Photochemical and Photoelectric Applications of II-VI Semiconductor Nanomaterials

Abhilash Sugunan

Licentiate Thesis
Stockholm 2010

Functional Materials Division
School of Information and Communication Technology
Royal Institute of Technology (KTH), Stockholm
Address

Functional Materials Division
School of ICT
Royal Institute of Technology
Isafjordsgatan 22
SE 164 40, Kista/Stockholm, Sweden

Supervisor

Prof. Mamoun Muhammed

Co-Supervisor

Assoc. Prof. Muhammet S. Toprak

TRITA-ICT/MAP AVH Report 2010:3
ISSN 1653-7610
ISRN KTH/ICT-MAP/AVH-2010:3-SE
© Abhilash Sugunan, 2010
Kista Snabbtryck AB, Stockholm 2010
Abstract

In this work we investigated fabrication of semiconductor nanomaterials and evaluated their potential for photo-chemical and photovoltaic applications. We investigated two different II-VI semiconductor nanomaterial systems; (i) ZnO oriented nanowire arrays non-epitaxially grown from a substrate; and (ii) colloidal CdTe nanotetrapods synthesized by solution-based thermal decomposition of organo-metallic precursors. In both the cases our main focus has been optimizing material synthesis for improving potential applications based on photon-electron interactions.

We have studied the synthesis of vertically aligned ZnO nanowire arrays (NWA), by a wet chemical process on various substrates. The synthesis is based on epitaxial growth of ZnO seed-layer on a substrate in a chemical bath consisting of an aqueous solution of zinc nitrate and hexamethylenetetramine (HMT). We have suggested an additional role played by HMT during the synthesis of ZnO nanowire arrays. We have also extended this synthesis method to fabricate hierarchical nanostructures of nanofibers of poly-L-lactide acting as a substrate for the radially oriented growth of ZnO nanowires. The combination of high surface area of the nanofibrous substrate with the flexibility of the PLLA-ZnO hierarchical nanostructure enabled the proof-of-principle demonstration of a ‘continuous-flow’ water treatment system that could effectively decompose single and combination of known organic pollutants in water, as well as render common waterborne bacteria non-viable.

We have studied another chemical synthesis that is commonly used for size controlled synthesis of colloidal quantum dots, which was modified to obtain anisotropic nanocrystals mainly for CdE (E=S, Se, Te) compositions. In this work we demonstrate by use of oleic acid (instead of alkylphosphonic acids) it is possible to synthesize CdTe and CdSe nanotetrapods at much lower temperatures (~180 ºC) than what is commonly reported in the literature, with significantly different formation mechanism in the low-temperature reaction.

Finally, we have performed preliminary photoconduction measurements with CdTe nanotetrapods using gold ‘nanogap’ electrodes fabricated in-house, and obtain up to 100 times enhancement in current levels in the $I–V$ measurements under illumination with a white light source.

Keywords: ZnO, nanowire arrays, photocatalysis, nanofibers, CdTe, nanotetrapods, Ostwald ripening photoconduction, nano-gap electrodes
List of Papers

This thesis is based on the following papers:


Other work not included in this thesis:


Contributions of the author

**Paper 1**: Planning of the experiments, performing the experiments, analyzing data, lead in writing the manuscript.

**Paper 2**: Planning of the major parts of the experiments, performing the experiments pertaining to material fabrication, analyzing material characterization data, lead in writing the manuscript. Development and measurements involving nano-gap electrodes was performed by the group of Prof. Klaus Leifer.

