailed contrast resolution and accurate determination of angular rotation between respective monolayer
sheets. Coupling the imaging analysis with either Fourier transform or Small Angle Electron Diffraction elucidates the rotational offsets from 1 to 30°. The manifestation of 12-fold quasicrystal symmetry at close to 30° demonstrates that the overlapping sheets are aperiodic in nature. This depth of analysis of multilayer nanorod assemblies reveals the additional patterns related to lateral shifting with no rotation, the interpretation of pattern formation in 3 or more layers and the heretofore unobserved influence of tetrapods on rod supercrystallisation. The interpretation is generally applicable to understanding and characterizing all nanorod assemblies irrespective of the nature of material (metal or semiconductor). This insight is particularly consequential and relevant given the rapidly expanding technological advances emerging from these solution-derived nanomaterials.

5.6 References


Chapter 6: Assembly of CuIn$_{1-x}$Ga$_x$S$_2$ Nanorods into Highly Ordered 2D and 3D Superstructures

6.1 Abstract

Here, we report self and directed assembly of CuIn$_{1-x}$Ga$_x$S$_2$ (CIGS) nanorods into highly ordered 2D and 3D superstructures. The assembly protocol is dictated by the ligand environment and is hence chemically tunable. Thiol capped nanorods spontaneously assemble into 3D aligned nanorod clusters over a period of hours with end to end and side to side order. These clusters can be disassembled by ligand exchange with an amine and subsequently re-assembled either at a substrate interface or as free floating 2D sheets by directed assembly protocols. This dimensional control of CIGS nanorod assembly, extending over device scale areas with high degrees of order, is highly attractive for applications utilizing these important quaternary photoabsorbers.

6.2 Introduction

Colloidal nanocrystal routes to the quaternary copper chalcogenide CuIn$_{1-x}$Ga$_x$S$_2$ (CIGS) offer attractive solution processing of this compound semiconductor.\textsuperscript{1-6} Formation as a nanocrystal locks in the correct stoichiometry, a major challenge in co-evaporation approaches where multiple phases occur particularly at grain boundaries.\textsuperscript{7-9} The direct band gap varies with (In/Ga) composition and can be tuned from 1.5 to 2.4 eV by judicious selection of metal precursor ratios during synthesis.\textsuperscript{3-5} The low toxicity, high radiation stability and high absorption coefficients of CIGS nanocrystals allows for wide ranging applications in photo-catalytic, thermoelectric and photovoltaic devices.\textsuperscript{1-6, 10-12} In nanocrystals, the wurtzite phase of copper chalcogenides is stable allowing for ligand assisted shape control with nanorod growth occurring along the (002) direction.\textsuperscript{12-16} This geometry
allows length dependent properties such as total absorption and conductivity to be harnessed independent of diameter dependent properties such as band-gap.\textsuperscript{17-19} Subsequent assembly allows for the possibility of large scale arrays with each nanorod vertically aligned and close packed thereby maximizing the collective properties in a densely packed superstructure.\textsuperscript{18,20}

The progress in understanding and hence controlling nanorod assembly has led to approaches ranging from simple evaporation, through to external perturbation by additives (depletion attraction), highly oriented pyrolytic graphite (HOPG) or electric fields.\textsuperscript{20-32} We have recently shown that coulombic interactions owing to the net charge and dipole on the nanorods exert the largest influence on the type of assembly that occurs.\textsuperscript{21-23} In ambient solutions, if the attractive interactions (dipole-dipole) outweigh the repulsive interactions (charge-charge) assembly will occur as a function of distance and hence concentration.\textsuperscript{21-23} In solution, this constitutes as assembly into 2D monolayers which deposit to the surface at a specific concentration. Alternatively, under an electric field the net charge results in electrophoretic migration with axial orientation due to the dipole.\textsuperscript{28} As the dipole is intrinsic to the wurtzite lattice and the charge can be modulated by a ligand, this gives a relatively facile approach to tailor the assembly formation as needed with up to centimeter scale areas reported.\textsuperscript{28} With copper chalcogenides, assemblies of binary (Cu\textsubscript{2}S) and ternary (CuInS\textsubscript{2}) nanorods have been demonstrated by slow evaporation of solutions over relatively small areas whereas Cu\textsubscript{2}S nanoplates have been shown to spontaneously organize into 3D supercrystals within the solution phase.\textsuperscript{16,33} We recently showed the synthesis and subsequent assembly of quaternary Cu\textsubscript{2}ZnSnS\textsubscript{4} (CZTS) nanorods from solution using charge/dipole interactions.\textsuperscript{15}

Here we show controllable assembly formation with the important CuIn\textsubscript{1-x}Ga\textsubscript{x}S\textsubscript{2} (CIGS) nanorods over two and three dimensions. The assembly was primarily enabled by a synthetic optimization to allow monodisperse nanorod formation (without L shaped
nanocrystals). The as-synthesized nanorods are thiol capped and over 4-5 hours spontaneously self-assemble into highly ordered 3D nanocrystal clusters (Figure 1). We further show that we can de-assemble these clusters by the facile introduction of an amine ligand; reverting the solution to a random nanorod dispersion. As these nanorods have a modified ligand environment (thiol/amine) and net charge, their assembly can be controlled by either optimizing the solution concentration (to form free floating 2D sheets) or by electrophoresis. The subsequent formation of monolayer to multi-layer assemblies of vertically aligned CIGS nanorods directly on substrates is therefore possible. This reversible assembly and disassembly protocol is extendable to a range of ternary and quaternary nanorods and creates a facile chemical process for modulating nanorod assembly over 2 and 3 dimensions in these important semiconductor materials.

