Ordered Layers of Nanocrystals through EPD

Department of Chemical and Environmental Sciences, University of Limerick

Saikat Bhowmick
Supervisors: Dr. Kevin M. Ryan
Dr. Ning Liu

Submitted to the University of Limerick for the Degree of Masters of Science (by Research)

October 2019
Declaration

I declare that the work presented in this thesis is my original research work, carried out in the University of Limerick. Any contributions from others in any context of the work has been indicated clearly, with due reference to the relevant literature and acknowledgements of collaborative research and discussions. The work has been carried out under the guidance and supervision of Dr Kevin M. Ryan and Dr. Ning Liu.

............................................

Saikat Bhowmick
Acknowledgements

I would like to thank my supervisors Dr. Kevin M. Ryan and Dr. Ning Liu for their constant help and support throughout. I would also like to thank all my excellent group members and friends of Bernal Institute for their immense help and support throughout the year.
Abstract

It is quite well-known that, deposition of highly-ordered layers of colloidal nanocrystals (mostly semiconductor and metal) onto different types of substrates is a really important aspect for various types of device fabrication and for other applications in many diverse areas. There are various different methods for forming these thin films/coatings of nanocrystals onto different substrates. But, among them, electrophoretic deposition (EPD) technique has attracted a lot of attention in the recent years due to its simplicity, high level of efficiency and cost-effectiveness. In this study, highly-ordered, close-packed, vertically-aligned, multi-layered assemblies of semiconductor nanorods (mainly CdSe) were deposited successfully by EPD process onto different types of substrates. Also, multi-layered, vertically-aligned, close-packed assemblies of two different types of semiconductor nanorods (CdSe and CdSeS) on the same substrate were obtained by EPD process. Apart from that, EPD of gold nanorods were also performed and good vertical alignment was obtained as well. Different parameters related to the EPD process have been studied in this work, which will help us in understanding the process of EPD in depth for various useful applications and device fabrication.
# Table of Contents

1 Introduction........................................................................................................... 6
  1.1 Nanotechnology............................................................................................... 6
    1.1.1 Properties of nanomaterials...................................................................... 7
    1.1.2 Effect of shape of nanocrystals on their properties......................... 10
  1.2 Colloidal synthesis route of different types of nanocrystals...................... 12
    1.2.1 Ligand chemistry in colloidal synthesis.............................................. 15
  1.3 Nanocrystal Assembly..................................................................................... 17
    1.3.1 Self-assembly of nanocrystals............................................................... 17
    1.3.2 External-field-assisted assembly......................................................... 27
  1.4 Electrophoretic Deposition (EPD)................................................................. 30
    1.4.1 Basics of electrophoretic deposition.................................................. 30
    1.4.2 EPD of nano-sized materials............................................................... 33
    1.4.3 Primary factors affecting the EPD process....................................... 35
  1.5 Different applications of nanocrystals and their assembled structures...... 42
  1.6 Semiconductor nanorods and their applications........................................... 45
    1.6.1 CdSe nanorods....................................................................................... 46
    1.6.2 CdSeS nanorods................................................................................... 47
  1.7 Metal nanoparticles and their applications................................................... 48
    1.7.1 Gold nanorods and their applications................................................. 49

References............................................................................................................... 51

2 General Experimental Procedures....................................................................... 63
  2.1 Synthesis of semiconductor nanocrystals....................................................... 63
    2.1.1 Hot-injection method.............................................................................. 63
    2.1.2 Washing of the prepared nanocrystals................................................. 67
  2.2 Synthesis of gold nanorods............................................................................. 68
  2.3 Electrophoretic Deposition (EPD)................................................................. 70

References............................................................................................................... 73

3 Characterization Techniques................................................................................ 76
  3.1 Scanning Electron Microscopy........................................................................ 76
  3.2 Transmission Electron Microscopy................................................................. 80

References............................................................................................................... 83

4 Results and Discussions(with experimental details)............................................ 84
  4.1 Primary aims of the project.............................................................................. 84
  4.2 Synthesis and EPD of CdSe nanorods............................................................ 85
  4.3 Co-deposition of CdSe and CdSeS nanorods.............................................. 118
  4.4 Some discussions about the EPD experiments with semiconductor nanorods... 123
  4.5 Synthesis and EPD of gold nanorods......................................................... 126

References............................................................................................................... 135

5 Conclusion............................................................................................................ 139

6 Future Work.......................................................................................................... 141

References............................................................................................................... 144
Chapter 1: **Introduction**

1.1 Nanotechnology

Richard Feynman, a visionary and great physicist and Nobel laureate, in his famous talk in 1959 titled “There’s Plenty of Room at the Bottom” proclaimed that “The principles of physics, as far as I can see, do not speak against the possibility of manoeuvring things atom by atom.” 1,2 But it was Norio Taniguchi, in 1974, who first used the word “nanotechnology”. Any object, which has one dimension, at least in the nanometer scale can be called a nanomaterial. The size of a nanoparticle typically ranges from one to a few hundred nanometers. 1

If the nanomaterials are solid and crystalline in nature, they are known as nanocrystals. Nanomaterials can be further subdivided into three main types. Nanomaterials are termed as “nanoparticles” if all their three dimensions are less than a few hundred nanometers. They are known as “nanotubes” or “nanorods” or “nanowires” if only two dimensions are lower than a few hundred nanometers. Lastly, nanomaterials are known as “nanofilms” or “nanolayers” if they have only one dimension less than a few hundred nanometers. 1 Nanomaterials have really become very popular in the scientific research community due to the fact that these
materials show unique physical and chemical properties in the nano level, which are not present in their bulk counterparts and are immensely useful in various applications.  

1.1.1 Properties of Nanomaterials

As we go down to the nano regime, quantum confinement effects are observed within nanocrystals. This happens due to the restriction in the motion of the charge carriers i.e. the electrons and holes. The nanocrystals can be regarded as infinite quantum wells in the nano-scale, with the crystal’s edges acting as the well’s boundaries. As a result, the particles (electrons, holes etc.) become confined spatially and the available energy levels get spread out. The minimum energy required to transport an electron from the valance band maxima to the conduction band minima is known as the band-gap in a bulk semiconductor type material. As a result of the transition, a hole is formed in the valence band. In the case of radiative recombination, a photon is emitted as a result of the excited electron coming back to the ground state. If we go down to the nanoscale below a particular size known as the Bohr radius (a material dependent constant), the exciton (created electron-hole pair) energy becomes confined and increases. The fact that the sizes of the nanomaterials relative to the Bohr radius define their physical properties, makes the nanocrystals so useful for various applications.

Due to quantum confinement effects, an increase in bandgap is observed in a semiconductor type material (Figure 1).
Figure 1: Energy band diagram of a molecule, nanocrystals of different sizes and bulk material (from left to right). \(^6\) HOMO and LUMO means highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively.

The fact that the size of the nanocrystals can determine the bandgap, means that by controlling their size we can change their respective bandgaps and thus can fine tune their various properties.

It has been observed that by effectively controlling the sizes of the cadmium sulphide (CdS) nanocrystals, tuning of their bandgap can be achieved over a range of 4.5 – 2.5 eV. \(^7\)

Thus, we see that by simply controlling the nanocrystal sizes, we can effectively control their electronic and optical properties. This fact makes the nanocrystals immensely useful for various photovoltaic \(^8\) and light-emitting diode (LED) applications \(^9\).

In Figure 2 UV-vis absorption and fluorescence spectra of CdSe nanocrystals are shown, which clearly indicates quantum confinement and tunability of size \(^10\).
Figure 2(a) UV-vis absorption (upper) and fluorescence (lower) spectra of CdSe semiconductor nanocrystals demonstrating quantum confinement and tenability of size;

(b) Effect of shape on the electronic and surface properties of semiconductor nanocrystals.
1.1.2 Effect of shape of nanocrystals on their properties

One dimensional (1D) nanomaterials such as nanorods and nanowires are formed when one axis of a zero dimensional (0D) material gets elongated. The properties of these 1D materials are quite different from 0D or bulk materials. It was noted that, in case of CdSe nanorods, the absorption peak’s position does not change with the variation of the length of the nanorods. However, a redshift of the absorption peak was observed with gradual increase in the width of the nanorods and the color of the nanorod dispersion also changed. Thus, it can be inferred from this that the width of the 1D nanomaterials specify their respective bandgaps. It has also been observed that efficient electrical conduction pathways are generated along the longer axis of the elongated structure.
Figure 3: This figure shows the absorption spectra of CdSe nanorods of (a) varying length ($a = 12.5$, $e = 35$ nm) and fixed width, and (b) varying width ($a = 3.5$, $e = 5$ nm) and fixed length. (c) depicts the effect of aspect ratio on the absorption characteristics of gold nanorods.

In the same manner, high chemical stability, conductivity, reactivity and mechanical strength are observed in two dimensional (2D) nanomaterials such as nanoplates, graphene sheets, transition metal dichalcogenide sheets, nanosheets etc. 

---

11
Thus, we see that the shapes of the nanocrystals have important implications on their properties and we can tailor the sizes of these nanocrystals to control these properties, which makes them really useful for diverse applications.

1.2 Colloidal synthesis route of different types of nanocrystals

The colloidal synthesis is a cost-effective method for production of different types of nanomaterials. This method is mostly used for the production of semiconductor and metal nanocrystals.

Wet chemical method is generally used for synthesis of Colloidal II–VI semiconductor nanocrystals like CdX, CuX, ZnX, PbX and their alloys, where X is S, Se or Te. By using this approach, the morphologies of these semiconductor nanocrystals can be controlled with extremely high precision. The primary ingredients for this type of synthesis mainly consist of metal salt or organometallic compound precursors, solvent, chalcogenide ion precursors and capping ligands. For controlling the binding of chalcogenide ions and metal cations and for their transformation from small nuclei to particles in the nano-level, organic molecules with their functional groups acting as capping ligands are used. A particular type of colloidal synthesis process known as “hot injection” method was first introduced by Murray et al. In this method, the chalcogen and metal precursors were mixed at first and then injected into a coordinating solvent which was preheated. A sudden supersaturation of chalcogenide was observed causing the nucleation of the nanocrystals (figure 4A). Now, nanocrystals were grown to the desired size by heating further. A really high level of monodispersity can be
achieved by this. The increase in the size of the nanocrystals is attributed to the continuous deposition of monomers and also by a process called “Ostwald ripening”, in which, as a result of higher stability of larger sized crystals towards disintegration, the size of the concerned nanocrystals increases $^{24,26}$. The latter can be successfully avoided by stopping the reaction, and as a result, consequently monodisperse nanocrystals can be obtained. Again, this method can be varied a little by heating the metal precursors and the solvent from before, followed by hot injection of the chalcogen precursor$^{24,26}$.

Thus, we see that different properties of the nanocrystals such as size, monodispersity, phase are determined by different things such as the type of ion precursor and metal salts chosen, functional head groups of organic ligands, concentration of reagents, temperature etc $^{23}$.

The experimental set up for the hot injection method is shown in Figure 4B.
There are some typical advantages and disadvantages in the hot-injection route of synthesis of nanocrystals. The typical advantages include cost-effectiveness and very good quality of the nanocrystals formed. Also, another great advantage of this method lies in the fact that the nanocrystal’s morphology and sizes can be tuned to a high degree of precision enabling to control various electronic and optical properties, which makes them very useful for diverse applications.  

On the other hand, a typical disadvantage of hot-injection method of synthesis is that large quantities of nanocrystals cannot be produced by this. However, quantities in the scale of grams have been produced in a single reaction by this method. Droplet reactors can be used to overcome this difficulty, as demonstrated by recent advances in this field.
1.2.1 Ligand chemistry in colloidal synthesis

In colloidal synthesis method, ligand or surfactant materials are put inside the reaction apparatus. This is done to control the morphology and size of the nanocrystals. Sometimes a “coordinating solvent”, like oleylamine, is used as a ligand. The main function of the ligands is to adsorb on the surface of the nanocrystals and create a shell which stabilizes them in the solvent and also helps in maintaining the nanocrystal growth to a particular desired size. In general ligands are organic molecules having long chains and functional groups like amines, phosphonic acids or thiols. The shapes of the concerned nanocrystals can be effectively controlled by variation of the ligand’s binding energies on different facets of the nanocrystals.

The dispersibility of nanocrystals in various solvents is determined by the ligand shell present on the surface of the nanocrystal. It has been observed that, hydrophobic ligands like long-chain organic molecules such as oleylamine and 1-ddt, aid in stabilizing nanocrystals in non-polar, organic solvents like hexane, toluene etc. On the other hand, dispersion of nanocrystals in polar solvents like water, isopropanol is achieved by hydrophilic ligand molecules such as short polar molecules like S\textsuperscript{2-}, formamide etc.

Figure 5 depicts the stabilization of colloidal nanocrystals.
Figure 5: a) This figure shows the CdSe nanocrystals which are Oleate-capped and dispersed in non-polar phase like Toluene (upper left) and the same nanocrystals transferred to polar phase in solvents like formamide (upper right) as a result of oleate ligands for potassium sulphide b) Nanocrystals capped with organic molecules having long chains (top) and nanocrystals capped with short polar molecules (bottom). c) This figure shows the plot of interaction potential energy with the nanocrystal’s interparticle distance $r$ in a good solvent and non-solvent $^{37}$. 

Ligand exchange is also very useful for dispersion of colloidal nanocrystals and also for their behaviour with respect to an applied electric field like in the case of electrophoretic deposition. This is because ligand exchange aids in tuning the zeta potential of nanocrystals in a particular dispersion $^{38}$. 
1.3 Nanocrystal Assembly

Assemblies of nanocrystals into closely packed bigger superstructures is necessary for implementation of various novel properties of nanomaterials for device fabrication. Bottom-up assembly of these nanomaterials decreases their cost of production in comparison to techniques like chemical vapour deposition, sputtering etc., which are top-down techniques. Additionally, by precisely controlling the nanocrystal’s shape and the ligands involved, the type of the assembly (like ordered arrays, chains etc) can be controlled in an effective manner.24.