**Paper 3**: Planning of the major parts of the experiments, performing the experiments pertaining to inorganic material fabrication, analyzing data, lead in writing the manuscript.
### List of abbreviations, symbols and non-standard definitions

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0D, 1D, 2D, 3D</td>
<td>0, 1, 2, 3 dimensions</td>
<td>0, 1, 2, 3 dimensions</td>
</tr>
<tr>
<td>Anisotropic</td>
<td></td>
<td>Non-spherical morphologies, usually like rod/wire</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td></td>
<td>Ratio of length to width</td>
</tr>
<tr>
<td>ATR</td>
<td></td>
<td>Attenuated total reflectance</td>
</tr>
<tr>
<td>CdE</td>
<td></td>
<td>Common notation for CdS, CdSe, CdTe</td>
</tr>
<tr>
<td>DPA</td>
<td></td>
<td>Diphenylamine</td>
</tr>
<tr>
<td>EBL</td>
<td></td>
<td>Electron beam lithography</td>
</tr>
<tr>
<td>Exciton Bohr radius</td>
<td></td>
<td>Bohr radius of the excited electron orbital</td>
</tr>
<tr>
<td>FIB</td>
<td></td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>FTIR</td>
<td></td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>HMT</td>
<td></td>
<td>Hexamethylenetetramine (hexamine)</td>
</tr>
<tr>
<td>I–V</td>
<td></td>
<td>Current – voltage</td>
</tr>
<tr>
<td>Ligand</td>
<td></td>
<td>Molecule that coordinates to the surface atoms</td>
</tr>
<tr>
<td>MCP</td>
<td></td>
<td>Monocrotrophos</td>
</tr>
<tr>
<td>Micelles</td>
<td></td>
<td>Droplets of oil/water suspended in water/oil, stabilized by amphiphillic surfactant molecules</td>
</tr>
<tr>
<td>Monomers</td>
<td></td>
<td>Precursor (or its fragment) that will eventually take up a lattice position in the crystal usually after undergoing a chemical reaction in the vicinity of the lattice.</td>
</tr>
<tr>
<td>Nanogap electrodes</td>
<td></td>
<td>Conducting strip with a nanoscale gap</td>
</tr>
<tr>
<td>NTP</td>
<td></td>
<td>Nanotetrapod</td>
</tr>
<tr>
<td>Nuclei</td>
<td></td>
<td>Initial cluster of atoms/molecules formed immediately after supersaturation</td>
</tr>
<tr>
<td>NWA</td>
<td></td>
<td>Nanowire-array</td>
</tr>
<tr>
<td>ODE</td>
<td>1- Octadecene</td>
<td>1- Octadecene</td>
</tr>
<tr>
<td>Optical wavelength</td>
<td></td>
<td>Range of wavelengths of light from ultra-violet to infrared</td>
</tr>
<tr>
<td>Photocatalysis</td>
<td></td>
<td>Catalysis reaction activated by light</td>
</tr>
<tr>
<td>PLLA</td>
<td></td>
<td>Poly-L-lactide</td>
</tr>
<tr>
<td>Polytypism</td>
<td></td>
<td>Co-existence of two or more stable crystallographic phase</td>
</tr>
<tr>
<td>ppm</td>
<td></td>
<td>Parts per million</td>
</tr>
<tr>
<td>Precursor</td>
<td></td>
<td>Reactants</td>
</tr>
<tr>
<td>Quantum dot/wire/well</td>
<td></td>
<td>Materials with three/two/one dimension smaller than its exciton Bohr radius</td>
</tr>
<tr>
<td>RF</td>
<td></td>
<td>Radio frequency</td>
</tr>
<tr>
<td>RON</td>
<td></td>
<td>Radially oriented nanowiers</td>
</tr>
<tr>
<td>Seeds</td>
<td></td>
<td>Small clusters of material onto which further precipitation and/or epitaxial growth is to occur</td>
</tr>
<tr>
<td>Term</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>-----------------------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
<td></td>
</tr>
<tr>
<td>Surfactant</td>
<td>Molecules that can interface with both oil and water phases due to its amphiphillic structure</td>
<td></td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
<td></td>
</tr>
<tr>
<td>TOP, TOPO</td>
<td>Trioctyolphosphine, trioctyolphosphine oxide</td>
<td></td>
</tr>
<tr>
<td>TOP-Te, TOP-Se</td>
<td>Trioctyolphosphine-telluride, Trioctyolphosphine selenide</td>
<td></td>
</tr>
<tr>
<td>[TOP-Te]</td>
<td>Molar concentration of, here of TOP-Te</td>
<td></td>
</tr>
<tr>
<td>Twinning</td>
<td>Two separate crystals sharing some of the same crystal lattice points in a symmetrical manner.</td>
<td></td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible</td>
<td></td>
</tr>
<tr>
<td>V_{R.M.S.}</td>
<td>Root mean square value of voltage, R.M.S value is a statistical amplitude of an alternating signal</td>
<td></td>
</tr>
<tr>
<td>Wurtzite</td>
<td>A type of hexagonal crystal structure</td>
<td></td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
<td></td>
</tr>
<tr>
<td>Zinc blende</td>
<td>A type of cubic crystal structure</td>
<td></td>
</tr>
<tr>
<td>$\theta/\theta$</td>
<td>Angles of sweep of X-ray detector during XRD measurement.</td>
<td></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength (in this work, unit is nm)</td>
<td></td>
</tr>
<tr>
<td>$\mu E$</td>
<td>Micro Einstein; number of photons expressed in terms of Avogadro’s number</td>
<td></td>
</tr>
</tbody>
</table>
# Table of Contents