6.3 Experimental

Materials

All reagents were used as received without any further purification. Copper (II) acetylacetonate (Cu(acac)2, 99.99%), Indium (III) acetylacetonate (In(acac)3, 99.99%), Gallium (III) acetylacetonate (Ga(acac)3, 99.99%), 1-dodecanethiol (1-DDT, >97%), tert-dodecanethiol (t-DDT, 98.5%, mixture of isomers), oleylamine (OLA, 70%, technical grade) and 1-octadecene (ODE, 90%, technical grade) were purchased from Aldrich. Trioctylphosphine oxide (TOPO, 99%) was purchased from Strem Chemicals.

Synthesis of CuIn0.75Ga0.25S2 (CIGS) Nanorod

CIGS nanorods were synthesized using a modification of previously published procedure. For a typical synthesis of CIGS nanocrystals, Cu(acac)2 (0.2618 g, 1mmol), In(acac)3 (0.3091
g, 0.75mmol), Ga(acac)₃ (0.0918 g, 0.25mmol) and TOPO (1.3532 g, 3.5mmol) were mixed with 10 mL of 1-octadecene in a three-neck round-bottom flask and evacuated at room temperature for 30 minutes. The solution was then heated to 250 °C-270 °C in 15-20 min under an argon atmosphere. At 155 °C, a mixture of 0.5 mL 1-DDT and 1.5 mL t-DDT was injected into the flask which resulted in an immediate colour change from dark green to light yellow. After injection, the reaction was allowed to proceed for 10-15 minutes with continuous stirring. Subsequently, the heating mantle was removed and the reaction vessel was allowed to cool to 80 °C. 2-3 mL of anhydrous toluene was added initially to quench the reaction. The nanorods were then washed in a 2:1 ratio of toluene to ethanol and centrifuged at 4000 rpm for 10 minutes to yield a dark red centrifuged product. The key step for synthesis of monodispersed CIGS nanorod is the increase in 1-DDT concentration in the reaction and growth time for the nanorod formation. As 1-DDT binds more strongly to facets other than the (002) allowing nanorod growth in this direction.

**Synthesis of CuInS₂ Nanorod**

For a typical synthesis of bullet shape CuInS₂ nanorods, Cu(acac)₂ (0.2618 g, 1mmol), In(acac)₃ (0.2919 g, 1mmol), and TOPO (1.3532 g, 3.5mmol), 10 mL of 1-octadecene were loaded in a three-neck round-bottom flask and degassed at room temperature for 30 minutes. Further the solution was then heated to 270 °C in 30 minutes under an argon atmosphere. When the temperature reach 155 °C, a mixture of 0.25 mL 1-DDT and 1.75 mL t-DDT was injected into the flask. After injection, the reaction was allowed to proceed for 30-60 minutes with continuous stirring. After that the nanocrystal growth was terminated by removal of the heating mantle. The nanocrystal was washed thrice with 1:1 ratio of toluene and acetone and centrifuged at 3000 rpm for 5 minutes to yield a black solid. The resultant nanocrystal redispersed in toluene for further analysis.
**Ligand Exchange**

For ligand exchange, 100 µl of oleylamine is carefully added to 5 mL toluene solution of as-synthesized CIGS/CIS nanorods. With the addition of amine solution there is immediate change in the dispersion of nanorods solution is visualized. Further, the resulting solution sonicated for 10 min in the sonication bath. The solution was washed with 1:1 ratio of toluene and ethanol and centrifuged at 4000 rpm for 5 min and the supernatant discarded. An important extra care will be taken during ligand exchange; the oleylamine-capped nanocrystals were washed 3-5 times with non-solvent (ethanol, methanol) to remove any excess oleylamine in the nanocrystal solution. As nanocrystal shows etching behaviour over the time in the presence of excess oleylamine (images not shown here). Similar behaviour of etching of nanocrystal due to excess oleylamine was previously seen on CuInSe$_2$.\textsuperscript{49,50}

**Monolayer Assembly of Nanorods**

The self-assembly of CIGS and CIS nanorods was undertaken by drop-casting the nanorod solution with various concentration ranging from $10^{-8} \text{ mol L}^{-1}$ to $10^{-2} \text{ mol L}^{-1}$ on to a carbon supported Cu-TEM grids. The solvent was allowed to evaporate slowly under constant evaporation rate (in an argon glove box, with 0% relative humidity). The optimum concentration for vertical assembly was found to be $5 \times 10^{-5} \text{ mol L}^{-1}$. The strict concentration dependence of nanorods solution is typical for perpendicular nanorod assembly where outside of certain window; randomly deposited nanorods are found on the substrate.

**Multilayer Assembly of Nanorods by Electrophoresis**

A toluene solution of CIGS nanorods (10% w/v) was used for electrophoresis. During Electrophoresis, the silicon substrates (10 mm × 10 mm) were attached onto the negative
electrodes, of a two parallel gold coated copper electrodes which are separated at 2 mm apart and the electrode are completely immersed in a nanorod solution and a potential of 150-200 V was applied to the substrate for 3 min 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 millimetre.

**Electron Microscopy**

The CIGS/CIS nanorods and their assemblies were characterized by transmission electron microscopy (TEM), angular dark-filed scanning transmission electron microscopy by using a JEOL JEM-2011F operating at an accelerating voltage of 200 kV. High resolution scanning electron microscopy (SEM) of the nanorods assembly on a Si (111) substrate was performed by a Hitachi SU-70 machine.

**X-ray Diffraction Analysis**

The sample for X-ray diffractograms analysis was prepared by drop-casting the nanorod solution on glass substrate. The analysis was carried out on a PANalytical X’Pert MPD Pro using Cu Kα radiation with a 1-D X’Celerator strip detector.

**UV-vis Absorption Spectroscopy**

Uv-vis spectroscopy of the nanorod solutions were carried on a PerkinElmer’s LAMBDA 45 and 35 UV-vis spectrophotometer operated at a resolution of 1 nm.
Fourier Transform Infrared Spectroscopy

All spectra were taken in transmission mode on a model Perkin-Elmer-Spectrum at a spectral resolution of 4 cm$^{-1}$. FTIR measurements were carried out for the nanorod solution drop casted on Si or glass substrates.