1.3.1 Self-assembly of nanocrystals

The field of nanotechnology has become very interesting and exciting due to the fact that nanomaterials have the tendency to organize by themselves into larger superstructures, which exhibit collective properties that are unique and can be exploited for various interesting applications.39 In general, self-assembly refers to the assembly of nanocrystals into organized superstructures by themselves, without any applied electric field or any other external agencies. Weak inter-particle forces are the main driving factors for this kind of assembly, with evaporation of solvent40 and spontaneous dispersion41 playing important roles in the process. The particular case of self-assembly of one-dimensional (1D) nanocrystals is very interesting for various reasons 24. This is because of the fact that the elongated shape of the nanorods makes effective charge
transport and efficient separation of charge possible, which makes them suitable for photovoltaic and photocatalytic applications \(^{39,42-44}\).

These organized superstructures can be broadly classified into two categories namely close-packed and non-close-packed structures. Depending on the nature of arrangement of the nanocrystals, the organized structures can be further categorized, based on alignment (side-by-side and end-to-end), orientation (horizontal and vertical) ordering (nematic and smectic) and also on the structure’s dimensionality (2D and 3D) \(^{39}\).

Figure 6 shows the different types of self-assemblies of nanocrystals.
1.3.1.1 Close-packed structures

When colloidal 1D nanocrystals are arranged in a very compact manner, close to each other, and with a very high level of orientational ordering, these configurations are known as close-packed assembly structures. As stated earlier, close-packed structures can be further
categorized into three ways. Firstly, based on the nature of alignment of the deposited nanocrystals on the substrates, their orientation can be either vertical or horizontal (Figure 7). Secondly, depending on the two types of liquid crystal phases that the 1D colloidal nanocrystals resemble, their close-packed ordering can be classified into two types namely-nematic and smectic (Figure 8). 1D colloidal nanocrystals, having no positional ordering but possessing long-range orientational ordering is referred to as nematic ordering. In smectic ordering, 1D colloidal nanocrystals have some additional degree of positional ordering, besides the general orientational ordering \(^{39}\).

Thirdly, the closed-packed assembly of 1D colloidal nanocrystals is referred to as two – dimensional (2D) monolayers, when the constituent nanocrystals are self-organized into a single layer of very close and densely packed structure, resembling a sheet. A three-dimensional (3D) multi-layered structure is formed when these different 2D monolayer structures are arranged on top of one another (Figure 9) \(^{39}\).
Figure 7: This figure shows horizontal and vertical orientational ordering. (A) and (B) shows the TEM images of horizontally and vertically assembly of CoP nanowires. (C) shows the TEM image of a horizontally oriented assembly of core–shell CdSe–CdS nanorods (having an aspect ratio of 13.6). (D) shows the TEM image of a vertically oriented CdS nanorods, (having an aspect ratio of almost 3), assembled in a vertical orientation.\(^{39}\)
Figure 8: (A) and (B) shows electron microscopy images of colloidal nanorods, showing nematic ordering, whereas (C) and (D) shows smectic ordering. Some of the rods are shown in yellow and the direction in which the nanorods are oriented are shown by white arrows. (A) and (C) are actually TEM images of core–shell CdSe–CdS nanorods, whereas (B) and (D) are SEM images of Au nanorods.\textsuperscript{39}
Figure 9: This figure shows the SEM images of (A) 2D monolayer and (B) 3D multilayer assembly structures consisting of vertically oriented CdS nanorods, which are vertically oriented. (C) is a TEM image of two layers of CdS nanorods, which are vertically oriented by AB stacking and shows a Moiré interference pattern. (D) refers to the schematic description of the pattern shown in (C). (E) and (F) refers to TEM images of 2D monolayer
and 3D bilayer assembly structures which are formed by Ag$_2$S nanowires, having horizontal orientation $^{39}$.

### 1.3.1.2 Non-close-packed structures

When 1D colloidal nanocrystals are assembled into loosely packed structures, shaped like rings or flowers or chain and stripe like structures, these assemblies are known as non-close-packed structures $^{39}$.

The 1D constituent nanocrystals are arranged into either of two types of alignment namely end-to-end or side-by-side. A combination of these two types of alignment are also observed in some cases. Alignment of 1D colloidal nanocrystals into stripe-like patterns (also referred to as rail-tracks or ribbons in the scientific community) is known as side-by-side assembly (Figure 10). These 1D structures are independently arranged with respect to one another with enough spacing in between and can reach upto mesoscopic length scales. Though most of these strip-like patterns are almost linear, some amount of bending can also be observed in some of these structures. End-to-end alignment of 1D colloidal nanocrystals is achieved by selective functionalization of the tips or end faces of the 1D nanocrystals with molecular linkers. In the solution, this brings the ends of the constituent nanocrystals together (Figure 10) $^{39}$. 


Multi-layered arrays of aligned nanorods can be formed by self-assembly. Precise control over the type of assembly like end-to-end or side-by-side, was achieved by Ryan et al. They were able to achieve this by modulating the net particle charge (Figure 11 and 12) [45]. It was noted by Singh et al. that the concentration of the nanorods, polarity or volatility of the solvent used and surface charge are some of the primary factors that affect the assembly of CdS and CdSe nanorods [40].
fringes of the assembly of CZTS nanorods, obtained by drop-casting (C) DF-STEM of 2D assembly of CdSe$_x$Si$_{1-x}$ nanorods, arranged in multilayers. (D) low resolution TEM image of assembly of CdSe$_x$S$_{1-x}$, arranged in a 1D rail-track structure.$^{45}$

Figure 12: (A) Low resolution TEM images of CIGS nanorods, arranged in clusters (B) higher resolution image showing nanorods inside clusters, aligned in an end-to-end and side-by-side manner. (C–D) DF-STEM images of these supercrystal’s side on and end on view.$^{45}$

1.3.2 External-field-assisted assembly

Application of external fields (like electric or magnetic) is very common for getting highly ordered assemblies of colloidal nanocrystals. Anisotropic nanocrystals require both orientational and positional ordering for forming their structured assemblies. This is facilitated by application of external fields. External–field-directed assembly is especially interesting for 1D nanocrystals. This is because, due to the presence of an external field, perfect alignment of the longitudinal axes of these types of nanocrystals along the direction of the field lines can be achieved.
1.3.2.1 Electric-field-assisted assembly

1D colloidal nanocrystals, possessing a net charge and/or a permanent electric dipole moment can be assembled into highly organized structures by applying a directed external electric field \(^{46-49}\). Let us, consider \(d_1\) and \(d_0\) as the induced and the permanent electric dipole moments respectively and \(d = d_1 + d_0\) is the total electric dipole moment of the system of nanoparticles. Alignment of the nanocrystals is obtained, when due to the presence of an external electric field (\(E\)), the total electric dipole moment \(d\) produces an alignment energy \(U_{\text{alignment}} = E \times d\), which is sufficient enough to overcome the thermal excitation energy at room temperature (\(k_B T = 26\) meV, where \(k_B\) denotes the Boltzmann constant) \(^{48}\). We can infer from this that for considerable alignment of the 1D nanocrystals, a minimum electric field \(E_{\text{min}}\) is required.

Highly-oriented structures of 1D colloidal nanorods of cadmium chalcogenides can be obtained by applying direct current (DC) electric fields \(^{46,48}\). 1D colloidal nanocrystals of binary cadmium chalcogenoides have a noncentrosymmetric wurtzite lattice. This type of lattice structure creates a permanent electric dipole moment in these types of 1D nanocrystals, which increases with the volume of the nanorods \(^{47}\). When an external electric field is applied, the nanorods feel a torque which rotates them and causes alignment of the long axis of the nanorods with the direction of the electric field \(^{39,49}\). The direction of the electric field and hence the orientation of the nanorods on the substrate between the electrodes is determined by, where the electrodes are placed. The nanorods align in the plane of the substrate, if the electrodes are coplanarly placed (Figure 13A). On the other hand, the nanorods are oriented perpendicular to the substrate, if the electrodes are arranged in a top-
down manner (Figure 13B) \(^{39}\). It has been observed that when the solvent evaporates with a slower rate, better positional ordering is noted \(^{46}\).

Sometimes, AC (alternating current) electric fields are also used to form highly-organized assemblies of 1D colloidal nanocrystals. The main advantage of using AC electric fields is that the interference due to electrochemical and electro-osmotic effects (which can be observed when DC fields are used) can be avoided \(^{39,51}\).

Figure 13: This figure shows the schematic representations of the experimental set-ups for assemblies of 1D nanocrystals under the influence of external fields like electric (A and B) or...
magnetic fields (C). (A) shows Au electrodes arranged in a coplanar manner, causing nanorod alignment in the plane of the substrate. The TEM image of CdSe nanorods (denoted as red bars) is shown. (B) shows that electrodes arranged in a top-down manner gives rise to perpendicular orientation of the nanorods with respect to the substrate. The TEM image shows CdS nanorods, oriented vertically. (C) shows the experimental set-up of magnetic field directed assembly. The SEM images show Fe$_2$O$_3$–SiO$_2$ core–shell ellipsoids (which are magnetically active), assembled into a close-packed 3D structure.$^{39,46,48,50}$

### 1.3.2.2 Magnetic-field-assisted assembly

In some cases, highly-organized assemblies of magnetically-active anisotropic nanomaterials (possessing permanent or field-induced magnetic dipole moment) can be achieved by application of an external magnetic field (Figure 13C), with their long axis aligned to the magnetic field lines.$^{39,52}$ The orientation of the magnetically active nanoparticles is determined by the magnet’s position. On the other hand, the positional ordering of these nanoparticles depends on their magnetic dipolar interactions.$^{39,53}$

### 1.4 Electrophoretic Deposition (EPD)

#### 1.4.1 Basics of electrophoretic deposition

Electrophoretic deposition (EPD) is a very efficient, simple and cost-effective technique of creating tightly-packed coatings and films of different types of materials. EPD is conventionally used for ceramic materials coating.$^{55}$

Historically, the phenomenon of electrophoretic deposition (EPD) was first discovered in 1808 by the Russian scientist Ferdinand Frederic Reuss, when he observed the movement of clay particles in water due to the application of an external electric field. But, the first
practical application of the EPD technique happened in 1933, when thoria particles were deposited on a platinum cathode, which acted as an emitter for applications in the electron tube. This was patented in USA. The basic concepts of EPD were well known to people from long back and a huge amount of research was ongoing on this topic for a long time. But, it was Hamaker who first studied EPD in the field of ceramics and during 1980s, this technique became quite popular in the field of advanced ceramics. Apart from the field of ceramics, EPD technique is used extensively in various diverse areas like chemistry, biology, materials science, bio-engineering etc.

In the recent past, extensive research is being done in the fields of nanoscience and nanotechnology. Due to their extremely small size, controlling of the nano-sized materials has always been a big problem and challenge for scientists. Although there are various techniques available for efficient controlling of these nano-materials, electrophoretic deposition (EPD) technique is very much appropriate for creating highly-organized structures and deposition of these nano-materials onto different types of substrates. Using this technique, closely and tightly packed coatings and films of different types of nano-materials like nanodots, nanorods etc. can be obtained.

In the EPD technique, due to application of an external electric field, charged particles which are dispersed in a liquid medium, get deposited on the conductive electrodes (which are immersed into the liquid medium). Figure 14 shows a typical EPD experimental set-up and Figure 15 shows a schematic representation of the movement of the suspended charged particles in a liquid medium when an external electric field is applied.
Figure 14: A typical experimental set-up for EPD.\cite{note38}

Figure 15: Figure 15 shows a schematic representation of the movement of the suspended charged particles in a liquid medium when an external electric field is applied.\cite{note54}

There are several factors that influence this EPD process. Some factors are related to the suspension of the charged particles like concentration, morphology of the concerned particles, surface charge, viscosity and dielectric constant of the dispersing medium. Other
factors like voltage used in the process, time of deposition, surface chemistry of the substrate etc. also play an important role in the EPD process \(^{23,54}\).

In comparison with other techniques of forming coatings, EPD has several advantages like it requires a very short time to process, the experimental setup is quite cheap, different types of substrates can be used for deposition and lastly the morphology and thickness of the deposited films can be precisely controlled in an effective manner. On the other hand there are some drawbacks and limitations of the EPD process as well. For example, non-conductive substrates are not suitable for performing the EPD process \(^{23}\).

### 1.4.2 EPD of nano-sized materials

Although EPD technique is mostly used in the field of advanced ceramics, recently it is being used in a very effective manner to form highly-ordered assemblies of nanomaterials and to form tightly-packed films and coatings on different types of substrates. A DC (direct-current) voltage is generally used in a conventional EPD. EPD is considered to be a very useful technique for forming highly-ordered assemblies and films of nanomaterials because different important aspects such as the size and scale of the film, tight-packing of the nanomaterials and thickness of the deposition can all be controlled and manipulated in an effective manner by using this technique \(^{57}\).

Nanocrystal assemblies can be obtained in their original solvents much quickly using EPD, than with the evaporation-dependent assembly techniques.

EPD can be combined with a patterned substrate to fabricate patterned arrays of nanoparticles, which can be optically tuned (Figure 16a) \(^{59}\).
Figure 16: (a) These images describe and show a patterned array of nanoparticles obtained by using ultraviolet light and EPD \(^{59}\). (b) This figure shows how the CdS nanorods respond under the influence of a square-wave electric field \(^{60}\).

Generally, the nanocrystals need to be dispersed in a non-polar, organic solvent having a low value of dipole moment and dielectric constant, in order to form specific, ordered assemblies. Additionally, the dispersibility of the concerned nanocrystals depends on the ligands involved in the process. The overall dielectric constant is also determined by the surface charge and free ligands in the suspension \(^{23}\).

Herman et al. changed the concentration of the phosphine oxide and phosphine capping ligands and studied their effect on the EPD mechanism of CdSe nanocrystals, having different surface charges \(^{61,62}\). It has been concluded from this study, that the role of the
ligands is very vital during deposition and for determining the morphology of the deposited film as well.