Abstract .......................................................................................................................... i
List of Papers.................................................................................................................. ii
List of abbreviations, symbols and non-standard definitions ......................................... iii

1. Introduction ............................................................................................................... 1
   1.1 Overview ............................................................................................................. 2
   1.2 Electrons: The Negative ................................................................................. 3
   1.3 The Nanoscale Effects: Strains, Surfaces and Confinement ............................. 4
   1.4 Dimensionality: 0D, 1D, and 2D nanomaterials ............................................... 6
   1.5 One dimensional nanomaterials ....................................................................... 9
       1.5.1 Solution chemistry routes for 1D nanomaterials ...................................... 10
   1.6 Applications of 1D semiconductor nanomaterials ............................................. 14

2. Experimental .............................................................................................................. 17
   2.1 Materials and Synthesis .................................................................................. 17
       2.1.1 Vertically aligned nanowire arrays of ZnO .............................................. 17
       2.1.2 Colloidal CdTe nanotetrapods .............................................................. 18
   2.2 Methods of Characterization ........................................................................... 19
       2.2.1 Characterization ...................................................................................... 19
       2.2.2 Continuous flow photocatalytic treatment of aqueous organic molecules .................................................................................................................. 20
       2.2.3 Continuous flow treatment of water contaminated with Escherichia coli.......................................................................................................................... 20
       2.2.4 Nanogap electrode fabrication ................................................................. 20
       2.2.5 Trapping of CdTe nanotetrapods between the nanogap electrodes ............ 21

3. Results and discussions ............................................................................................. 22
   3.1 Aligned ZnO NWAs ......................................................................................... 22
       3.1.1 Structural characterization ....................................................................... 22
       3.1.2 Hierarchical nanostructures ...................................................................... 26
       3.1.3 Photocatalytic Effects ............................................................................. 27
   3.2 Colloidal nanotetrapods of CdTe ....................................................................... 30
       3.2.1 Effect of temperature .............................................................................. 31
       3.2.2 Growth mechansim ............................................................................... 32
       3.2.3 Photoconduction measurements of CdTe nanotetrapods ......................... 35

4. Summary and conclusions ......................................................................................... 39

5. Future work ............................................................................................................... 41

Acknowledgement ........................................................................................................... 42
References ....................................................................................................................... 43
1. Introduction

Nanotechnology has been steadily receiving significant attention during the past decades both in scientific & engineering communities as well as in popular media. Nanometer-scale materials or ‘nanomaterials’ often have distinctly different physical and chemical properties in comparison to their bulk form. The origin of some of the novel properties will be described in the later chapters. Unlike the connotation of the word, nanotechnology is not a single technology, in the sense that it is not a jargon for a particular manufacturing process or a particular design for a device. Instead, it is a broad umbrella covering interdisciplinary research on fabrication of nanomaterials, tuning their properties and applications of these novel properties.