X-ray Photoelectron Spectroscopy

XPS measurement of the as synthesized and ligand exchanged CIGS nanorods were carried out using a Kratos Axis 165 spectrometer. High-resolution spectra were taken using monochromated Al Kα radiation of energy of 1486.6 eV at fixed pass energy of 20 eV. For peak synthesis, a mixed Gaussian-Lorenzian function with a Shirley type background subtraction was used. Samples were flooded with low energy electrons for efficient charge neutralization. Binding energies (BE) were determined using C 1s at 284.8 eV as charge reference.

Dynamic Light Scattering

The size of CIGS and CIS ANCs was measured by Dynamic Light Scattering (DLS) using Zetasizer Nano ZS DLS system (Malvern Instruments Ltd., England). The laser specifications for this Zetasizer were 4mW He or Ne laser with a 633 nm wavelength. DTS applications 5.10 software was used to analyse the data. For each sample, four DLS measurements were conducted with a number of runs.

Zeta-potential Measurement

Zeta-potential of as-synthesised and ligand exchanged CIGS nanorod was measured in toluene solution by using Zeta PALS (Zeta Potential Analyzer, Brookhaven Instruments
Corporation, US) using low and high electric-field, \( E = 137 \text{ Vcm}^{-1} \) and \( 274 \text{ V cm}^{-1} \), across the palladium electrodes and measured zeta-potential values was constant from two fields which was averaged from 10 repeated experiments. The mean zeta-potential value was calculated by Zeta PALS software.

### 6.4 Result and Discussion

Highly monodisperse CIGS nanorods 11±0.5 nm in width and 24±1 nm (Figure 2a) were synthesized using a modification of procedure from Gupta et al (see experimental section).\(^{14}\)

The nanorods are defect free wurtzite single crystals (XRD inset Figure 2a) with elongation occurring along the [002] direction and with a \( d \)-spacing of 0.318 nm (TEM Figure 2b).

Spontaneous nanorod assembly occurs in a solution of these thiol-capped nanorods when left for a period of 4-5 hours resulting in sub-micron sized aligned nanorod clusters (ANCs) consisting of close packed rods stacked end-to-end and side-by-side. The size of the clusters varies from 500-800 nm (Figure 2c). In Figure 2d, the hexagonal symmetry of the ANCs is evident suggesting that the nanorods prefer to adopt hexagonal close packed (hcp) packing arrangements to attain the highest packing efficiency and minimize the potential energy.\(^{35-37}\)

Elemental mapping of an ANC (figure 2e) further confirms that Cu, In, Ga, and S are evenly distributed with chemical composition close to \( \text{CuIn}_{0.75}\text{Ga}_{0.25}\text{S}_2 \). The formation of ANCs in solution was further investigated by dynamic light scattering (DLS) showing an average hydrodynamic size at 500-800 nm (Figure 3) in good agreement with TEM and SEM data. The degree of order and resolute close packing in these ANCs is highly attractive for applications where the collective properties of the nanorods can be exploited at a sub-micron length scale, e.g. labeling, lighting etc.\(^{18-20}\)

The ANCs show a broad UV-vis absorbance in comparison to well dispersed nanorods as seen in Figure 4a. This can be attributed to increased dipole coupling between the nanorods in the closed packed arrangement when
Figure 1: Schematic representation shows the assembly and deassembly of CIGS nanorods.
Figure 2: Low-resolution angular dark-field STEM (DF-STEM) of monodispersed CIGS nanorods with inset XRD pattern confirming their wurtzite structure. (b) HRTEM image of nanorod. (c) Low-resolution DF-STEM image showing the CIGS ANCs with inset high-resolution DF-STEM image. (d) HRSEM image shows the side-by-side alignment of nanorods in individual ANC. (e) HAADF STEM image of CIGS ANC with corresponding EDS elemental mapping images.
Figure 3: DLS size distributions of CIGS ANCs.

Figure 4: (a) UV-vis absorption spectra of CIGS ANCs (red) and after deassembly by oleylamine (green). (b) Tauc plot of CIGS nanorods to calculate direct optical band gap of 1.85 eV by extrapolation $(\alpha h\nu)^2$ versus energy, where $\alpha$ represents the absorption coefficient and $h\nu$ is the photon energy.
compared to the non-assembled nanorods. Similar behavior was recently reported for pseudo spherical \( \text{Cu}_{1.97} \text{S} \) nanocrystals.\(^{34,38,39} \) The CIGS nanorods have a band gap of \(~1.85\) eV (Figure 4b) determined by extrapolating the linear region of a plot of \((\alpha h\nu)^2\) versus energy, where \(\alpha\) represent the absorption coefficient and \(h\nu\) is photon energy, in good agreement with previous reports.\(^{14} \)

While these ANCs can be deposited from solution in high density (Figure 5) to form a thin-film there is no preferred axial orientation of the nanorods in the final layer (given the random packing of the ANCs). As resolute vertical alignment of nanorods in a thin-film is attractive for absorber layers, we investigated cluster de-assembly in solution for subsequent reassembly at a substrate interface. This was achieved using partial ligand exchange with oleyamine where a rapid solution transformation from opaque to translucent occurred upon addition (Figure 6a). DLS measurements confirmed the cluster de-assembly with the hydrodynamic radius \(~25\) nm consistent with the length of a discrete nanorod (Figure 6b).