Figure 16b shows how the CdS nanorods respond to an externally applied electric field. It is observed during this study that when the electric field is turned on, CdS nanorods are oriented in an orderly manner, whereas, they get randomly oriented when the electric field is turned off. Ryan et al. later, used EPD technique to obtain a close-packed film, consisting of CdSe and CdS nanorods, arranged vertically.

1.4.3 Primary factors affecting the EPD process

In a standard EPD process, due to an externally applied electric field, charged particles suspended in a liquid medium are deposited onto an electrode. As stated earlier, there are two types of parameters that play important roles in the EPD process. One is related to the suspension of charged particles in the liquid medium and the other is related to the dynamics and parameters directly related to the process itself.

The current is contributed by both the charged particles and the free ions, present in the suspension, for the EPD of the concerned particles. But, if the amount of free ions is not much (such as in organic suspensions like ketones), the current carried by them can be ignored. It is believed that, the deposition rate is subsequently diminished by the accumulated cationic and anionic charges at the electrodes, during the process of electrophoresis. However, in the initial period of deposition, effect of accumulated ions can be neglected.
It was Hamaker who for the first time tried to correlate the deposition amount with the associated depositing conditions \(^\text{56}\). Later, Ishihara et al. \(^\text{64}\) and Chen and Liu \(^\text{65}\) modified on the model and came up with an equation for the weight \((w)\) of deposited charged particles per unit area of the electrode. The charge of the free ions was ignored in this calculation.

\[
w = \frac{2}{3} C \varepsilon_0 \varepsilon_r \zeta \left( \frac{1}{\eta} \right) \left( \frac{E}{L} \right) t,
\]

where, \(C\) is the particle concentration, \(\varepsilon_0\) is permittivity of vacuum, \(\varepsilon_r\) is the relative permittivity of the solvent, \(\zeta\) is the particles’ zeta potential, \(\eta\) is the viscosity of the solvent, \(L\) is the distance between the electrodes, \(E\) is the applied electric field potential and \(t\) is the time of deposition \(^\text{54}\).

Some key parameters, which play an important role in the EPD process are discussed below.

### 1.4.3.1 Suspension related parameters

**Size of the constituent particles**

According to the scientific literature, there is no clear boundary or set range, about the size of the particles for the EPD process. But, in order to get a uniform and smooth deposition, the concerned particles need to be well dispersed and stable in the appropriate solvent. But, in the case of larger particles, obtaining a uniform deposition is very difficult, as they tend to form sediments due to gravity. Avoiding sedimentation as a result of gravity, is a big problem. Additionally, when dealing with EPD of larger particles, either a very high surface charge is required, or the size of the resultant electrical double layer region must increase.
It is also observed that when relatively smaller particles were used, fewer cracks were noticed in the resultant film/deposition \(^{66,67}\). From this, it can be concluded that the size of the particles plays an important role in determining the morphology of the deposited film/coating \(^{54}\).

**Dielectric constant of the liquid**

An optimum value of the dielectric constant of the dispersing liquid is required for successful operation of the EPD process. If the value is very low, the liquid does not have sufficient dissociative ability and hence the obtained deposition is not satisfactory. On the other hand, if the value of the dielectric constant is very high, the size of the electrical double layer and hence, the electrophoretic mobility gets diminished, as a result of the high concentration of the ions present in the liquid.

An investigation of the beta-alumina suspensions in various organic solvents, was carried out by Powers \(^{68}\) and noted a sharp increase in conductivity with dielectric constant. Powers \(^{68}\) could only obtain depositions with liquids having dielectric constants in the range of 12-25.

**Zeta potential**

The charge that develops at the interface of a solid surface and a liquid, is known as the Zeta potential. Zeta potential is dependent on different associated parameters like particles’ surface charge, the composition and type of the suspension medium and also the interfacial adsorbed layer \(^{70}\). Zeta potential is one of the key parameters in the EPD process. It determines the repulsive interaction between the suspended charged particles and hence plays a vital role regarding the stability of the suspension. Zeta potential also determines the particles’ velocity and direction, during the EPD process \(^{54}\).
The interaction between the constituent particles in the suspension determine the stability of
the system. This interaction mostly depends on the electrostatic and van der Waals forces. To
get rid of agglomeration of the constituent interacting particles in the suspension, high
electrostatic repulsion is required. It has been observed that the constituent particles tend to
coagulate if the charge is low and gives deposits like sponge, whereas, particles, having a
high surface charge, tend to repel each other during deposition process and form tightly and
closely packed assemblies\textsuperscript{71,54}. Different charging agents like acids, bases and
polyelectrolytes help in controlling the zeta potential\textsuperscript{72}.

It has been shown by Zarbov et al.\textsuperscript{72} that the rate of deposition is directly related to the zeta
potential. But, again, the zeta potential is determined by the charging additive, which in turn,
influences the ionic conductivity of the suspension. Again, the drop in potential in the bulk of
the suspension which is the primarily responsible for the migration of the particles to the
electrode, is related with the ionic conductivity\textsuperscript{54}.

\textbf{Solvent used in the EPD process}

Although, theoretical calculations predict that the deposition amount increases with
increasing value of the dielectric constant, it has been noticed that in a realistic system, a very
high value of the dielectric constant of the solvent used results in reduction of the size of the
double layer region. The constituent nanocrystals tend to aggregate as a result of this and the
electrophoretic mobility is reduced. Thus, a low value of the dielectric constant and a low
ionic concentration in the suspension are favourable conditions for EPD\textsuperscript{23}.

From various observations during several experiments, it can be inferred that, in only stable
dispersions of the constituent particles, maximum packing density of particles can be
successfully obtained. On the other hand, for weak inter-particle interactions, non-uniformly
packed structures are obtained. Some important physical constants of some polar and non-polar solvents are listed in Table 1.  

Table 1: Some important physical constants of useful polar and non-polar solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Viscosity (mP.s)</th>
<th>Relative dielectric constant</th>
<th>Dipole moment (Debye)</th>
<th>Vapor pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.544</td>
<td>32.7</td>
<td>2.87</td>
<td>12.8</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>2.038</td>
<td>17.9</td>
<td>1.66</td>
<td>4.4</td>
</tr>
<tr>
<td>Water</td>
<td>0.89</td>
<td>80.1</td>
<td>1.8546</td>
<td>1.75</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.560</td>
<td>2.38</td>
<td>0.375</td>
<td>2.9</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.3</td>
<td>1.88</td>
<td>0.08</td>
<td>160</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.894</td>
<td>2.02</td>
<td>0</td>
<td>10.4</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>0.753</td>
<td>5.62</td>
<td>1.69</td>
<td>1.2</td>
</tr>
</tbody>
</table>

a. Relative dielectric constant of a material is its absolute permittivity expressed as a ratio relative to the permittivity of vacuum. The permittivity of vacuum is $8.854 \times 10^{-12} \text{C}^2 \text{V}^{-1} \text{m}^{-1}$.

b. The unit of Dipole moment is Debye. 1 Debye $= 3.33654 \times 10^{-30} \text{C} \cdot \text{m}$.

c. The values of vapor pressure is extracted at 20°C. vapor pressure is used to reflect the solvent drying speed in EPD.

1.4.3.2 EPD process related parameters

Deposition Time

It has been detected by Basu et al. that if the applied electric field is kept constant at a fixed value, then the rate of deposition decreases with increase in deposition time. Chen et al also arrived at the same conclusion through their experiments.
Figure 17 shows the typical relationship between the thickness of deposition and the deposition time for ZnO coatings on copper electrode at different applied electric field potentials. From the figure we can say that during the initial stages of deposition, deposition is quite linear. But, we can see, that as time progresses, the rate of deposition decreases and after a considerable amount of time reaches a plateau.

![Graph showing the relationship between thickness and time for different electric fields.](image)

**Applied Electric Field**

From Hamaker and others’ calculations, it can be said that the thickness of deposition should increase with corresponding increase in the applied electric field. But, in the case of some nanocrystal films, the rate of deposition increases very rapidly with high values of the applied electric field. This prevents good positional ordering in the closely-packed assembly of the nanocrystals. Basu et al. observed that if the applied electric field is of moderate
value (25–100 V/cm), good quality uniform films can be obtained. On the other hand, usage of high applied electric fields (>100 V/cm) result in bad quality films, which are not quite uniform in nature.

Actually, if the applied electric field is very high, the resulting coating/film will get affected adversely during deposition process, due to turbulence formed in the suspension. It has been observed by Negishi et al. that in the absence of any powder, the current density of n-propanol solvent was proportional to the applied voltage and it had a tendency to get unstable with increase in the applied voltage (Figure 18). It can be concluded that, the quality and morphology of the resulting deposition depends on the unstable current density.

Figure 18: This figure shows the stability of n-propanol’s current density for various different applied voltages.

Concentration of the constituent nanoparticles in suspension
It has been observed that the concentration of solid nanoparticles in the suspension have a lot of influence on the EPD process, especially for the multi-component EPD. It has been noted that in some cases, even if the group of particles have the same type of electrical charge (like positive or negative), their deposition rates may vary due to the concentration of the solids in the suspension. It can be concluded that the deposition of nanocrystal powders occurs at an equal rate, if the solid’s volume fraction in the suspension is relatively high, whereas, the deposition rates of the constituent nanoparticles are proportional to their individual electrophoretic mobility, if the volume fraction of the solids in the suspension is relatively less.\textsuperscript{54,76}

*Deposition substrate*

In order to obtain a good quality coating/film by EPD, the conductivity and uniformity of the deposition substrate are two parameters which are really very important. It was observed by Peng and Liu\textsuperscript{77} that low conductivity of the La\textsubscript{0.9}Sr\textsubscript{0.1}MnO\textsubscript{3} (LSM) substrate results in slow deposition and a non-uniform film. Stability of the final deposit also depends on the interaction between the substrate and the concerned nanoparticles and also on the surface chemistry of the substrate. Chemical or plasma treatment techniques can be used to improve on the stability of the deposited film/coating\textsuperscript{78,23}.

1.5 Different applications of nanocrystals and their assembled structures
There has been a growing interest in studying colloidal nanocrystals in the scientific fraternity in the past few decades. This is because these types of nanocrystals and their assembled superstructures have several important material properties and are very promising for applications in different diverse areas. In the recent years, different types of nanomaterials ranging from quantum dots (QDs), nanowires (NWs) and nanorods (NRs) have been synthesized successfully and are used quite effectively in optoelectronic and electronic devices. These types of nanomaterials can be used in different ways and have vital roles to play in these devices such as electrodes or conducting layers, electron or hole-transporting layers, semiconducting channels, light-absorbing or light-emitting layers etc.\textsuperscript{79,114}

For manufacturing transparent electrodes, colloidal metallic nanocrystals (dispersed in ink) have been widely used. A transparent electrode is a very crucial component in optoelectronic devices such as LEDs, photodetectors, solar cells etc. Conventionally, transparent electrodes are made of thin films of doped metal oxides such as aluminium zinc oxide (AZO), indium zinc oxide (IZO) and indium tin oxide (ITO). But brittleness, very high cost are some of the drawbacks that limit their usage in effective device fabrication. For this reason, scientists have tried to incorporate different types of nanomaterials such as ITO nanocrystals, silver nanowires etc., as alternatives to the previous conventional materials for preparing transparent electrodes.\textsuperscript{79}

Light-emitting diodes (LEDs) have nowadays become very popular as novel optoelectronic devices, because of their brightness and high level of efficiency. Especially semiconductor colloidal nanocrystals are popular ingredients in LEDs like in the colour filter, the electron-transport layer and the emitting layer.\textsuperscript{80} Nowadays, for getting good colour purity in various types of displays, quantum dot films are effectively used on the backlight units.\textsuperscript{79} In 1994, Alivisatos’s group reported the first QLEDs.\textsuperscript{81} They spin casted CdSe nanocrystals with a p-phenylene vinylene hole-injecting layer for making these QLEDs.\textsuperscript{79,81}
Photovoltaics based on colloidal nanocrystals is very promising due to the cost-effective manufacturing process involved, uniformity in composition etc. In general, assembled structures of nanocrystals are mostly used for practical device application.  
Solar cells based on colloidal nanocrystals are considered to be very promising for applications in energy-harvesting devices. Solar cells based on quantum dots are very efficient and are generally of four types namely: quantum dots sensitized solar cells, Schottky solar cells, hybrid nanocrystals–polymer solar cells and depleted heterojunction solar cells. Lots of well-established detection apparatus such as charge-coupled devices, photoresistors, photodiodes and photomultiplier tubes are available for operating in the spectral range of visible light. Most advanced photodetectors use silicon as their main component, but silicon is not able to absorb light in the infrared region. But, colloidal quantum dots are promising candidates for usage in photodetectors since they have tunable band-gaps and can be effectively used in the infrared spectral range as well. 

Semiconductor nanocrystals are quite promising for components for electronic devices as well. As we know, different types of electronic devices like inverters, amplifiers and logic gates can be fabricated using a perfect combination of n and p-type transistors. It has been noted that field-effect transistors (FETs), based on nanocrystals can be effectively used as basic components for integrated circuits. The main advantages of using colloidal nanocrystals in FETs and other associated devices are that they are very compatible with different types of substrates, they can be solution processed over large areas and lastly, the cost of the materials, processing and manufacturing, is quite low. 

Efficient and reliable memory devices based on nanocrystals have become quite popular in recent times due to their small size, scalability and high speeds in reading, writing and erasing.
Cadmium-based nanocrystals and their assembled structures are widely used in different electronic and optoelectronic devices such as in transistors, photoelectrodes, LEDs etc. It has been observed that superstructures made up of closely-packed core-shell type nanocrystals show spontaneous emission and lasing effect. Some examples of these superstructures are microcavities, which are cylindrical in shape and having CdSe/ZnS core-shell nanorods and CdSe/CdS nanorods arranged into a coffee ring type structure. The assemblies of anisotropic nanocrystals have some interesting features like tunability of corresponding band-gap and polarized emission. The overall performance of these types of devices is dependent on both the inherent properties of each individual nanoparticle and also on the type of assemblies they form.

Apart from electronics, optoelectronics, photovoltaics and memory devices, nanocrystals also have tremendous applications in next-generation catalysts, as biosensors etc.