Indeed several size-dependant phenomena makes nanomaterials attractive in terms of potential applicability compared to their bulk form, justifying the importance and attention such research is receiving. Methods of obtaining nanomaterials vary and mostly depend on the material, its morphology and also the targeted applications. Physical techniques for fabricating nanomaterials including tribology, vapor-phase depositions, electric discharges, were investigated in order to study the size dependant physical properties as a proof-of-concept. Currently physical techniques are usually limited to specialized vapor deposition techniques for obtaining epitaxial deposition of thin layers and clusters of materials with precision down to atomic layers on various substrates. Other techniques extensively involve solution chemistry and are favored when synthesis of large quantities of nanomaterials at relatively lower costs is required.

In the past decades chemical routes for nanomaterials fabrication have matured and there is a very good control over the size, shape and most importantly yield when considering a per-batch basis. Applications of nanomaterials cover a wide range of fields including bio-medicine, electronics, optoelectronics, and water purification amongst many others. Traditionally nanomaterials investigated for (opto)electronic applications were fabricated by variations of vapor deposition techniques, although recent advances in the chemical routes, allowing synthesis of nanomaterials with good control over its shape (in addition to size) has led to a shift in this trend. This work will be limited to synthesis of group II-VI semiconductor nanomaterials and some applications arising from interactions of its valence electrons with light, with the main focus on the materials chemistry perspectives.
1.1 Overview
The focus of this work is to investigate the fabrication of semiconductor nanomaterials and evaluate their potential for photo-chemical and photovoltaic applications. Our main motivation is to consolidate the significant recent advances in the multidisciplinary domain of nanotechnology to gain a better understanding of the fabrication processes, development of more efficient fabrication techniques and preliminary assessment of environment-friendly applications.

Here we have investigated two different II-VI semiconductor nanomaterial systems; (i) ZnO oriented nanowire arrays grown non-epitaxially on a substrate; and (ii) colloidal CdTe nanotetrapods synthesized by solution-based thermal decomposition of organo-metallic precursors. In the case of both these II-VI semiconductor materials, their valence electrons are known to interact with optical wavelength photons* resulting in interesting potential applications.

In the presence of ultra-violet light, ZnO catalyzes the decomposition of several toxic organic chemicals dissolved in water. This occurs at the surface of ZnO and enhanced surface area of nanoscale structures aids this reaction significantly. In this thesis we describe new insights on the mechanisms of formation of ZnO nanostructures (in the form of nanowire-arrays on a substrate) by a solution-chemistry route. Furthermore we developed a practical route to obtain large quantities of such nanowire arrays on a novel flexible substrate and demonstrate a proof-of-principle of a ‘continuous-flow’ water purification system.

Towards another environmental friendly application, CdTe is a promising material for solar-cells due to its high carrier mobility and broad absorption of light covering the entire visible spectrum. In the form of nanocrystals, CdTe is employed as active components in several novel solar cell architectures. In this thesis, we developed a novel low temperature synthesis of CdTe tetrapodal nanocrystals and describe the nanocrystal formation mechanism in our low temperature reactions. We compare the formation mechanism with the already established mechanisms describing formation of nano-tetrapod (NTP) morphologies at higher temperatures. We also describe perhaps the first photoconductivity measurements of CdTe NTPs employing ‘nano-gap’ electrodes of gold. The significance of the photoconduction measurement technique described here is mainly due to the artefact-free photoconduction data, which is difficult to obtain with contemporary strategies for measurement of electrical transport properties of nanocrystals. Such ‘exotic’ measurements are

* Optical wavelength here refers to the range covering ultraviolet to near infrared (roughly $\lambda = 300–2000$ nm)
important as they can potentially bring out the mechanisms of charge transport within a single nanocrystal, thus aiding the design of efficient futuristic solar-cells.