Fourier transform infrared spectroscopy (FTIR) confirmed the partial ligand exchange where in addition to the characteristic \(\text{S–H}\) vibration peak at \(2570\) cm\(^{-1}\) (from the thiol), the anti-symmetric and symmetric vibration modes of \(-\text{N–H}\) are observed between \(3300\) and \(3500\) cm\(^{-1}\) with \(\text{NH}_2\) scissoring modes at \(1570\) cm\(^{-1}\) respectively (Figure 7).\(^{34} \) The survey XPS spectra of as-synthesized CIGS nanorods (Figure 8) show the presence of \(\text{Cu}, \text{In}, \text{Ga}, \text{S}, \text{O}, \text{C}\) with \(\text{N}\) detected after ligand exchange. The high-resolution spectra of \(\text{S}\ 2p\) (Figure 9a) from the as-synthesized CIGS nanorods can be fitted well with two spin–orbit doublets of intensity ratio1:2 for \(2p_{1/2}\): \(2p_{3/2}\) and doublet separation of \(1.2\) eV. The doublet with \(\text{S}\ 2p_{3/2}\) peak at \(161.7\) eV is attributed to sulphide ions of the nanorods.\(^{40} \) The second doublet at \(162.7\) eV can be assigned to thiolate sulfur bonded to the nanorod surface.\(^{41} \) The \(\text{S}\ 2p\) spectrum from the ligand exchanged nanorods (Figure 9b) can be fitted in a similar manner yielding a relatively low fraction of thiolate sulfur which is expected as the amine displaces thiols forming
Figure 5: Low-resolution SEM images of ANCs on silicon substrate

Figure 6: (a) Photograph of solutions of ANCs of CIGS nanorod and after deassembly of CIGS ANCs by oleylamine. (b) DLS size distributions of CIGS nanorod after ligand exchange with oleylamine.
Figure 7: (a) FTIR spectra of CIGS ANCs after partial ligand exchange with oleylamine, black arrow for aliphatic alkyl chains, green for thiols and red for oleylamine respectively.

Figure 8: Survey spectra of (I) as synthesized nanorods (II) oleylamine exchanged nanorods.
Figure 9: High-resolution XPS spectra of as-synthesized and ligand exchange CIGS nanorods.

stronger bonds with the surface atoms. An additional broad peak at ~ 169 eV is attributed to oxidized sulfur in the form of sulfone or sulfate species. The related N 1s spectrum of the amine exchanged CIGS (Figure 9c) shows the presence of nitrogen in two different chemical states. The peak at 399.3 eV corresponds to neutral C-N bonding in amine and the prominent shoulder at higher binding energy of 401.3 eV to positively charged nitrogen (C-N\(^+\)) resulting from coordination of the N in the amine to the metal ions.\(^{42}\)

The thiol/amine-capped nanorods did not undergo spontaneous super-crystallization regardless of time. In contrast, thiol/amine capped nanorods only self-assemble at an optimal concentration, forming 2D superstructures which drop to the surface under gravity sedimentation correlating with the charge/dipole based mechanism previously reported.\(^{21-23}\) Figure 10a shows low resolution TEM images of a monolayer of vertically aligned thiol/amine-capped CIGS nanorods that self-assemble at an optimal concentration of (5×10\(^{-5}\) mol L\(^{-1}\)). The inset FFT pattern demonstrates the resolute hexagonal ordering. Further magnified HRTEM images are shown in Figure 10b with the inset top-down HRTEM image of a single nanorod showing the d-spacing in the lattice fringes is 0.318 nm, which matches with the (002) plane of wurtzite structure. The influence of charge and dipole can be further utilized to achieve perpendicular assembly over large (device scale areas) using electrophoresis. Here the charge ensures field driven migration whereas the dipole ensures...
orientational order in the deposit. Using field strength of 150-200 V, highly ordered deposits over device scale areas and over several multilayers were obtained (Figure 10c). The further HRSEM image in Figure 10d shows that the nanorods are vertical oriented in all the layers.

The greater ζ potential of the thiol/amine-capped nanorods, ~ 33±4 mV, to that of the thiol capped nanorods, ~ 7±3 mV, (Figure 11) significantly impacts their respective assembly protocols. The thiol/amine-capped nanorods have large cumbic repulsion in solution, which maintains the dispersion such that no assembly is occurring outside of an optimized concentration. The 2D assembly of thiol/amine-capped nanorods in solution therefore follows the expected lowest energy consideration with a distance (concentration) dependence that balances attractive and repulsive interactions for assembly. In contrast, for the thiol-capped nanorods, dipole-dipole forces are much stronger as the cumbic repulsion is less prominent. The spontaneous clustering of the thiol capped nanorods at low dilution for the formation of 3D assemblies clearly occurs by a different mechanism. The time dependence (3-4 hours) suggests that this assembly is predominantly entropy driven where the free energy of the system increases when solute molecules are eliminated from between the nanorods. For supra-crystals to form the nanorods need to find their preferred place on the growing crystal structure before locking in resulting in the most energetically stable configuration (3D versus 2D) yielding the greatest entropy gain.43-48 Clearly other inter-particle interactions cannot be discounted. Van der Waals studies in nanorods have shown the length of the ligand will predicate the preference for end to end or side to side assembly (or both) with shorter lengths increasing the propensity for end to end.43 Here the thiols are shorter than the oleylamine in good agreement with the simultaneous occurrence of end to end and side to side. In support of this, if thiol capped nanorods are rapidly assembled from an evaporated solvent before clustering occurs, end-to-end patterns form in preference to side by side (Figure 12).
Figure 10: (a) Top down TEM image of monolayer sheet of vertically assembled CIGS nanorods with inset FFT pattern. (b) TEM images showing the closed-packed 2D superlattice with inset HRTEM image of single nanorod. (c) SEM cross-section image shows the multi-layered assembly of nanorods. During sample cleaving, the multilayer nanorod film has delaminated resulting in the dark feature between the layer and substrate (d) High-resolution SEM image shows the vertically alignment of CIGS nanorods.
Figure 11: The zeta potential of the ANCs CIGS nanorods, shown in (a), was found to be 7 ± 3 mV. After ligand exchange with oleylamine, the CIGS nanorods having much higher zeta potential value of 33 ± 4 mV as shown in (b).