1.6 Semiconductor nanorods and their applications

Different types of semiconductor nanocrystals like spherical-shaped, elongated-shaped, platelets/membranes etc. are quite popular for their different types of applications in various diverse areas. But, among them, the elongated nanocrystals (rod-shaped), typically called nanorods in the scientific community, are the ones that are mostly studied after the spherical-shaped nanocrystals.
Typically, the lengths of these nanorods range from tens to few hundreds of nanometres, whereas, their diameters are generally between few nanometres. In general, the length of the nanorods are greater than their Bohr radius. For this reason, the charge carriers (electrons, holes, excitons etc.) are confined strongly along two dimensions only. As a result, the charge carriers are free to move along the length/long axis of the nanorod. This phenomenon generates the one-dimensional exciton \(^{14,88}\). This new kind of quantum confinement in nanorods, which are absent in spherical nanocrystals like quantum-dots gives rise to a number of important properties in them, related to their symmetry, electronic structure, band-gap energies, polarization properties etc \(^{14}\).

1.6.1 CdSe nanorods

In this work, we have mostly focussed on CdSe nanorods. Actually, CdSe nanorods are one of the mostly studied semiconductor nanorods because of their interesting and novel optoelectronic properties. The lattice structure of CdSe nanorods and other cadmium chalcogenides are of noncentrosymmetric (i.e. does not have inversion symmetry) wurtzite type. Due to this lattice structure, these nanorods have a permanent electric dipole moment which increases with their volume \(^{39,89}\). This makes these types of nanorods suitable for EPD using external electric fields.

The motion of the electrons in nanorods are permitted only along the long axis of the rod and thus has a one-dimensional character. This gives rise to some unique optical properties in them, which are absent in conventional spherical nanocrystals (quantum dots in general), such as radiative and non-radiative transitions and their relationship on the size and temperature of the nanorods, photoluminescence and polarization \(^{14}\).
Another important character of these nanorods is that charges have a natural tendency to distribute on their surface, which has direct effects on their optical properties, such as energy of emission and its intensity\textsuperscript{14}.

We know, that the bandgap of any semiconducting material is a very important property for studying its electronic structure and for effective fabrication of electronic and opto-electronic devices. It has been observed that in the nano-regime, the bandgap of any semiconducting material can be altered by varying their sizes. Thus, by precisely controlling the sizes of the nanomaterials, their electrical and optical properties can be effectively tuned for successful applications in various sectors\textsuperscript{90,91}.

In recent times, a really successful synthesis route for effective variation of the length of the CdSe nanorods has been reported, which has enabled scientists to study the dependence of bandgap with their length and size\textsuperscript{90,92-94}.

1.6.2 CdSeS nanorods

CdSeS based nanorods have attracted lot of attention in recent times due to their unique and novel properties like transport phenomena confined to a particular dimension\textsuperscript{95,96} and precisely tunable physical properties related to their size and composition\textsuperscript{95,97}. CdSeS based nanorods can be effectively used for fabrication of highly-efficient electronic and opto-electronic devices\textsuperscript{95} such as lasers\textsuperscript{98,99}, waveguides\textsuperscript{100}, photosensors\textsuperscript{101}, photovoltaic cells\textsuperscript{102}, photodetectors\textsuperscript{103} and field-effect transistors\textsuperscript{104}.

Ryan et al.\textsuperscript{105} have successfully synthesized homogeneously alloyed CdSe\textsubscript{x}S\textsubscript{1-x} nanorods using the standard hot-injection method. The nanorods bandgap range from 1.77 to 2.03 eV and exhibit tunable photoluminescence. It was observed from this study, that the relative molar amounts of sulphur and selenium used in these nanorods determine their structural and
optical properties. A direct band edge photoluminescence (PL) emission was noted over a range of 200 nanometres, which could be tuned by precisely changing the selenium/sulphur ratio.

1.7 Metal nanoparticles and their applications

Metal nanoparticles can absorb and scatter light strongly in the visible part of the spectrum. This property can be effectively used for various types of applications. Metals have delocalized, free electrons in the form of a gas, with positively charged nuclei around them. These free electrons can absorb low-energy photons and hence can occupy vacant energy levels in the same band or vacant energy levels of an overlapping band. Application of an external electric field can generate collective oscillation in these free electrons. The phenomenon of resonance occurs when the frequency of the collective electron oscillation matches with the frequency of the incident electromagnetic field. At resonance, the energy from the incident radiation gets absorbed strongly, followed by eventual transformation into light and heat. The electrons are displaced from the nuclei as a result of these collective oscillations of the electrons. As a result of this, different types of surface charge distributions get created. A particular mode of oscillation is associated with every distribution of surface charge and are known as localized surface plasmons. Due to collective coupling of the plasmons in the metal nanoparticles, the incoming optical signals get amplified. The supercrystals of these metal nanoparticles can also show a considerable optical shift in the localized surface plasmon resonance. This aspect of metal
nanoparticles make them suitable for effective application in the areas of sensing and photonics $^{14,107-109}$.

1.7.1 Gold nanorods and their applications

Extensive studies on metal nanoparticles have revealed that their shape and morphology have significant effects on their optical properties. The plasmon mode in metal nanorods is divided into a longitudinal mode and a transverse mode $^{14}$. Among all the different types of metal nanoparticles, gold nanoparticles are particularly interesting for several reasons. Firstly, oxidation processes are absent in gold nanoparticles. So, theoretical studies regarding gold nanoparticles become much easier as the surface oxide layer does not need to be considered. Secondly, nanoparticles can be synthesized now in a controlled manner in various shapes and sizes and can be used successfully in different types of applications $^{14}$.

Among all the different morphologies possible with gold nanoparticles, gold nanorods have attracted a lot of attention. This is due to the fact that, gold nanorods produce really strong plasmonic fields and they can be tuned very effectively in a controlled manner. Also, they are quite suitable for biological applications $^{111}$.

The phenomenon of surface plasmon resonance can be customized to a particular wavelength, in case of gold nanorods $^{111-113}$. This has several benefits in applications. Over the past few years, different efficient synthesis routes, especially the seed-mediated growth approach, have been able to produce highly stable and monodispersed gold nanorods.
Another speciality of gold nanorods is that, they can form alternatively aligned assemblies. This gives rise to optical anisotropies, which can be effectively used in novel photonic devices \(^\text{111}\).

It has been well established that assemblies of nanoparticles (especially nanorods) into different types of superstructures is very useful. This is because the assembled superstructures possess unique qualities of an ordered structure containing the physical properties from the constituent particles making up the assembly \(^\text{111}\). Different types of assembly processes like self-assembly, chemically-driven assembly, assembly using polymers as hosts, electric-field-induced assembly etc. have been used in the case of gold nanorods \(^\text{111}\).

In the recent times, gold nanorods have become quite popular for various types of biological and biomedical applications as well, such as bio-sensing, gene and drug delivery and biomedical imaging \(^\text{111}\).
References


38) Liu, P.; Singh, S.; Bree, G.; Ryan, K. M. Complete Assembly of Cu:ZnSnS$_4$ (CZTS) Nanorods at Substrate Interfaces Using a Combination of Self and Directed Organisation.


58) [http://www.electrophoretic-deposition.com](http://www.electrophoretic-deposition.com)


70) [https://www.brookhaveninstruments.com/what-is-zeta-potential](https://www.brookhaveninstruments.com/what-is-zeta-potential)


72) Zarbov, M.; Schuster, I.; Gal-Or L. Methodology for selection of charging agents for electrophoretic deposition of ceramic particles. In: *Proceedings of the international*


77) Peng, Z.; Liu, M. Preparation of dense platinum-yttria stabilized zirconia and yttria stabilized zirconia films on porous La$_{0.9}$Sr$_{0.1}$MnO$_3$ (LSM) substrates. J Am Ceram Soc. 2001, 84(2), 283–8.


Chapter 2: **General Experimental Procedures**

### 2.1 Synthesis of semiconductor nanocrystals

Different methods can be adopted for successful synthesis of nanocrystals, such as, heat-up, solvo-thermal and mechano-chemical methods. In this thesis, we are mostly concerned about colloidal semiconductor chalcogenide and metal nanocrystals. In this work, colloidal synthesis route has been followed, in which the relevant precursors are decomposed thermally in a solvent, having a high boiling point. In the “heat-up method”\(^1-^4\) of colloidal synthesis, all precursors are put inside a reaction flask and heated together, whereas, in the typical “hot-injection method”\(^5-^7\) cationic and anionic precursors are heated separately and then one is injected to the other.

#### 2.1.1 Hot-injection method

The most commonly used method for synthesis of semiconductor nanocrystals is the “hot-injection method”. The reaction apparatus for this method typically consists of a three-neck round bottom flask, a Schlenk line system, a thermocouple, a temperature controller and a condenser (Figure 1).
Figure 1: a typical hot-injection experimental set-up $^{10-12}$.

Generally, in a hot-injection method, the required metal cationic precursors and solvents are put together in a three-neck round bottom flask (or some other type of reaction vessel). Then they are mixed with the appropriate ligands. These ligands play a very important role in precise controlling of the growth of the concerned nanocrystals. Then, the previously formed mixture is degassed to get rid of any water and oxygen. After that, the mixture is generally heated to a particular temperature and the required ion precursor is injected. The nucleation mechanism starts soon after this step and a colour change of the mixture is also observed in most cases $^8$. 
There are two basic stages for the gradual synthesis and formation of perfect nanocrystals of interest. According to LaMer’s model \(^{14}\) (Figure 2) these two basic stages are the nucleation stage and the crystal growth stage. The chemical reaction between the required precursors produce the necessary monomers, after the initial dispersion of the precursors in appropriate solvents. After that, with the rise in concentration of the monomers to the level of supersaturation, corresponding nuclei will be formed due to accumulation and self-nucleation of monomers. Then, as the monomers constantly aggregate on these already-existing nuclei, the growth process of the nanocrystals starts and continues till the monomer concentration falls below the critical value. During the growth stage of the nanocrystals, new nuclei can also be formed which results in an eventual increase in the nanocrystals’ size distribution \(^{13}\).

Figure 2: This figure shows the schematic representation of the nanocrystals’ nucleation and growth processes \(^{13}\).
2.1.1.1 Controlling the size of the colloidal semiconductor nanocrystals

The important parameters which help in controlling the sizes of the colloidal semiconductor nanocrystals are the following: a) the reaction time and temperature, b) the temperature in which the appropriate reactant is injected in the hot-injection method, c) effect of surfactant, solvent, pH, d) the precursors’ concentration and reactivity. The kinetics of the nucleation and growth process mainly determine the size distribution of the concerned nanocrystals. As discussed earlier, it is noted that the simultaneous occurrence of nucleation and growth gives rise to poor size distribution of the nanocrystals. So, in order to achieve a proper size distribution, at first, at sufficiently high temperature, the precursors are injected into the corresponding solvents and after that, the reaction temperature is deliberately reduced. This effectively separates the co-existence of the nucleation and growth mechanisms. This method was successfully employed by Murray et al. in 1993 for effective synthesis of monodispersed nanocrystals of cadmium chalcogenides. In their work, at 300 C, the appropriate cadmium precursors were injected into the organic solvents. Then the reaction was continued at different temperatures. In this way, by controlling the temperature of the reaction, the size distribution of the CdSe nanocrystals could be effectively controlled. Thus, we see that the hot-injection method is a very useful and effective method for synthesis of high-quality colloidal, semiconductor nanocrystals.
2.1.2 Washing of the prepared nanocrystals

After the synthesis of the colloidal semiconductor nanocrystals, a purification or washing step is very much necessary to get rid of the excess ligands, unreacted reactants in the solution, excess residual solvents etc. In general, the reaction for synthesis of nanocrystals is quenched by adding an organic solvent like, toluene, hexane etc. and after that the product solution formed is left undisturbed for some time (like for 10-15 minutes).

In the washing process, at first, the solution product obtained is taken in a small amount and dispersed in an appropriate non-polar solvent (generally) like toluene, cyclohexane, n-hexane etc. Secondly, a polar anti-solvent like IPA (isopropanol), ethanol, methanol etc. is added for precipitation. All these solvents and anti-solvents are added in specific ratios and sometimes the ratios are changed each time while washing, to get better results. Then, the obtained product is put under centrifugation and the required nanocrystal sediment is collected from the bottom of the centrifuge vials/containers. This process of centrifugation and re-dispersion can be continued several times, depending on the situation and requirement.

The role of the polar anti-solvent is to cause accumulation of the nanocrystals, which is necessary for collecting them after centrifugation. The other excess material like excess ligands (dissolved as well as adsorbed on the surface of the nanocrystals), unreacted precursors and excess solvent which remain in the supernatant, is then discarded.\(^8,9\)

The washing steps are performed several types to get clean, high-quality nanocrystals, which can be put to effective use in different areas. The number of washings is actually very crucial for conducting the EPD technique with these nanocrystals. The reason for this lies in the fact that the number of washings determine the concentration of the ligands, which again, is
related to the nanocrystals’ charge, which is an important factor for the effectivity of the EPD process.8,9,17.

2.2 Synthesis of gold nanorods

The most challenging issue in the synthesis of metal nanoparticles is effectively controlling their size and shape. Generally, the metallic nanorods are synthesized in presence of surfactants or by using templates.18 A typical seed-growth method is conducted in an aqueous surfactant media (CTAB in our case) and nanoparticle seeds are added in it, in order to get highly monodispersed gold nanorods.18,19 Addition of the strong reducing agent NaBH₄ to the solution of the gold salt, facilitates the formation of the appropriate gold seeds. For slow and steady growth on seeds, Au³⁺ is reduced to Au by using a weak reducing agent like L-ascorbic acid.

Figure 3 shows the schematic representation of the mechanism of gold nanorod formation.