The generation of electron and hole pairs in II-VI semiconductor nanomaterials when excited by light is the driving force for the two applications in seemingly different fields of research. This opto-electronic interaction in semiconductor nanomaterials can potentially lead to several other applications.

1.2 Electrons: The Negative

In order to explain and bring out various novel phenomena and applications of nanomaterials, or even general chemistry, a proper introduction is justified for the most potent elementary particle in our length/size scales, namely the electron.

Electrons play a central role in many physical phenomena such as electricity, magnetism, and thermal conductivity. When electrons oscillate, or more specifically (de/)accelerate they absorb or radiate energy in the form of photons, This phenomenon is commonly used in radio-frequency (RF) devices such as antennae. Generation and detection of photons of higher energies (optical, X-rays, etc) also involve excitation of electrons, although in this case quantum mechanical properties are involved rather than the ‘simpler’ oscillations. Moving into chemistry, size of an atom (by extension also size of a molecule) is largely determined by the number and quantum state of the outermost electrons.

Yet in an extreme irony, such a potent elementary particle has been assigned to have a ‘negative’ charge! As a charged particle, and knowing that there are two equal and opposite kinds of elementary charge, they could have just as well been positive. This ‘injustice’ can be attributed to the multi-skilled American scientist Benjamin Franklin.\(^\text{17}\) At least as early as the time of ancient Greeks it was known that amber (they called it ἠλέκτρον, or ēlektron), when rubbed with fur attracted small objects. C. F. du Fay and Hawksbee independently showed two different kinds of this frictional property (the term electrostatics was not known then), one from rubbing glass and another from rubbing amber. It was Benjamin Franklin who proposed that these were two opposite kinds of a same property and assigned the property taken by glass to be positive and by amber, negative. It was shown much later that glass lost electrons, while amber gained electrons to become charged and continuing with the naming convention (established for over a century by then) electrons unfortunately came to possess a negative charge.

All chemical bonds involve exchange, sharing, or ‘loan’ of electrons and in some cases the redistribution of electrons within an already bonded molecule causes additional inter/intra-molecular
bonds. The strength and nature of these chemical bonds determines most physical and chemical properties of matter, such as melting and boiling points, hardness, conductivity, chemical reactivity, etc. Even the absence of electrons (in a particular energy state) is important enough to be assigned a name (holes) and, as will be shown later chapters, play an important role in all contemporary and future ‘high-tech’ gadgets.

1.3 The Nanoscale Effects: Strains, Surfaces and Confinement

The nature and strengths of the chemical bonds largely determine the properties of matter. Small atoms with few electrons (low atomic number) tend to competitively share or exchange electrons with other atoms to achieve stable octet forming covalent or ionic bonds, respectively. Larger atoms have a lot of electrons, allowing several of such atoms pooling in their electrons to collectively satisfy their stable octet, forming what is called ‘free electron gas’ model of metallic bonds.

Most solid matter with ionic, covalent or metallic bonding exists with a long range periodic order in the arrangement of the atoms forming crystals. The exact arrangement, which includes the distances, strength of attachment, and the number of atoms attached to an atom in a particular lattice, determines the many of the physical and chemical properties of the crystalline material.

For example in ionic and covalent bonds, the atoms fiercely compete for their electrons and once the bonds are formed, they are rigidly held in place (changing the bond lengths would be difficult without redistribution of the already short supply of electrons). Hence they are usually brittle, have higher melting points, and are nonconductors. Contrarily, the relatively free electrons in metallic bonds, allow considerable freedom to metallic atoms to change their bond lengths and making metals malleable, have lower melting points and good conductors. The lattice parameters are applicable to a bulk lattice, i.e. for bonds deep with a crystal. At the outermost surface of any crystal, there are atoms which have unsatisfied bonds, and this is compensated within a crystal by strained lattice parameters of the surface atoms with their penultimate atoms. This ‘tweaking’ usually goes unnoticed in most materials, due to sheer abundance of bulk lattice bonds compared to the strained surface bonds.