Figure 12: (a,b) Low and high-resolution TEM images show end-to-end assembly of nanorods.
Figure 13: (a) Low-resolution SEM images of ANCs of CuInS$_2$ nanorods. (b) HRSEM of individual ANCs, where side by side alignment is clearly revealed. (c) DF-STEM image shows deassembly of CuInS$_2$ ANCs after ligand exchange with oleylamine. (d) TEM image shows the close-packed vertical assembly of nanorod obtained by slow evaporation of nanorods solution on carbon coated Cu-TEM grid with inset HRTEM of single nanorod.

6.5 Conclusion

In summary, the reversible assembly and disassembly of CIGS nanorods is demonstrated over 2 and 3 dimensions from solution. This approach is generally applicable to copper
chalcogenide nanorods synthesized with thiol ligands (See comparable assemblies demonstrated with ternary CuInS$_2$ nanorods: Figure 13). We show that the assembly protocol is dictated by the ligand environment and is hence chemically tunable. This approach allows the collective properties of CIGS nanorods to be harnessed either as micron size clusters, or in monolayer and multi-layer assemblies extending over device scale areas. The density of packing, perpendicular order and evidence of absorption enhancement in the assemblies make these structures highly attractive for scalable application in photovoltaic devices.

6.6 References


Chapter 7: Highly Ordered Nanorod Assemblies Extending over Device Scale Areas and in Controlled Multilayers by Electrophoretic Deposition

7.1 Abstract

Here we describe the formation of vertically aligned nanorod assemblies over several multilayers using CdS and CdSe nanorods by electrophoretic deposition. The presence of both charge and dipole on the rods allows both field driven deposition and orientational order to form close packed arrays where each rod is vertically aligned. Comparing assembly formation in electrophoresis to spontaneous assembly in solution gives important insights into nanorod organization by these different mechanisms. We show the influence of ligand environment on net charge (zeta potential) and its influence on assembly formation in CdSe nanorods that have long chain alkyl ligands (low charge) or pyridine ligands (high charge). The experimental observations show that highly charged rods deposit too quickly to allow close packing to occur with perpendicular alignment only occurring with a lower net charge. This is supported by simulation predicting a lower energy configuration with a preference for perpendicular alignment as the charge state decreases. The resolute order that is retained over device scale areas and over several multilayers combined with inherent scalability of electrophoretic deposition makes this approach highly attractive for large-scale nanorod integration in electronic, photonic or photovoltaic devices.

7.2 Introduction

Colloidal nanorods are an important material set where electronic and optical properties are size tunable in both length and diameter and hence controllable.1-4 Organization of nanorods into assemblies at practical length scales using reproducible protocols is important if their
predicted impacts in wide ranging applications from photovoltaics to energy storage are to be realized.\textsuperscript{1,5-8} Shape anisotropy in nanorods creates a barrier to rational assembly although successful approaches in solution have been achieved by addition of external additives either as excess surfactants, polymers or solvents to induce depletion attraction.\textsuperscript{1,5,9-14} Alternatively, external directing agents such as highly oriented pyrolytic graphite or drying under an electric field have been successful over small areas.\textsuperscript{15-18} We have recently shown that the net charge and dipole moment on nanorods has a significant influence on their assembly. In the absence of external forces on a solution, the charge dipole interactions have a distance hence concentration dependence which when optimized allows for spontaneous clustering of the rods into 2D sheets that drop to the surface under gravity sedimentation.\textsuperscript{19-22} As these interactions are Columbic, they can be calculated allowing for predictive control of assembly (whether 1D or 2D) by tuning the net charge through ligand exchange. A limitation is that large area coverage is attained by overlapping of these pre-formed sheets, leading to non-uniform construct unsuitable for reproducible application.

Electrophoretic deposition as a viable route to layer formation with colloidal particles is known, yet it is only recently that this approach has been optimized to form assemblies of nanocrystals with a high degree of order at a surface.\textsuperscript{23-38} We have shown that electrophoretic deposition is an effective route for the formation of close packed assemblies of both spherical and rod-shaped nanocrystals. The presence of a net charge on the as-synthesized colloidal nanocrystals allowed their controlled deposition.\textsuperscript{26} In the case of spherical nanocrystals, the electrophoretic route allowed not just close packed order but localization of assemblies to discrete lithographic trenches.\textsuperscript{38} With rods the charge allowed deposition with the inherent dipole moment due to the non-centrosymmetric wurtzite lattice ensuring orientational order in the final deposit.\textsuperscript{39-40} The nanorods were organized into close packed assemblies with each rod vertically aligned extending over centimeter scale areas.
Here we expand on this electrophoretic route for nanorod assembly demonstrating accurate control over the number of nanorod layers deposited on a surface with each layer perfectly aligned and close-packed. We further show the importance of nanorod charge in addition to dipole on the electrophoretic assembly process expanding on interactions in the solution state. We extend the protocol to CdSe and show how differences in charge, dipole and rod shape in comparison to CdS rods affects the assembly. The as-synthesized rods having a low net charge can be induced to form ordered assemblies whereas when the charge is dramatically increased by ligand exchange the rods no longer form perfect assemblies. The balance between field driven (electrophoresis) and entropic assembly is discussed in detail with both needed for optimum ordering in the array. A theoretical treatment of assembly correlates well with the experimental results confirming that field driven effects are dominant in solution to push the nanocrystals to the surface with entropic considerations manifesting to allow close packing at the interface.

7.3 Experimental

Materials

Cadmium oxide (>99%), trioctylphosphine (TOP, 90%), tri-n-octylphosphine oxide (TOPO, 99%), sulfur (99.98%) and selenium (99.98%) were purchased from Aldrich. n-octadecylphosphonic acid (ODPA), n-tetradecylphosphonic acid (TDPA), n-hexylphosphonic acid (HPA) were obtained from PolyCarbon Industries, Inc. (PCI). All the chemicals were used as received.