Figure 3: Schematic representation of gold nanorod formation.19.
For getting monodispersed gold nanorods, secondary nucleation should be avoided and the following factors like: the concentration of silver ions (for single-crystal rods the aspect ratio increases with increasing concentration), concentration of ascorbic acid (the aspect ratio decreases with increasing concentration), amount of seed involved in the reaction (the lesser the amount of seeds, larger will be the size of the nanorods), values of pH (the kinetics of the growth process will be slow, if the values of pH is less and will produce nanorods with high aspect ratios), temperature of growth (30°C overnight) etc. should be controlled carefully with high precision. The gold nanorods are separated from the growth solution in the usual way by centrifuging it at sufficiently high speeds and the washing procedure is repeated for a number of times.

2.2.1 Phase transformation of gold nanorods

The gold nanorods thus synthesized and washed are in the aqueous phase. But for using these gold nanorods, for the purpose of EPD, they need to be transformed to a non-polar, organic phase. After the excess surfactants are removed by centrifugation, the collected gold nanorods are generally re-dispersed in distilled water. Then, the original surfactant cetyltrimethylammonium bromide (CTAB) was replaced on the gold nanorods’ surface into mercaptosuccinic acid (MSA) molecules. Actually the purpose of doing this to replace the original surfactant i.e. the CTAB by ligands having stronger functional groups like –SH of MSA and other types of alkylthiols. After that a solution of TOAB (tetraoctylammonium bromide, which acts as a necessary catalyst for the phase transformation), in an appropriate
organic solvent like chlorobenzene or toluene, is mixed with the aqueous solution of the gold nanorods. The two-phase solution, thus obtained is kept under vigorous stirring for some minutes. Finally, due to the electrostatic interaction between the molecules of MSA and TOAB in the non-polar organic solvent (like chlorobenzene or toluene), the gold nanorods capped with negatively-charged MSA (or some other negatively-charged ligand) in aqueous phase are eventually transformed to the required organic phase. A detectable colour change of the nanorod solution is generally associated with this kind of phase transformation 8,21,22.

2.3 Electrophoretic Deposition (EPD)

Electrophoretic deposition (EPD) is a simple and cost-effective technique for obtaining high-quality, uniform, thin films/coatings of different types of ceramic and other types of nanomaterials on different types of substrates. EPD is mainly based on the principle of electrophoresis, where colloidal charged particles in a solution are deposited to the oppositely charged electrodes, due to application of an external DC electric field. AC electric fields are also used in some cases. But in this work, we have only used DC electric fields.

The EPD experimental set-up used in this work consists of the following basic parts: a high-voltage generator, a programmable dip-coater apparatus, a substrate holder and a vial/container containing the colloidal solution of the concerned nanoparticles. The dip-coater apparatus (manufactured by Nadetech Innovations) can be programmed by using a suitable software, using a simple computer. There are several important parameters concerning the
process of deposition such as angle (where the vial containing the solution is placed and where the substrate holder will come down for dipping into the electrolyte solution), immersion and withdrawal speeds (the speed in which the substrate holder holding the substrates are immersed into the solution and lifted from it after the deposition process), down waiting time (the time for which the substrates are dipped into the solution with a high voltage applied for deposition), up waiting time (the time for which the substrate holder containing the substrates remain in fixed position before moving downwards for dipping into solution), dips (the number of dips of the substrate holder containing the substrates in a single run) etc. All these parameters can be effectively controlled remotely by the software on a computer. After the deposition step is finished, the substrates are lifted from the solution and are left undisturbed for several minutes for drying. A high-voltage power supply (TECHNIX SR-5-F-300, S/N: BU08/04971) is used for the EPD process in our work and the voltage is monitored carefully by a digital multimeter. The high-voltage power supply unit is connected to the dip-coater apparatus and deliver the voltage to the substrates (which act as electrodes in this case and are attached to the substrate holder). In our case, the substrates are silicon or ITO/glass substrates. The substrate holder is made of plastic and is not conductive. So, the substrates are attached to the holder with carbon-tape or electrical-tape, which are conductive. In this way, the high voltage is transferred to the substrates (while dipped in the electrolyte solution), which act as electrodes in this case.

The EPD apparatus used in this study is shown in figure 4.
Figure 4: The EPD apparatus used in this study.
References


Chapter 3: Characterization Techniques

3.1 Scanning Electron Microscopy

Any modern optical microscope has a maximum magnification power of about 1000x and its resolution capacity and image quality is limited due to the wavelength of the light used and also due to the number of lenses used. The de-Broglie wavelength of an electron is much lesser than the wavelength of light and hence, when electrons were used for illuminating the sample for microscopy, they offered much better resolution and good image quality.\(^1\)

There are different types of electron microscopy techniques in operation in the scientific research community and industry, like Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Scanning Transmission Electron Microscopy (STEM) etc. For scanning electron microscopy (SEM) technique, an incident beam of high energy electrons is accelerated, passed through a combination of lenses and apertures and lastly a focused beam is directed towards a sample. After that, these incident, focused electrons interact with the sample and the subsequent signals arising due to these interactions are detected efficiently. SEM is a non-destructive technique and can be efficiently used for acquiring detailed information about the sample’s surface topography, chemical composition, crystalline structure, electrical behaviour etc.\(^1-4\).

Figure 1 shows the interaction between the high energy beam of electrons and the sample specimen.
Figure 1: This figure shows the interaction of high energy beam of electrons with the sample.  

A schematic diagram of a standard scanning electron microscope with all its different components is shown in Figure 2.
In general in scanning electron microscopy, the electron beam after being generated under high vacuum, is accelerated through a voltage (generally between 2-40 kV). After that, the electron beam is focused by employing a number of lenses (objective and condenser) on the specimen of interest. After the electrons hit the sample, they can be elastically or in-elastically scattered. In the case of elastic scattering process, there is no net transfer or change in energy, whereas for in-elastic scattering process, there is a net transfer or change in energy.
These different types of interactions between the incident electrons and the specimen give rise to a number of signals, which can be detected by suitable detectors. Mostly, secondary electrons, back-scattered and Auger electrons, diffracted back-scattered electrons and X ray photons constitute these typical signals $^{2,3,4}$.

Secondary and back-scattered electrons are in general mostly used for typical imaging purposes. Secondary electrons generally have energies below 50 eV and are ejected from almost the surface layer of the specimen or very near to it. Mainly, topographic information is furnished by these electrons $^2$. The electron beam is raster scanned over a small area of the sample to acquire an image. At each point, secondary electrons are collected and this gives rise to the required contrast in the acquired images.

Back-scattered electrons have high energy and primarily provides compositional and crystallographic information about the sample $^2$.

When an incident high-energy electron kicks out another electron from the inner-shell of an atom, an outer-shell electron of higher energy fills up the vacant state, thus created. The difference in energy is released as X-ray photons, for energy conservation. These are known as characteristic X-rays. These characteristic X-rays provide information regarding elemental composition of the sample. Energy dispersive X-ray spectroscopy (EDX) is an additional attachment to most SEMs for providing high resolution elemental analysis of the concerned sample $^{2,3}$.

Samples which are studied in the scanning electron microscope, must be conducting in nature. Otherwise the sample gets charged up i.e. the incident electrons get accumulated in an area of the sample and thus, further electrons from the incident beam cannot reach the sample. So, in order to look at samples which are non-conductive in nature, they are sometimes coated with a thin layer of gold.
3.2 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is another type of electron microscopy technique, used as a characterization tool for obtaining high-resolution, good-quality images of samples and their analysis. In general, a transmission electron microscope provides much better resolution than a standard scanning electron microscope. Apart from providing high-quality, ultra-high-resolution imaging, TEM is also used for getting important information about the crystal structure and also the chemical composition of the samples under study.

In typical TEM, a uniform electron beam is used for studying thin samples. Generally, an accelerating voltage between 100-200 kV is applied to get a focussed beam of electrons for irradiating the sample under study. The primary difference from SEM is that, in the case of TEM, the transmitted electrons are detected. So, the samples need to be quite thin, otherwise most of the electrons will be lost due to interactions (elastic and in-elastic scattering of the electrons by the atoms of the sample) within the sample. For medium or high-voltage set-ups, voltages between 200 kV to 3 MV are used. Electron emission in the electron gun occurs by the process of thermionic emission, field emission or by Schottky emission. If, very high gun brightness and coherence is required, then field emission is used. Figure 3 gives a schematic representation of a typical transmission electron microscope. The illumination aperture and the area of the illuminated part of the sample can be changed and controlled by using a three or four stage system of condenser lenses. Imaging of the distribution of the electron intensity behind the sample onto a fluorescent screen is generally accomplished by using a system of three to eight lenses. The corresponding image thus formed can be acquired and stored by direct exposing of an image plate or photographic emulsion in vacuum.
the resultant image is acquired digitally via a fluorescent screen which is connected to a CCD camera by a fibre-optic plate. The image, thus obtained is then stored in the computer for further analysis and study.

Figure 3: Schematic representation of a standard transmission electron microscope.
In 1931, Max Knoll and Ernst Ruska made the world’s first transmission electron microscope. Presently, transmission electron microscopes can reach atomic level resolution. In a transmission electron microscope, only those electrons which do not interact with the sample and are transmitted through, are detected. In bright-field TEM, the direct, un-scattered electron beam is taken into consideration for imaging purpose. So, in the corresponding image, the white or bright part represents vacuum and the dark part represents the sample. In dark-field TEM, the scattered electron beam is used for imaging and the direct beam is blocked. So, the dark part in the image represents the vacuum and the brighter part represents the sample under consideration.

For studying the defects in crystals in crystalline samples, a combination of bright-field and dark-field modes of imaging is necessary, which provides diffraction contrast. In modern TEM, extremely small electron probes ranging from 0.2 to 10 nm in diameter, can be generated by using a system consisting of three or four stage condenser lens. This facilitates the instrument to work in scanning transmission mode. A finely focussed electron beam is raster scanned across the sample in scanning transmission electron microscopy (STEM) mode.
References

1) https://www.nanoscience.com/techniques/scanning-electron-microscopy/


5) Liao, Y. *Practical Electron Microscopy and Database*.


9) https://www.princetoninstruments.com/applications/fluorescence-phosphorescence-photoluminescence
Chapter 4: *Results and Discussion (with experimental details)*

### 4.1 Primary aims of the project

We have seen that deposition of highly-ordered layers of colloidal nanocrystals (mostly semiconductor and metal) onto different types of substrates is a really important aspect for various types of device fabrication and for other applications in many diverse areas. There are various different methods for forming these thin films/coatings of nanocrystals onto different substrates. But, among them, electrophoretic deposition (EPD) technique has attracted a lot of attention in the recent years due to its simplicity, high level of efficiency and cost-effectiveness.

The main aim of this project was to create highly-ordered, multi-layered, close-packed assemblies of semiconductor and metallic nanocrystals (especially nanorods) consisting of continuous arrays of nanorods, with their long axes perpendicular to the used substrate and extending over centimetre scale areas. Another goal of this project was to achieve bimodal assembly on a single substrate, where two different types of nanocrystals are co-deposited simultaneously. Actually, both vertically-aligned and horizontally-aligned assemblies are important for device fabrication. Studies on these types of assembled superstructures of nanorods have shown that, vertically-aligned assemblies are more suitable for fabrication of sandwich-type structures (like composite multi-layer LEDs and solar cells), while horizontally-aligned assemblies are suitable for realization of optoelectronic devices (like planar-type photodetectors), having planar electrode type structure $^{13}$. In this work, we have mostly focussed on creating vertically-aligned assemblies of different types of nanorods, having good closed-pack ordering.
4.2 Synthesis and EPD of CdSe nanorods

It has been experimentally detected that, as a consequence of quantum confinement effects below the Bohr radius, nanorods possess unique opto-electronic properties that are not present in their bulk counterparts. Just by changing the size of these nanorods, their different properties can be tuned accordingly. These nanorods have important applications in diverse areas such as photovoltaics \(^1,2\), field-effect transistors \(^3,4\), biological sensing \(^5,6\), light-emitting applications \(^7,8\) etc. Especially, nanorods which are made from II- VI materials deserve special mention due to their unique optical and electronic properties \(^9\).

There are different types of methods used for synthesis of these types of nanorods, such as solvo-thermal, hydro-thermal, one-pot, hot-injection method etc. Among all these methods, hot-injection method is a very useful colloidal synthesis route because controlling the morphology and size of the nanocrystals can be much easily achieved by this method. In this work, hot-injection method has been used for synthesis of semiconductor nanorods.

Detailed discussion on hot-injection method is done in chapter 2 of this thesis.
4.2.1 Experimental Details (Synthesis of CdSe nanorods)

**Chemicals used**

The following chemicals were used for synthesis of CdSe nanorods as received from their respective companies without any further purification:

1) Cadmium oxide (CdO, >99 %), purchased from Fluka.
2) Tetradecylphosphonic acid (TDPA), purchased from PCI Synthesis.
3) n-octylphosphonic acid (OPA), purchased from PCI synthesis.
4) trioctylphosphine (TOP, 97 %), purchased from Sigma-Aldrich.
5) trioctylphosphine oxide (TOPO, 99 %), purchased from Sigma-Aldrich.
6) Selenium (99.8 %), purchased from Sigma-Aldrich.

**Synthesis methodology**

The hot-injection method was followed for the synthesis of CdSe nanorods 12. At first 0.2 g of CdO, 0.71 g of TDPA, 0.20 g of OPA and 3 g of TOPO was taken in a 25 ml three-neck flask. This was done very carefully, inside a M-Braun glove-box. Then a Schlenk line arrangement was used to heat the above mentioned mixture to 120 °C in argon atmosphere. A magnetic stirrer was placed inside the three-neck flask prior to the heating step. The mixture was kept under constant stirring. After that, the mixture was degassed under vacuum for 60 minutes at a pressure of 0-300 mTorr. Then, again the mixture was heated to 300 °C in argon and an optically clear solution was obtained. After that, 1.5 g of TOP was injected to the resulting solution inside the three-neck flask and the temperature was raised to 310 °C.
In the next step, about 750 μl of Selenium/TOP stock solution (which was prepared by mixing 0.146 g of selenium with 0.832 g of TOP and was kept under constant stirring with a magnetic stirrer, inside a glove-box) was injected into the solution and a gradual colour change to reddish-brown was observed. Then, the resulting solution was kept for about ten minutes for growth. After that, the three-neck flask was cooled down to about 80 °C, by removing the heating mantle. Then, about 4 ml of toluene was injected into the resulting solution to completely stop the reaction.