If we were to break a chunk of a crystal into two, we increase its exposed surface area, thereby slightly increasing the ratio of strained surface bonds to the bulk bonds. If we keep breaking up this

---

* The term atom here is usually limited to the nuclei and their inner-shell electrons, while the outer-most electrons actively participate in the various bond formations.

† Breaking the bonds in an ionic crystal due to melting or dissolution in polar solvents creates mobile ions thereby increasing the electrical conductivity.
crystal, a time will come when the surface bonds will dominate over the bulk bonds. The particle will have to be very small for this to happen, but it is possible. Theoretical calculations and experiments showed that this cross-over occurs when dimensions of the matter is hundred nanometers or less.\textsuperscript{18,19} This is the most intuitive ‘nano-size’ effect: dominance of surface atoms. This concept is schematically shown in Figure 1, where the nanocrystal on the right has only the four inner bonds with bulk parameters. The strained bonds of the surface atoms now determine the new properties of the material.\textsuperscript{20} The ability to exchange, share, or loan electrons largely determines the chemistry of an atom (or molecule), which in turn is affected by the changes in the lattice bonds in a crystalline material. Hence the properties of a material changes when they are in the form of nanocrystals. Among the several manifestations of the dominance of the strained surface bonds include lower melting points for nanomaterials.\textsuperscript{21} The dominance of surface atoms, leads to a heightened chemical reactivity and for this reason, aluminum metal in the form of a fine powder acts as fuel for rocket engines, including the booster stages that were used in space shuttle launches. Part of this work will focus (detailed in chapter 1.8) on a well known catalytic reaction occurring on the surface of metal oxides (commonly TiO$_2$ and ZnO) which is known to be very efficient when employing the oxides in the form of nanomaterials.

Another distinct nano-scale effect is the changes in the quantum mechanical states of the electrons in a nanomaterial. Building up from Bohr’s postulate that electrons in an atom can reside only on specific ‘allowed’ orbits (now known to be orbitals) corresponding to specific energies, this implies that electrons in an atom can absorb or lose discrete quanta of energies to move from its current energy state to the next allowed energy state. For single atoms there are distinct energy states that the electrons can occupy. When millions of atoms come together to form a bulk lattice, due to inter-atomic interactions several closely placed energy states are now available for an excited electron to reside only if the exciting energy is at least enough to reach the lowest of the allowed excited state (this minimum energy is called the band-gap), as shown schematically in Figure 2. The availability of allowed states for an excited electron with respect to energy (per unit volume of the material) is called the ‘density of states’ and for most bulk crystals, there are enough available states to form a continuum called

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{A schematic comparison of lattice of a bulk crystal (left) with a nanocrystals (right).}
\end{figure}
conduction band. The corresponding ground states merge to form the valence band. In other words the density of states is smooth and continuous for bulk crystals.

However when we have a very small crystal (nanocrystal), due to lack of enough atoms, the availability of energy states for electrons become discreet and far apart (Figure 2). Such nanocrystals are characterized as atomic clusters and are called quantum confined systems. The requirement for quantum confinement is that the size of the nanocrystals should be smaller than the exciton Bohr radius of the material, which in simple terms is the Bohr radius of the electron residing in the first allowed excited state. This means that an excited electron is physically constrained by the small dimension of the nanocrystal. This spatial confinement can be in only one dimension (1D), two dimensions (2D), or in all the three dimensions (3D). For quantum confined nanocrystals, the band-gap and the density of states becomes sensitively dependant on the size of the nanocrystal (along the confined direction). The band gap energy and the separation between available states for an excited electron in a nanocrystal become larger with decreasing size. This is another distinct nano-size effect, wherein, below a certain material dependant critical size, the electrons in a nanocrystal becomes ‘quantum confined’ leading to novel size dependant interactions of the valence electrons to specific energies of excitation (notably photons and electric field).