Synthesis of CdS Nanorods

CdS nanorods were synthesized according to previously published methods in an inert atmosphere using standard air free techniques. In detail, 0.21 g 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 120 °C under Argon gas flow at which CdO, ODPA and TOPO were dissolved. The mixture is further evacuated at 120 °C for 20 minutes with a vacuum range of 150-200 mTorr to remove any impurities and moisture (first degas). Next, the mixture is ramped to 300 °C under Argon flow at which CdO completely dissolves and the solution becomes optical clear. The solution is cooled to 120 °C and further degassed for another 45 minutes. After this second degas, the mixture was heated to 310 °C under argon flow at which sulfur stock solution (~ 800 µl) containing 64 mg of sulfur in 7.64 mg TOP is rapidly injected and nanocrystal were allowed to grow for 30 minute before removal of the heating mantle. When the temperature reached ~80°C, the reaction was quenched via the addition of 2~3 mL of anhydrous toluene. The nanorods were purified by 3-4 times by dissolution in toluene and precipitation from acetone.

**Synthesis of CdSe Nanorods**

CdSe nanorod was also synthesized in a procedure similar to that of CdS nanorods. Briefly, CdO (0.20 g), n-tetradecylphosphonicacid (TDPA, 0.71 g), n-hexylphosphonic acid (HPA, 0.16 g) and tri-n-octylphosphine oxide (TOPO, 3.00 g) in a three-neck flask equipped with a condenser and a thermocouple adapter. The mixture is heated to 120 ºC in an atmosphere of Ar and then evacuates for 1 hr. The mixture is further heated up to 300 ºC under Argon atmosphere so that CdO decomposed and give optical clear solution. Once clear solution was achieved add 1.5 g of Trioctylphosphine (TOP) to the mixture, and the temperature was further raised to 310 ºC. Next inject rapidly Selenium (~500 µl) stock solution containing 73 mg of selenium in 416 mg of TOP and the resulting nanocrystal were further allowed to grow for 5-10 min at 310 ºC. The growth of nanorods was terminated by removal of the heating mantle, and at 80 °C adds 2-4 ml anhydrous toluene to the mixture to quench the reaction.
The nanorods were washed three times in a 1:1 toluene: isopropanol mix to remove any excess surfactants.

**Electrophoretic Deposition**

A toluene solution of CdSe (5% w/v) and CdS nanorods (10% w/v) was used for deposition. Prior to deposition, the nanorod solution is sonicated for 5-10 min to get well dispersion of nanorods in toluene. During deposition, the silicon substrates (10 mm × 10 mm) were attached onto the negative electrodes, of a two parallel gold coated copper electrodes which are separated at 2 mm apart and the electrode are completely immersed in a nanorod solution and a potential of 200 V was applied to the substrate for 3 min 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 millimeter. After deposition, the electrodes are pulling out from nanorod solution bath and dried slowly. The silicon substrate is put in the desiccator to remove all solvent before further characterization.

**Ligand exchange (Pyridine) of CdSe nanorods**

For ligand exchange of CdSe nanorods with pyridine, 1 ml of as-synthesized CdSe nanorod solution was dispersed in anhydrous pyridine (5-7 ml) followed by vortex for 10 min and then sonicated for 30-45 min. The solution then centrifuged at 13000 rpm for 10-15 min. The filtrate was discarded and the resulting nanorod was redispersed in toluene.

**Analysis**

The as-synthesized CdS and CdSe nanorods was imaged on Cu coated TEM grids are characterized by transmission electron microscopy (TEM) by using a JEOL JEM-2011F
operating at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) of the nanorods assembly on a Si (111) substrate was performed by a Hitachi S-4800 machine. 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 $274 \text{ V cm}^{-1}$, across the palladium electrodes and measured zeta-potential values was constant from two fields which was averaged from 10 repeated experiments. The X-ray diffractograms analysis was carried out on a PANalytical X’Pert MPD Pro using Cu Kα radiation with a 1-D X’Celerator strip detector.

7.4 Results and Discussion

There are a multitude of influential factors to be considered when nanorod assembly is investigated in solution. The physical properties of the rod such as size, shape, net charge, dipole moment and ligand environment are significant. A low degree of polydispersity in rod length and diameter is a necessary pre-requisite if close packed ordering is to be attained. While the dipole moment is inherent to the crystallographic structure (non-centrosymmetric wurtzite lattice in the case of rods), the remaining physical properties are largely controllable through repeated synthetic optimization. Figure 1a shows a TEM image of CdS nanorods (7 x 30 nm) with a very low polydispersity that are routinely achievable. In a solution of these rods, the strongest rod-rod interactions are Coulombic meaning a distance hence concentration dependence determines whether assembly occurs spontaneously in solution or dispersion is maintained. Modulating the concentration of the rods in (a) results in their spontaneous assembly into discs that drop to the surface under gravity sedimentation (b) and (c) As the ligand capped rods are designed to be solubilized in organic solutions, the nature of the solvent interaction is also important with solubility (dispersibility of the rods), volatility, viscosity and polarity all contributing either positively or negatively to the resultant
Figure 1: (a) Low-resolution TEM of highly monodispersed CdS nanorods of dimension (7 × 30 nm). (b) & (c) Low-resolution TEM and SEM images show the drop-cast assembly of CdS nanorod. (d) Schematic representation shows the EPD set-up. (e) & (f) Low-resolution and high-resolution SEM cross-section images shows multilayer vertically aligned CdS nanorod over large area obtained by electrophoretic deposition.
assembly. For example, the screening effect of the solvents on the Coulombic interactions needs to be considered in determining the optimum assembly protocol. The presence and influence of unwanted impurities in this solvent particularly excess surfactant, is often overlooked, but can be highly detrimental to assembly formation if not controlled. Under the influence of an electric field, all these factors are equally relevant although the driving force for assembly is clearly different. Advances in understanding of the kinetics of electrophoretic deposition allow correlation of the properties of the colloidal suspension such as concentration and zeta potential to the external factors of field strength, deposition area and deposition time. In our studies, we work in a normalized system with equally sized flat planar electrodes (Figure 1d) and toluene as a solvent.