**Washing procedure of the nanorods**

After the synthesis of the nanorods, lots of surfactants, unreacted precursors, excess ligands and excess residual solvents (mostly organic) remain in the solution. So, a purification or washing step is necessary to get rid of these unwanted by-products and separate the desired nanorods from the resulting solution.

The prepared nanorod solution (dark-brownish in colour), was washed in the following way. First, a non-polar organic solvent like toluene was added with some amount of the nanorod solution. Then, a polar anti-solvent like isopropanol (IPA), was added to the nanorod solution. The mixing of the solvent and anti-solvent was done in different proportions each time (at first 80 % toluene and 20 % IPA was used, then 60 % toluene and 40 % IPA, then 50 % toluene and 50 % IPA). After each mixing step with toluene and IPA, the nanorod solution was vortexed for few minutes and was put under centrifugation for 10 minutes at 13000 rpm. The whole washing process with different proportions of toluene and IPA was repeated several times (for 14 to 17 times). Then after that, the excess solution was discarded and the desired nanorod sediment was collected from the bottom of the centrifuge tubes/vials. The collected nanorods were then stored in toluene for future deposition-related experiments by EPD.
Some TEM and SEM images of the prepared CdSe nanorods

The following are some SEM images of the prepared CdSe nanorods, used in this study.

Figure 1: SEM image of CdSe nanorods, obtained by drop-casting the sample on a piece of silicon which was coated with gold.
Figure 2: SEM image of CdSe nanorods, obtained by drop-casting the sample on a piece of silicon which was coated with gold.

In figures 1 and 2 we can see the typical rice-shaped CdSe nanorods.

The silicon piece was coated with gold before drop-casting the CdSe nanorod sample. This was done to avoid any charging effects which may arise due to incident electrons getting accumulated on a certain area of the sample and restricting further electrons to reach the sample, causing damage to the sample under consideration.

The size of the nanorods were about 20 nm x 10 nm, in general.

The following are some bright-field TEM images of the prepared CdSe nanorods, used in this study.
Figure 3: CdSe nanorods obtained via drop-casting on a TEM grid.
From the above SEM and TEM images, it can be observed that the synthesized CdSe nanorods are rice-shaped, rather than typical columnar-shaped like CdS nanorods. Previous studies on CdSe nanorods by Ryan et al. $^{12}$ have also reported the same type of rice-shaped morphology/structure.
SEM studies were done with Hitachi SU-70 and Hitachi S-4800 scanning electron microscopes. The TEM study was done with a JEOL JEM-2010 field emission transmission electron microscope.

4.2.2 Experimental Details (EPD OF CdSe nanorods)

The electrophoretic deposition (EPD) experimental set-up used in this work, is already described in details in section 2.3 of chapter 2 of this thesis. A programmable dip-coater set-up (manufactured by Nadetech Innovations), high-voltage power supply (TECHNIX SR-5-F-300, S/N: BU08/04971) and a digital multimeter was used for effectively carrying out EPD.

4.2.2.1 EPD of CdSe nanorods on silicon substrates

The CdSe nanorods after synthesis and subsequent washing were dispersed in toluene in varying concentrations. The CdSe nanorods after centrifugation were collected and were
dispersed in toluene by sonicating it in a sonicator for about 45 minutes. The resulting nanorod solution was also vortexed for about 5 minutes, so that the nanorods were well dispersed in the solvent (toluene in this case). After that, two pieces of silicon (1.5 cm x 1 cm) were washed properly by sonicating them in a bath of acetone, IPA and de-ionized water, separately for 15 minutes each. Then, the substrates were blow dried in nitrogen till they were completely dried. Then, EPD was performed with these nanorods. After the deposition process was finished, the electric field was turned off and the substrates were pulled out from the nanorod solution and was dried for about 10 minutes in toluene atmosphere.

**Effect of different parameters on the EPD process of CdSe nanorods on silicon substrates**

Different parameters like concentration of the colloidal nanocrystals (CdSe nanorods in this case) in a non-polar dispersing medium (toluene in this case), voltage used for deposition (DC electric field in this case), time of deposition etc., all play an important role for obtaining high-quality, uniform films/coatings (with high degree of alignment of the nanoparticles), carried out through EPD.

In the recent past, EPD technique has proven to be a very useful one for deposition of nanomaterials. But, works in this area were mostly confined to metal nanocrystals, semiconductor nanocrystals (0-dimensional) or carbon nanotubes. But, work in nanorods, in general, started a bit later. Some researchers like Khoo et al. have done EPD of WO₃ nanorods on ITO substrates. But, ordered assembly was not reported in these works. Our research group has done extensive research work on the vertical assembly of different types
of semiconductor nanorods by EPD technique \(^{12,15-19}\). It can be inferred from several experiments and numerical simulations that the most important requirements for successful EPD are presence of a net charge in the nanorods and the electric field which is applied for the deposition should be uniform over space (to avoid effects due to dielectrophoresis) \(^{13}\). Ryan et al. \(^{13}\) have used an interaction energy model (based on the value of the deposited nanorods’ permanent dipole moment) to assess the minimum value of the net charge, which is essential for attaining optimum conditions of deposition. It was determined by experiments and numerical modelling, that each nanorod should possess a minimum net charge of +4\(e\). If the value of net charge is lesser than this value, at the time of deposition onto the substrate, a net positive interactive potential will not act on the nanorod. \(^{13}\).

In this work, CdSe nanorods have been synthesized by the hot-injection method. After that, those nanorods have been used for EPD.

*Effect of concentration of the nanorods, dispersed in solution*

In this work, it has been shown that the concentration of the CdSe nanorods in the dispersing solution (toluene in this case), plays a really important role in forming vertically-oriented assemblies on different substrates.

The concentration of the nanorods was determined and fixed in the following way:

At first, an empty vial was taken and it was weighed very carefully in a sensitive weight balance. After that, the nanorods were washed in this vial by centrifugation and vortexing. Then the vial, containing the washed nanorods (after proper drying in the desiccator) were weighed again. Then, by subtracting the weight of the empty vial from the weight of the vial, containing the nanorods, the weight of the nanorods (in mg) was determined. Then, it was dispersed in a certain volume (in ml) of toluene. In this way, the concentration of the nanorods (in percentage weight/volume) was determined and changed according to the requirements for the experiment.
i) At first, the EPD of CdSe nanorods were performed with a concentration of 20% weight/volume, the average voltage used was 301.08 volts and the deposition time was about 7 minutes.

The following are some SEM images, related to the above mentioned experiment.
Figure 5: Low-resolution top-down SEM image of CdSe nanorods on (flat surface of) silicon substrate.
Figure 6: High-resolution top-down SEM image of CdSe nanorods on (flat surface of) silicon substrate.
Figure 7: High-resolution top-down SEM image of CdSe nanorods on (flat surface of) silicon substrate. Red circles in the figure show vertically aligned patches of CdSe nanorods.

Figure 5 is a low-resolution SEM image of the flat surface of the silicon substrate deposited with CdSe nanorods by EPD. From the image, it can be observed that the deposition is quite uniform and there are almost no holes on the substrate. Presence of holes or vacant areas on the substrate is not suitable for satisfactory functioning of any fabricated electronic device. Figures 6 and 7 are high-resolution SEM images of the flat surface of the silicon substrate deposited with CdSe nanorods by EPD. From these images, it can be observed that only few of the deposited CdSe nanorods are vertically aligned perpendicular to the substrate. The vertically aligned patches of CdSe nanorods are shown in Figure 7 by red circles.

ii) Secondly, EPD of CdSe nanorods were performed with a concentration of 25% weight/volume, the average voltage used was 301.95 volts and the deposition time was about 7 minutes.

The following are some SEM images, related to the above mentioned experiment.
Figure 8: High-resolution top-down SEM image of CdSe nanorods on (flat surface of) silicon substrate.
Figure 9: High-resolution top-down SEM image of CdSe nanorods on (flat surface of) silicon substrate.

It can be observed from Figures 8 and 9 that, in this case, most of the deposited CdSe nanorods are vertically aligned perpendicular to the substrate.

iii) Next, EPD of CdSe nanorods were performed with a concentration of 30% weight/volume, the average voltage used was 311.33 volts and the deposition time was about 6 minutes.

The following are some SEM images, related to the above mentioned experiment.

Figure 10: High-resolution top-down SEM image of CdSe nanorods on (flat surface of) silicon substrate.
Figure 11: High-resolution top-down SEM image of CdSe nanorods on (flat surface of) silicon substrate.

It can be observed from figures 10 and 11 that most of the deposited CdSe nanorods are not vertically aligned perpendicular to the substrate.

From the above studies, it can be clearly understood that the concentration of the CdSe nanorods in the dispersing media (toluene in this case), plays a very important role in forming vertically-aligned assemblies on silicon substrates. We observe that, 25% concentration (weight/volume) of the CdSe nanorods in toluene is best for obtaining vertically-aligned assemblies of nanorods on silicon substrates. We see, that in order to get good vertical alignment of the CdSe nanorods, their concentration should have an optimum value, not too high or too low. If the concentration is too low, the rate of deposition of the nanorods may be proportional to their own individual electrophoretic mobility i.e. they will not be deposited at the same rate. On the other hand, if the concentration of the nanorods are too high, due to
their mutual interaction with one another, they may tend to aggregate with one another before migrating to the electrodes for deposition and thus, vertical closed-pack ordering cannot be achieved successfully.

**Effect of the applied voltage used in the EPD process**

Another important parameter, which plays a really important role in the EPD process is the applied voltage used for depositing the nanorods. Studies on CdSe nanorods have shown that, they possess a permanent dipole moment of approximately 250 D (8.34×10\(^{-28}\) C. m)\(^{21}\). This permanent dipole moment in the CdSe nanorods can be attributed to their non-centrosymmetric P63mc system lattice structure\(^{21,22}\). So, it is quite evident from this that the value of the applied electric voltage will influence the migration of the nanorods in the solution.

In this study, a DC electric field was used.

While conducting the process of EPD for this study, the electric field was varied, keeping other relevant parameters like concentration, deposition time etc. almost same.

The following are some SEM images of CdSe nanorods on silicon substrates obtained via EPD process with varying voltages, but keeping other parameters almost same.
Figure 12: High-resolution top-down SEM image of CdSe nanorods on (flat surface of) silicon substrate. Voltage used was 252.22 volts and the concentration was 25% weight/volume. The circular regions marked in red in show some areas containing vertically-aligned CdSe nanorods.
Figure 13: High-resolution top-down SEM image of CdSe nanorods on (flat surface of) silicon substrate. Voltage used was 252.22 volts. The circular regions marked in red show some areas containing vertically-aligned CdSe nanorods. The previous image and this one are of the same sample but taken on different areas of the substrate.
Figure 14: Low-resolution top-down SEM image of CdSe nanorods on (flat surface of) silicon substrate. Voltage used was 301.95 volts.

Figure 15: High-resolution top-down SEM image of CdSe nanorods on (flat surface of) silicon substrate. Voltage used was 301.95 volts.
Figure 16: High-resolution top-down SEM image of CdSe nanorods on (flat surface of) silicon substrate. Voltage used was 325.63 volts. The circular regions marked in red show some areas containing vertically-aligned CdSe nanorods.
Figure 17: High-resolution top-down SEM image of CdSe nanorods on (flat surface of) silicon substrate. Voltage used was 325.63 volts. The circular regions marked in red show some areas containing vertically-aligned CdSe nanorods.

Figure 18: High-resolution top-down SEM image of CdSe nanorods on (flat surface of) silicon substrate. Voltage used was 375.34 volts. The circular regions marked in red show some areas containing vertically-aligned CdSe nanorods.
Figure 19: High-resolution top-down SEM image of CdSe nanorods on (flat surface of) silicon substrate. Voltage used was 395.26 volts. The circular regions marked in red show some areas containing vertically-aligned CdSe nanorods.

From the above images, it becomes quite evident that the externally applied voltage plays a very important role in obtaining good vertical alignment of CdSe nanorods on silicon substrates. We can clearly notice from images 12 and 13 that, when an electric potential of 252.22 volts was used, vertical alignment of the CdSe nanorods was obtained only in certain areas of the substrate. From images 14 and 15, we notice that when 301.95 volts was used as external voltage, very good vertical alignment of CdSe nanorods was obtained almost everywhere on the substrate. From images 16-19, we can clearly notice that for voltage values of 325.63 volts and 375.34 volts, moderate vertical alignment of the CdSe nanorods could be observed over certain areas (marked in red circles) on the silicon substrate. But,
when a voltage of 395.26 volts was applied, we can clearly see from figure 19 that there is almost no visible vertical alignment of CdSe nanorods on the substrate.

From the above images, it is also quite evident that a certain range of applied voltage is necessary for obtaining a good closed-pack ordering and vertical alignment of the CdSe nanorods on the silicon substrate. In this study, we can observe that, the voltage range between 300 volts to 375 volts is very much suitable for getting good vertical alignment and ordering of CdSe nanorods on the silicon substrate. We also notice that, in our case, a voltage of about 300 volts is most appropriate for obtaining good quality films and good vertical alignment and closed-pack ordering of the CdSe nanorods. The vertical alignment and closed-pack ordering gradually decreases with increasing values of the applied voltage. Almost no vertical alignment can be observed, when a voltage of about 395 volts was applied.