Toluene has a low dielectric constant ($\varepsilon_r = 2.38$) and a viscosity of (0.56) resulting in relatively low electrophoretic mobilities in comparison to higher dielectric solvents such as water. We have previously shown that the charge is influenced by the structure of the coordinating ligand with 8 nm × 100 nm CdS nanorods having a zeta potential of ~50 mV and organizing into perpendicular arrays under electrophoresis. The shorter aspect ratio rods, Figure 1a have a zeta potential of 9 ± 5 mV which is the expected charge reduction as the surface area decreases given the previously determined influence of ligand on the charge state. This approximates to similar mobility values given the proportional reduction in volume (hydrodynamic radius). Under similar assembly conditions 200 V, parallel electrodes 1 cm apart, highly ordered close packed arrays are obtained with each rod vertically aligned. The LRSEM image in Figure 1e and HRSEM image in Figure 1f are cross-section images of centimeter scale deposits showing the extraordinarily resolute order throughout the layer. In Figure 1f, the perfect axial alignment and close packing in each layer is evident with rods spaced at ~2 nm by the ligand spacers. In contrast to our previous reports, no additional surfactant deposits between the layers such that the film thickness is an exact multiple of the
Figure 2: (a-d) SEM images show the control on number of layers with respect to deposition time from 30, 60, 120 and 180 seconds.

rod lengths. This was achieved by carrying out sufficient anti-solvent precipitations of the as-synthesized solution to remove all organic material except for ligands directly bound to the rods. This resolute assembly at a substrate interface would not be possible in non-field driven approaches and demonstrates the effectiveness of EPD for thin-film formation from nanorod suspensions. Extending the deposition time to 30, 60, 120 and 180 seconds allows the number of layers to be accurately controlled with 2, 4, 6 and 9 sequential layers of rods
attained as seen in Figure 2. Importantly no loss of ordering is observed when subsequent layers are deposited on pre-formed layers indicating that as each layer formed acts as a planar surface for the next depositing layer. The close packing of the rods is interesting, as this will only occur in a dynamic situation with a rod finding its preferred location on the deposit before locking in. This strongly suggests that whereas the particle migration to the electrodes is field driven, inter-particle forces are dominating at the interface to allow the lowest potential energy (close packing) of the final deposit to be reached. This is in good agreement with similar evaluations of potential energy interactions with spherical nanocrystals under EPD reported by Dickerson.41

Extension of EPD deposition to CdSe nanorods was evaluated to show the general applicability of this system. CdSe nanorods are typically rice shaped in comparison to the perfect columnar shape of CdS and are therefore more difficult to assemble in general (Figure 3a). The as-synthesized rods are capped in phosphonates/TOPO and after several washings show a zeta potential of ~ 5 mV with an aspect ratio of 3. The reduction in net charge is again consistent with the reduced surface area of the rice shape and will again result in comparable mobilities to the CdS rods given the associated volume reduction. The rods have a low barrier to aggregation in solution and the optimum conditions for EPD required a lower concentration under 200 V to achieve assembly. Figure 3b shows a cross-sectional SEM image of the resulting deposit after 5 minutes deposition. Again the rods are vertically aligned in the deposit with areas of side-by-side ordering although not as resolute as the CdS rods. This can be largely attributed to the rice shape being inherently less suitable for close packing in 2 or three dimensions. The conservation of vertical orientation with comparable density of packing is important as these materials are important photo-absorbers and this EPD route is an ideal low cost replacement for expensive vacuum processes.1, 3 When the ligands are exchanged for pyridine, the zeta potential dramatically increases to ~35 mV. EPD
of these rods leads to disordered assemblies at the substrate regardless of solution concentration (Figure 3c, d). The increased charge will correlate with an order of magnitude increase in electrophoretic mobility, resulting in deposition of the particles to the surface at a rate that prevents inter-particle forces and or entropic considerations to allow the lowest potential energy state of the final deposit to be reached. Lowering the voltage does increase the order although the deposition time becomes a limiting factor for practical application.

Figure 3: (a) TEM image show the rice-shape CdSe nanorod. (b) SEM cross-section image shows multilayer vertically assembly of CdSe nanorod. (c & d) SEM images show the cross-section and top down image of randomly lying pyridine washed CdSe nanorod where no preferential ordering is seen.
To further elucidate the influence of charge on assembly formation we performed non-equilibrium MD simulations of EPD to obtain molecular level insights to approximate the experimental results.\textsuperscript{42-45} Two charge states (0.2e, 0.4e) were applied to small, charged CdSe nanorods (18 Å in height and 5 Å in diameter- comparable aspect ratio to experimental scaled to allow for limitations of model). The EPD simulation was carried out in external electric fields $E$, of 0.03 V/Å in the -z direction in toluene. Once deposition was complete, it was found that the rods remained relatively stable in situ with the energy of the deposited system for the 0.2 e-charged rods lower than that of their more highly-charged counterparts. The post-deposition probability distributions of the orientation angles of the rod’s axes with respect to the surface-normal are shown in Figure 4. For the 0.2 e-charged rods, the slower deposition affords greater scope for a greater extent of dipolar rotational alignment with the applied field vis-à-vis the 0.4 e surface-charge cases. Therefore, there is a greater likelihood of more perpendicular alignment to the surface (i.e., a smaller absolute value of the angle relative to the surface normal) once deposited; quantitatively, the likelihood was found to be about 70\% within ±20° for the 0.2 e case, as compared to around 30\% within this range for the 0.4 e scenario. While this model is highly idealized, it does confirm the experimental finding in relation to the effect of charge, dipole and deposition speed on ordering in the final deposit. The lower energy consideration of the more slowly deposited rods suggests that entropy driven crystallization does play an important role in the formation of ordered arrays by electrophoretic deposition.

After EPD, the removal of the substrate from the solvent can lead to drying induced cracking in the deposited layer. This is a well-known phenomenon that occurs when trapped solvent molecules evaporate causing intrinsic strain and stress as the distance between the particles decrease.\textsuperscript{28} Figure 5 a-b shows examples of cracks propagating in a rapidly dried CdS nanorod film. The cracks propagate laterally and to a depth of several multilayers as
Figure 4: (a) Normalized probability distribution of the rods’ axes vis-à-vis the normal to the surface for the 0.2e-charged rods, (b) for 0.4 e-charged rods.

Figure 5: (a-d) SEM images show the effect of solvent drying on deposited nanorod film evident in the higher magnification image (5c). The absence of delamination between the layers shows that the end-end and side-side packing is still conserved with random cleavage
along the interdigitated surfactant between rods where the greatest strain is accumulated. If the electrodes are dried very slowly in the saturated solvent vapor atmosphere, the cracking is eliminated (Figure 5d). The organic ligand does play a role in accommodating the strain under controlled evaporation conditions such that ligand coverage, ligand length and film thickness are influencing factors on the formation of defect free deposits.

7.5 Conclusions

EPD of semiconductor nanorods from toluene allows their deposition into close packed layers with resolute vertical alignment extending over device scale areas. In sequential multi-layers, the perpendicular order is conserved with up to 9 layers shown with the number of layers controlled by the deposition time. The extension of EPD from CdS to CdSe is successfully demonstrated where although the ligand environment is different; the similar mobilities allow assembly formation with the retention of vertical alignment. The shape of the particle is further shown to have an influence on the final deposit with the rice shaped CdSe not allowing for a similar degree of end to end order as achieved with the CdS. The influence of net charge on the assembly is outlined for the first time where after a pyridine wash the higher charged CdSe no longer assemble, as the deposition is too fast to allow the lowest energy consideration to be reached. This is confirmed by simulation of a model system of rod deposition in toluene where net charge and relative deposition rates are shown to impact the rod ordering and hence the energy consideration attainable. The effect of solvent evaporation on crack propagation shows similar behavior to spherical nanocrystal assemblies with conformal deposits attained by drying in a solvent rich environment. The results show the effectiveness of EPD for the creation of highly ordered nanorod assemblies at length scales amenable to real application with outstanding possibilities for photovoltaic and photoemission devices.


7.6 References


41. Dickerson, J. H.; Boccaccini, A. R. Electrophoretic Deposition of Nanomaterials; Springer **2012**.


Chapter 8: Conclusions

In this thesis, both the synthetic and assembly aspects of semiconductor nanorods are presented. The solution synthesis methods developed in this thesis allow the formation of multicomponent copper chalcogenide (Cu$_2$ZnSnS$_4$) nanorods. These nanorods, along with other binary (CdS, CdSe) and ternary-quaternary nanorod (CuIn$_{1-x}$Ga$_x$S$_2$) have been assembled over micron to centimetre scale by exploring various self-assembly methods from simple drying mediated to EPD.

Chapter 2 gives a detailed investigation of the synthesis of 1D nanostructure (nanorods) of earth abundant quaternary copper chalcogenide (Cu$_2$ZnSnS$_4$). The selection of cationic and anionic precursors along with the correct ligand and solvent choice is vital in this synthesis. The use of thiols as a ligand and sulphur source is shown to be critical to form the wurtzite phase. Modulating the combination of ligands allows different shapes from spherical to rod-like to be achieved. The additional ability to assemble these CZTS nanorods vertically by a drying mediated assembly protocol is also shown. This is the first report of CZTS nanorod and their vertical assembly.

Chapter 3 describes the charge based assembly method to assemble CdSe nanorods. This method precisely controls the assembly into either 1D or 2D/3D superstructures by manipulating the surface charge of nanorods. This study is further extended in Chapter 4 where additional factors such as solvent nature, rate of solvent evaporation and the concentration of nanorods was investigated. The charge on the nanorod surfaces can be easily tuned by ligand exchange with the concentration of nanorods impacting the optimum distance which allows nucleation of the nanorod assembly in solution. This simple charge based protocol is also extended to other semiconductor nanorods such as CdS. These 2D sheets are deposited on the substrate by gravity sedimentation. When these multilayers nanorod arrays are analysed under TEM or STEM, characteristic Moiré interference patterns are obtained.
These Moiré patterns are shown to depend upon the rotational offset and the number of layers between the subsequent 2D sheets. The patterns are analysed using SAED and FFT to find the exact rotational offset and the number of layers in the superstructure. This is discussed in detail in Chapter 5.

Chapter 6 discusses the reversible assembly de-assembly method for ternary and quaternary nanorod (CuInS$_2$ and CuIn$_{1-x}$Ga$_x$S$_2$) in solution. These as-synthesised nanorods are thiol capped and assembled into micron size 3D supercrystals in solution over a period of time. These nanorod superstructures show perfect close-packed alignment where nanorods are aligned side by side and end to end respectively. These superstructures are easily broken up into individual nanorods through the addition of a small amount of oleylamine in the solution. The oleylamine partially replace the thiol ligands on the surface of nanorods and increase the surface charge which influence there dispersibility in solution and increase the coulombic repulsion between the nanorods. By using the charge based assembly methods discussed in Chapter 3 and 4 and EPD, these nanorods are subsequently assembled into monolayer or multilayer of vertical aligned nanorods on the substrate.

In Chapter 7, the influence of external field such as DC field on the nanorod assembly is discussed. By using DC field in the nanorod solution (electrophoretic deposition), it is possible to deposited vertically aligned nanorods over device scale areas with a precise control over the number of layers shown. The influence of charge on the assembly and the general applicability of the electrophoretic deposition for different nanorods (CdS & CdSe) is shown.
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