EPD technique is based primarily on the phenomenon of electrophoresis, where due to application of an external electric field (DC, in our case), charged particles (nanorods in our case), dispersed in a dispersing media (toluene in this case), migrate and get deposited on the oppositely-charged electrode. Various theoretical and experimental studies have suggested that the amount of deposit, in general, increases with increase in value of the applied voltage. The rate of deposition also increases, but the quality of the coating/film deteriorates when very voltages are used. The alignment and ordering of the nanorods on the coating/film on the substrate is a kinetic phenomenon. So, the rate of deposition of the nanoparticles (nanorods in this case) is greatly related to the way they get assembled onto the substrate. A high value of the applied voltage can give rise to turbulence in the suspension. The effect of turbulence will adversely affect the positional ordering and orientation of the nanorods, due to flows in their surroundings during the process of particle migration and deposition. The faster the nanorods move in the suspension, the less time they have to occupy the most appropriate positions in
the assembly to form a dense, coherent closed-pack structure\textsuperscript{20}. On the other hand, if the value of the applied voltage is very low, that is also not ideal for getting a high-quality coating/film with good orientation and closed-pack ordering of the constituent nanoparticles. The cadmium chalcogenide nanorods (CdSe and CdSeS used in this study) have a fixed permanent electric charge and dipole moment. As discussed in details in section 1.3.2.1 of chapter 1 of this thesis, there is a minimum value of alignment energy (which is dependent on the applied electric field and hence applied voltage) that is required to overcome the thermal excitation energy of the nanorods in the dispersing media at room temperature and for getting good alignment. So, there is a minimum value of voltage corresponding to this minimum alignment energy. Any applied voltage which is below this threshold value will result in poor alignment of the nanorods\textsuperscript{22}. This threshold value will depend on the type of nanorods used, the values of their net electric charge and permanent dipole moment, the type of dispersing media, its viscosity etc.

In our case we see that the electric potential of about 252 volts was too low and 395 volts was too high for getting good vertical alignment of the CdSe nanorods on silicon substrates.

\textit{Effect of deposition time on the EPD process}

In this study, extensive study about the deposition time and the amount of deposit has not been done. But while conducting various EPD related experiments with CdSe and CdSeS nanorods, we have noticed that, during the initial stages of deposition, the rate of deposition generally increases with time. But, after a certain time, the deposition rate becomes constant and does not change much with time. This is expected because after a certain time when all the area of the substrate dipped in the colloidal solution gets coated with nanorods, arranged densely, the electrophoresis decreases since we are using a constant voltage throughout the
process. The time after which the rate of deposition becomes almost constant should depend logically on the concentration of the nanorods in the dispersing media as well.

The following are some cross-section SEM images of CdSe nanorods deposited onto silicon substrates.

![SEM Image](image)

Figure 20: High-resolution cross-sectional SEM image of CdSe nanorods on silicon substrate. Voltage used, time of deposition and concentration of nanorods in solution (toluene) were 325.54 volts, 5 minutes and 25 % weight/volume respectively.
Figure 21: High-resolution cross-sectional SEM image of CdSe nanorods on silicon substrate. Voltage used, time of deposition and concentration of nanorods in solution (toluene) were 325.54 volts, 5 minutes and 25 % weight/volume respectively.
Figure 22: Low-magnification cross-sectional SEM image of CdSe nanorods on silicon substrate. Voltage used, time of deposition and concentration of nanorods in solution (toluene) were 325.54 volts, 5 minutes and 25 % weight/volume respectively.

From these above images, we can observe a good uniform deposit of CdSe nanorods on the silicon substrate with very good vertical alignment.
4.2.2.2 EPD of CdSe nanorods on ITO/glass and ITO/glass-NiO substrates

In the previous sections, EPD of CdSe nanorods on silicon substrates was discussed. In this section we will focus on the EPD of the same type of CdSe nanorods onto Indium Tin Oxide (ITO)/glass substrates.

The experimental process of conducting EPD with CdSe nanorods on ITO/glass substrates are the same as with silicon substrates. Two pieces of ITO/glass of about 1.5 cm x 1 cm dimensions were washed properly by sonicating them in a bath of acetone, IPA and de-ionized water, separately for 15 minutes each. This was followed by blow drying them in nitrogen, till they became completely dried. After that, EPD deposition was performed on these ITO/glass substrates with the conductive side of ITO facing each other (spacing between two electrodes was 2.15 mm) and forming the deposition electrodes. After the completion of the deposition process, the electric field was turned off and the substrates were pulled out from the nanorod solution and was left undisturbed for about 10 minutes in toluene atmosphere to let them completely dry. The ITO/glass substrates were then ready for further characterization.

The CdSe nanorods after synthesis and subsequent washing were dispersed in toluene in varying concentrations as before and were used for EPD experiments.
The following are some SEM images of CdSe nanorods deposited on ITO/glass substrates (the deposition occurs on the ITO side of the ITO/glass substrate).

Figure 23: High-resolution top-down SEM image of CdSe nanorods on (ITO side of) ITO/glass substrate. Voltage used was 350.03 volts and deposition time was about 8 minutes.
Figure 24: High-resolution top-down SEM image of CdSe nanorods on (ITO side of) ITO/glass substrate. Voltage used was 350.03 volts and deposition time was about 8 minutes.

From figures 23 and 24, we can observe that almost all of the substrate is covered by a uniform coating of CdSe nanorods and majority of the nanorods are densely packed and are vertically aligned.

Another type of substrate was also used in this study for depositing nanorods by EPD process. The ITO/glass substrates were sputtered with NiO on the ITO side. We were planning to fabricate a composite light emitting diode (LED) structure consisting of NiO sputtered on ITO/Glass substrate, CdSe and/or CdSeS nanorods and ZnO thin film. For that reason, CdSe nanorods needed to be deposited on NiO sputtered on ITO/glass substrates with good vertical alignment and close-pack ordering.

The following are some SEM images of CdSe nanorods deposited on NiO sputtered on ITO/glass substrates.
Figure 25: High-resolution top-down SEM image of CdSe nanorods on NiO sputtered on ITO/glass substrate. Voltage used was 350 volts and deposition time was about 5 minutes.

We can see from the above image that vertical alignment of the nanorods is not as good as the other cases, but some vertically aligned patches of CdSe nanorods (shown in red circles) could be observed.

We see that, when ITO/glass and NiO sputtered on ITO/glass substrates are used as deposition electrodes, a higher value of voltage and deposition time is required in comparison with silicon substrates, in order to get a good uniform coating with good vertical alignment of CdSe nanorods. This is because, the conductivities of these two types of substrates are different and the process of EPD will also depend on the surface chemistry of the substrate and its interaction with the suspension containing the nanorods.
4.3 Co-deposition of CdSe and CdSeS nanorods

Synthesis of CdSeS nanorods

CdSe$_x$S$_{1-x}$ nanorods were synthesized in the same way as CdSe nanorods, following the hot-injection method.

Chemicals used

The following chemicals were used for synthesis of CdSe nanorods as received from their respective companies without any further purification:

1) Cadmium oxide (CdO, >99 %), purchased from Fluka.
2) n-octadecylphosphonic acid (ODPA, > 99 %), purchased from PCI Synthesis.
3) n-octylphosphonic acid (OPA), purchased from PCI Synthesis.
4) trioctylphosphine (TOP, 97 %), purchased from Sigma-Aldrich.
5) trioctylphosphine oxide (TOPO, 99 %), purchased from Sigma-Aldrich.
6) Selenium (99.8 %), purchased from Sigma-Aldrich.
7) Sulfur (99 %), purchased from Sigma-Aldrich

Synthesis methodology

The synthesis methodology of CdSeS nanorods is almost same as that of CdSe nanorods. The same hot-injection method was followed for the synthesis of CdSe nanorods \(^{12}\). At first 0.11 g of CdO, 0.45 g of ODPA, 0.11 g of OPA and 1.45 g of TOPO was taken in a 25 ml three-neck flask. This was done very carefully, inside a M-Braun glove-box. Then a Schlenk line arrangement was used to heat the above mentioned mixture to 120 C in argon atmosphere. A
A magnetic stirrer was placed inside the three-neck flask prior to the heating step. The mixture was kept under constant stirring. After that, the mixture was degassed under vacuum for 45 minutes at a pressure of 0-300 mTorr. Then, again the mixture was heated to 300°C in argon and 0.84 g of TOP was injected to the resulting solution inside the three-neck flask and the temperature was raised to 330°C.

In the next step, about 500μl of Selenium, Sulfur/TOP stock solution (with a ratio of Selenium/Sulfur = 0.77) was injected into the solution and a gradual colour change was observed. Then, the resulting solution was kept for about 15 minutes for growth, under constant stirring. After that, the three-neck flask was cooled down to about 80°C, by removing the heating mantle. Then, about 4 ml of toluene was injected into the resulting solution to completely stop the reaction.

Washing procedure of the nanorods
The washing procedure for CdSeS nanorods was exactly similar as that of CdSe nanorods.

4.3.1 EPD of CdSe and CdSeS nanorods onto the same substrate

As discussed before, CdSe and CdSeS nanorods separately possess some unique electronic and optoelectronic properties and these properties can be tuned by controlling the size of the nanorods. Especially, for CdSeS nanorods, just by changing the ratio of Selenium and Sulfur in the stock solution, the photoluminescence emission and optical absorption can be tuned in an effective and precise way. Ordered multi-layered assemblies of two different kinds of nanorods onto the same substrate can be quite beneficial for realization of different types of photovoltaic and optoelectronic devices.
Two small rectangular shaped silicon substrates were used for the nanorod deposition by EPD. Spacing between Silicon substrates was 2.5 mm. At first CdSe nanorods (25% concentration weight/volume) were dispersed in toluene and EPD was performed on silicon substrates with an applied voltage of 325.39 volts for 5 minutes. Then, the silicon substrate were kept undisturbed to dry for 5 minutes and were again immersed in a solution of CdSeS dispersed in toluene (Se/S=0.77 and 22% weight by volume concentration) for EPD. The voltage used was 250.26 volts with a deposition time of 3 minutes.
The following are some SEM images from the above mentioned experiment.

Figure 26: High-resolution cross-sectional SEM image of CdSe and CdSeS nanorods on silicon substrate. Voltage used and time of deposition were 325.39 volts and 5 minutes and 250.26 volts and 3 minutes for CdSe and CdSeS nanorods respectively.
Figure 27: High-resolution cross-sectional SEM image of CdSe and CdSeS nanorods on silicon substrate. Voltage used and time of deposition were 325.39 volts for 5 minutes and 250.26 volts for 3 minutes for CdSe and CdSeS nanorods respectively.
Figure 28: High-resolution cross-sectional SEM image of CdSe and CdSeS nanorods on silicon substrate. Voltage used and time of deposition were 325.39 volts for 5 minutes and 250.26 volts for 3 minutes for CdSe and CdSeS nanorods respectively.

From the above figures, we can observe that both CdSe and CdSeS nanorods (CdSeS nanorods are comparatively longer in length) are arranged in multi layers with pretty good vertical alignment and closed-pack ordering. It would have been better if we could control layer by layer ordering of each type of nanorods. Maybe, it can be done by changing some parameters related to the EPD process and the suspension as well. But, one important observation from our experiments is that two different kind of semiconductor nanorods can be deposited onto silicon substrates with good vertical alignment and closed-pack ordering.

Another thing, which can be tried in the future is to disperse both the CdSe and CdSeS nanorods on the same solvent (maybe toluene) and then EPD can be tried with that sample. Depending on the difference in size and dipole moment of two types of nanorods, maybe a sequential deposit can be obtained.

4.4 Some discussions about the EPD experiments with semiconductor nanorods

The interaction between the nanorods in suspension is very much crucial for the process of EPD, which leads to deposition of uniform films/coatings on any substrate. In the absence of any external electric field, the electrostatic properties of the nanorods are responsible for their self-assembly from an evaporating drop of solvent. Although by this self-assembly approach, the nanorod solution concentration and the solvent evaporation rate can be controlled
precisely, but positional ordering of the nanorod assemblies cannot be manipulated effectively. The CdSe and CdSeS nanorods have inherent electrical charge and permanent dipole moment (due to their noncentrosymmetric, wurtzite lattice structure). EPD is a combination of the processes of electrophoresis and deposition. During electrophoresis, charged particles in a suspension move towards the oppositely-charged electrode due to application of a DC, spatially uniform electric field. After migrating towards the electrode, the charged particles deposit onto the depositing substrate or electrode and become densely packed with good orientational ordering.

From previous studies on cadmium chalcogenide nanorods (CdSe and CdS), it can be inferred that dipole-dipole interaction is primarily responsible for their self-assembly. But, specifically, in order to get more ordered assemblies with particular orientation and positional close-pack ordering, EPD technique is used. During EPD, the total force acting on the nanorods is simply qE, where q is the net charge on the nanorods and E is the externally applied electric field. So, the nanorods by virtue of their net charge will migrate towards the oppositely charged electrode, when an external electric field is applied. Another advantage of using EPD is that the nanorods by virtue of their inherent permanent dipole moment will feel a torque when an electric field is applied and will tend to align to the direction of the electric field. If $d$ is the inherent electric dipole moment then the alignment energy of the nanorods will be given by $E \times d$. When this alignment energy will overcome the thermal excitation energy given by $k_B T$ ($k_B$ is Boltzmann constant and $T$ is the temperature), good alignment of the nanorods can be achieved. If the applied electric field is not homogeneous, the whole process of deposition can be adversely affected, as a result of dielectrophoresis. During EPD process, the interaction between the nanorods is mainly governed by Coulombic interaction i.e. due to net charge, charge-dipole interaction and dipole-dipole interaction. The resultant potential energy on the nanorods consists of each of these interaction potentials. The electric field in a way compels the nanorods in the solution to align in the same direction.
The total interaction energy between the nanorods can be written as

\[ E_{\text{total}} = \left[ \frac{q^2}{4\pi\epsilon_0 r} \right] - \left[ \frac{(qp \cos \theta)}{4\pi\epsilon_0 r^2} \right] - \left[ \frac{p_1 p_2}{4\pi\epsilon_0 r^3} \right] \]

Here, \( \theta \) is the angle between two neighbouring nanorods, \( \epsilon \) is the dielectric constant of the solvent, \( p \) is the permanent dipole moment of each nanorod, \( r \) is the distance between the nanorods. It has been assumed that each nanorod in the solution has identical permanent dipole moment and net charge. It is also assumed that the nanorods are arranged side by side with their dipoles aligned with the electric field. As discussed before, the sum of all the three terms in the above equation contributes to the overall net potential on each nanorod due to its neighbour. The nature of the nanorod deposits can be analysed by studying each of these potentials in detail.

Sometimes, excess and unwanted impurities in the form of surfactants, ligands and organic material can influence the process of EPD and hence needs to be controlled effectively in order to get a high-quality deposit on the substrate.

The externally applied electric field is primarily responsible for the movement of the nanorods to the electrode, but their mutual interaction dominates at the interface, allowing the assembly to attain the lowest potential energy. It has been noted that although Coulombic repulsion is very important in the assembly process, the shorter range dipole-dipole interaction become predominant as the distance between the neighbouring nanorods decreases. This dipole-dipole interaction provides the necessary positive interaction energy for forming highly ordered, close-packed assembly onto the substrate. If we consider sequential deposition of nanorods into highly-ordered multi-layer structures, the negative interaction energies between adjacent deposited layers which is required for getting good ordering, are mainly provided by the charge-dipole and dipole-dipole interactions between the nanorods.
Previous works\textsuperscript{12,13} on EPD of CdSe and CdS nanorods have reported good vertical alignment of CdS nanorods. But satisfactory vertical alignment and ordering for CdSe nanorods was not achieved before. From the images presented in this thesis, we can observe a well-ordered, close-packed assembly of CdSe nanorods with good vertical alignment, in this work.

4.5 Synthesis and EPD of gold nanorods

In the next part of the thesis, we will discuss our work carried out on gold nanorods. The gold nanorods were synthesized by following the standard seed growth method\textsuperscript{28-30}.

4.5.1 Synthesis of gold nanorods

\textit{Chemicals used}

The following chemicals were used for synthesis of gold nanorods as received from their respective companies without any further purification:

1) Cetyltrimethylammonium bromide (CTAB, >95\%), purchased from Fisher Scientific.
2) Sodium borohydride (NaBH4, > 99 \%), purchased from Sigma-Aldrich.
3) Silver nitride (AgNO3, > 99 \%), purchased from Sigma-Aldrich.
4) L-ascorbic acid (≥ 99.0 \%), purchased from Sigma-Aldrich.
5) Gold (III) chloride trihydrate (HAuCl4·3H2O, ≥ 99.9 \%), purchased from Sigma-Aldrich.
6) Hydrochloric acid (HCl), purchased from Sigma-Aldrich.
7) Sodium hydroxide (NaOH, ≥ 97 \%), purchased from Sigma-Aldrich.
8) Mercaptosuccinic acid (MSA, 97 \%), purchased from Sigma-Aldrich.
9) Tetraoctylammonium bromide (TOAB, 98 \%), purchased from Sigma-Aldrich.
10) Chlorobenzene, purchased from Sigma-Aldrich.
Cyclohexane, purchased from Sigma-Aldrich.

**Synthesis Methodology**

**Seed solution preparation:** At first, freshly-prepared ice-cold aqueous solution of NaBH₄ (0.01 M, 1 ml) was mixed with an aqueous solution of CTAB (0.10 M, 9.75 ml) and HAuCl₄ (0.01 M, 250 μl). Then, the solution was kept under vigorous stirring (1200 rpm) for two minutes. From colourless, the solution turned bright yellow and then light brown.

**Growth solution preparation:** An aqueous solution of AgNO₃ (0.01 M, 150 μl) was mixed with the solution of CTAB (0.10 M, 19 ml). It was kept undisturbed for 15 minutes. After that, a solution of HAuCl₄ (0.01 M, 1 ml) was mixed with this solution under mild stirring (400 rpm).

Finally, HCl (0.8 ml, 1 M) and L-ascorbic acid (0.1 M, 220 μl) was added to the as prepared growth solution. Then, 170 μl of the gold seed solution was mixed with it. Then, the gold nanorods in the solution were kept overnight as it is, undisturbed without stirring at 30 °C, to let them grow.

The gold nanorods, thus synthesized were collected by centrifugation at 5000 rpm for 20 minutes and re-dispersing in water.

**Phase transformation of synthesized gold nanorods**

The gold nanorods obtained by the above described procedure were in aqueous phase. But, as we know, any aqueous dispersing media is not quite suitable for EPD. So, the as prepared gold nanorods were transferred to an organic phase of chlorobenzene following the procedure reported by Chen et al. At first, the concentration of CTAB was reduced by centrifuging and re-dispersing the gold nanorods twice. Then, the resulting sediment thus obtained, was dispersed in 3 ml of deionized water. In the next step, MSA ((3 ml, 10 mM) was mixed with 3 ml of the aqueous gold nanorod solution. Then, using dilute NaOH solution (1.7 ml, 0.1 M) under constant stirring, the pH was set to a value of 9. Then, 1.5 ml of a 50 mM solution of TOAB in chlorobenzene was added to the previously obtained solution. The mixture, thus
obtained, was kept under vigorous stirring for about 30 minutes and were then left undisturbed till the aqueous phase faded and the organic phase turned deep red. The gold nanorods from the bottom in chlorobenzene were collected very carefully by using a pipette and were transferred to a centrifuge tube. The obtained product was again centrifuged and the top layer (which has the possibility of containing some water) was discarded. Finally, the gold nanorod sediment, thus obtained, was dispersed in about 2 ml chlorobenzene for future use in experiments 27. The size of the gold nanorods were about 11 nm x 42 nm, in general.
**Some TEM images of gold nanorods**

Figure 29: A bright-field TEM image of gold nanorods obtained by drop-casting gold nanorods solution (in chlorobenzene) onto a TEM grid.
Figure 30: A bright-field TEM image of gold nanorods obtained by drop-casting gold nanorods solution (in chlorobenzene) onto a TEM grid.

From the above images we can observe that the synthesized gold nanorods are quite monodispersed in nature.
4.5.2 EPD of gold nanorods

The EPD apparatus used for carrying out different experiments with gold nanorods is the same as described before. Two rectangular pieces of silicon wafer of 1 cm x 2.5 cm dimensions were used as deposition electrodes for the EPD experiments. The silicon substrates were sonicated in acetone and IPA for 15 minutes in each and then were blow dried by nitrogen. The electrodes were kept parallel to one another with a separation of about 2.15 mm.

The as prepared gold nanorods in chlorobenzene were then added to the non-polar, organic solvent cyclohexane with varying concentrations and were vortexed and ultrasonicated for 2 minutes each. The voltage used for deposition was about 400 volts and the deposition time was 5 minutes. A concentration of 0.4 ml of gold nanorod solution (in chlorobenzene phase) was dispersed in 6 ml of cyclohexane for EPD.
Some SEM images of gold nanorods deposited onto silicon substrates

Figure 31: A high-resolution top-down SEM image of gold nanorods deposited on silicon substrate by the process of EPD.
Figure 32: A high-resolution top-down SEM image of gold nanorods deposited on silicon substrate by the process of EPD.
From the above SEM images, we can observe that most of the deposited gold nanorods are vertically oriented and are densely packed. But, we can also see that the whole of the substrate is not deposited with the gold nanorods. For device scale applications in various areas, uniform films/coatings are required without too much holes. Here, we find that although we could get closed-pack ordering with quite good vertical alignment of gold nanorods, the entire area of the silicon substrate (submerged in the suspension media) does not get covered with gold nanorods. But, from this work, it can be inferred that, EPD process can be considered as an appropriate, suitable and cost-effective method for obtaining good deposition of vertically-oriented gold nanorods. It can be expected that by precisely optimizing the different parameters such as the concentration of the nanorods, the applied voltage and the deposition time, the deposition area can be effectively extended to the entire substrate.
References


O’Dwyer, C.; Ryan, K.M. A facile spin-cast route for cation exchange of

20) Besra, L.; Liu, M. A review on fundamentals and applications of electrophoretic

21) Singh, A.; Gunning, R.D.; Sanyal, A.; Ryan, K.M. Directing semiconductor nanorod
assembly into 1D or 2D supercrystals by altering the surface charge. *Chem.
Commun. (Camb)*. **2010**, *46*, 7193.

22) Zhang, S-Y.; Regulacio, M.D.; Han, M-Y. Self-assembly of colloidal one-

23) Singh, S.; Singh, A.; Palaniappan, K.; Ryan, K.M. Colloidal synthesis of
homogeneously alloyed CdSe$_x$S$_{1-x}$ nanorods with compositionally tunable

24) Ahmed, S.; Ryan, K.M. Centimetre scale assembly of vertically aligned and close

25) Chen, F.; Liu, M. Preparation of Yttria-Stabilized Zirconia (YSZ) Films on
La$_{0.85}$Sr$_{0.15}$MnO$_3$ (LSM) and LSM–YSZ Substrates Using an Electrophoretic

Lee, S.H. Dielectrophoretic and electrophoretic force analysis of colloidal fullerenes in

27) Liu, P. Investigation of Electric field Assembly of ColloidalRod Shaped Nanocrystals
and Their Device Application. PhD Thesis **2016**, Department of Chemical and
Environmental Sciences, University of Limerick.


Chapter 5: Conclusion

The primary objective of this thesis was to obtain highly-ordered, close-packed deposit of semiconductor and metal nanorods on different substrates with good vertical alignment, by using the electrophoretic deposition (EPD) technique.

In this work, semiconductor nanorods (CdSe and CdSeS) were synthesized successfully, following the hot-injection approach. After that, using the EPD process, good vertically-aligned multi-layered, close-packed deposits of CdSe nanorods were obtained on different types of substrates, such as, silicon wafers, ITO/glass, NiO sputtered on ITO/glass. Detailed studies were done to analyse the effects of different EPD related parameters, such as, the concentration of the nanorods in the dispersing media, the applied voltage and deposition time, on the deposition formed on the substrates. From the studies, it can be inferred that, optimizing these parameters is required, in order to get high-quality films/coatings with good vertical-alignment of the nanorods. It is also noticed that washing of the nanorods after the synthesis step and a perfect ligand environment is very crucial for the EPD process. Another finding from this study is that, these EPD related parameters need to varied accordingly for different types of substrates.

Also, multi-layered, vertically- aligned, close-packed assemblies of two different types of semiconductor nanorods (CdSe and CdSeS) on the same substrate, were obtained by EPD process.

Lastly, gold nanorods were synthesized using the standard seed-growth method. Then EPD technique was used to deposit gold nanorods onto silicon wafer substrates. Although the entire area of the substrate could not be deposited with the gold nanorods, but good vertical alignment could be observed in most cases.
From this work, it can be concluded that, EPD is a simple and cost-effective technique for obtaining high-quality, close-packed films/coatings of semiconductor and metal nanorods on different types of substrates with very good vertical alignment. Thus, EPD technique can be further used for various types of applications in diverse areas such as electronics and opto-electronics and also for efficient device fabrication.
Chapter 6: **Future Work**

Cadmium chalcogenide nanocrystals are very much suitable for applications related to opto-electronic devices, especially in light emitting devices such as LEDs. For achieving that, one important step is deposition of these cadmium chalcogenide based nanocrystals on different types of substrates. A multi-layered composite nano-structure, consisting of sequentially arranged CdSe nanoplates of different types were reported by Rowland et al. The bandgaps of the nanoplates were slightly different. This structure is quite promising for realization of efficient LEDs, low threshold optical gain media and multiexcitonic solar-cells. Similarly, a highly-efficient, sequentially-arranged multi-layered nanostructured solar cell consisting of ITO/CdTe/CdSe:Te$_{1-x}$/ZnO/Al was reported by MacDonald et al. For realization of various types of complex structured opto-electronic and photovoltaic devices, like composite LEDs and solar-cells with different layers of materials, EPD technique can be effectively used along with other deposition techniques like Atomic Layer Deposition and Sputtering. In this work, CdSe nanorods deposited on NiO sputtered on ITO/glass has shown some PL. So, a sandwich-like LED structure consisting of ITO/glass/NiO/CdSe/ZnO can be fabricated in the future.

Metal nanoparticles and their assembled superstructures are particularly very important for sensing purposes and photonics related applications, because of the collective coupling of the plasmons present, which in turn is responsible for amplification of the optical signals. Moreover, hybrid superstructures of metals and semiconductors are also very interesting as they possess the properties of both types of materials. Besides that, due to inter-particle interactions, these hybrid superstructures also exhibit some novel characteristics such as very good charge transfer properties, reduced lifetime etc. Most works on hybrid
nanostructures have focussed on the selective growth of metals on nanorod and nanowire tips\textsuperscript{12} and also on hybrid supercrystals, consisting of 0 dimensional nanoparticles of gold with PbSe and CdSe nanocrystals \textsuperscript{2,8,13}. But, combined superstructures consisting of both semiconductor and metal nanorods are seldom reported. In this work, CdSe and gold nanorods have been deposited separately on silicon wafers by the EPD technique. This can be extended in the future to achieve bi-modal or multi-modal assembly of CdSe (or any other semiconductor nanorods or nanocrystals) and gold (or any other metal nanorods or nanoparticles) on the same substrate.

Zhu et al.\textsuperscript{14} have reported fabrication of thin films of gold nanoparticles by electrophoretic deposition method. These thin films could be used as highly sensitive surface-enhanced Raman scattering (SERS) substrates. Similarly, high-quality thin films consisting of vertically-aligned, close-packed gold nanorods can also be fabricated in the future, using the EPD process and hence can be used as good SERS substrates.

In this work, we have only used constant DC electric fields for our deposition purpose. But, in recent times, pulsed direct current (PDC) and alternating current (AC) electric fields have also been used for carrying out the EPD process \textsuperscript{15}. When DC electric fields are used, there are some electrochemical and electro-osmotic effects which may hinder the overall effectivity of the deposition process. These effects can be avoided if an AC electric field is used \textsuperscript{16}. An assembly of gold nanowires dispersed in a di-electric medium have been reported by Mayer et al. by applying an AC electric field \textsuperscript{17}. It has been observed that both the magnitude and the frequency of the applied AC voltage play important roles in the alignment process of the nanowires \textsuperscript{16}. So, in the future, AC or PDC electric fields can be used for getting good assembly of vertically aligned metal and semiconductor nanorods or nanoparticles, in a definite pattern, as required for various applications.
Thus, we see that EPD is a simple and cost-effective technique which can be effectively used in a variety of applications in the future and for realizing highly-efficient opto-electronic and photovoltaic devices.
References