1.4 Dimensionality: 0D, 1D, and 2D nanomaterials

A crystalline material having at least one dimension smaller than 100 nm is said to be a nanomaterial. A nanocrystal smaller than the exciton Bohr radius for that material, in at least one dimension is said to be quantum confined. A nanomaterial can be nano-sized along only one, two or all the three dimensions, in the form of a film, rod or a dot. There are several nomenclatures, to ascribe dimensionality to nanomaterials, and confusion arises due to the fact that some describe the number of dimensions of confinement (or nano-scale size), which is different from the number of bulk-like dimensions a nanomaterial seems to posses. Thus a thin film (quantum well) is confined in 1D, but is a
2D nanomaterial. Similarly a quantum wire is confined in 2D, but is a 1D nanomaterial and finally a quantum dot is confined in 3D and is a 0D nanomaterial.

The density of states of quantum confined nanocrystals has characteristic shapes for 2D, 1D and 0D nanomaterials, and the differences are due to the degrees of confinement of the electrons. For 0D nanomaterials, the excited electrons are completely confined in all the three dimensions and they behave analogous to atomic/molecular clusters with discreet states that are well separated in energy (Figure 3). For 1D nanomaterials, the excited electrons experience no confinement along the length of the material, and density of states is quasi-discreet (Figure 3) with respect to increasing excitation energy. Finally for 2D nanomaterials, the density of states shows a quasi-continuous step-like increase with increasing excitation energy (Figure 3). These changes in the density of states for excited electrons alters the way excitation energy interacts with the valence electrons, thus changing the fundamental properties with size as well as shape in quantum confined nanomaterials. In the case of larger nanocrystals (not quantum confined), size and shape of the nanocrystals also affects its properties due to differences in surface to volume ratio. For a given mass, 0D nanomaterials have the maximum exposed surface, followed by 1D, and finally 2D nanomaterials have the least.

Fabrication of 2D nanomaterials (including quantum wells) is usually accomplished on a substrate and over the past decades sophisticated techniques have been developed to achieve a controlled deposition down to single atomic layers. Fuelled by the advances in microelectronic fabrication processes, several matured vapor-phase techniques were extended to obtain controlled deposition of 2D nanomaterials. Although vapor-phase techniques are energy intensive and usually require exceptionally clean environments, the technology is mature enough to be commercially viable by large scale production. Indeed multiple quantum well laser diodes are now used in read/write heads for digital optical storage media. Alternative routes to obtain quasi-2D nanomaterials include spin-
coating of colloidal nanoparticles or layer-by-layer dip-coating processes (into colloidal suspension of nanoparticles). Both these techniques require synthesis of nanoparticles in colloidal form, by solution chemistry, and the obtained 2D material is usually textured and non-epitaxial. Such strategies have potential in applications where cost efficiency is more important over high-quality and repeatable performance, such as qualitative sensors.27 A newly discovered 2D nanomaterial, graphenes (single layer of graphite sheet) can be synthesized by solution-chemistry techniques and are not ‘grown’ on a substrate.28

1D nanomaterials, unlike films and particles, are unique due to the possibility of two axes of alignment with respect to a flat substrate. Planar deposition (parallel to a substrate) of nano-scale wires by extension of various microelectronic fabrication technologies such as chemical etching,29,30 electron (or ion) beam lithography31,32 has been demonstrated for metallic, or semiconducting materials. These demonstrations are on a small scale. Aligned nanowires of semiconductors are extremely interesting for optoelectronic applications and they will be described in greater details in the next section.

Since ancient times 0D nanomaterials particularly colloidal gold has been in use for several applications, including coloring agents for stained glass and potteries,33,34 as well as purported medicinal uses.35 In the mid 19th century, Michael Faraday performed the first modern scientific experiments with nanomaterials, and determined the particulate nature and size dependant optical properties of colloidal gold.36 There has been some interest in fabrication of 0D nanomaterials by physical processes like tribology37 and vapor phase epitaxial depositions38 followed up by lab-scale proof of principle demonstrations of potential applications.

Due to the extensive knowledge base in chemistry over the past centuries, the field of solution-chemistry based synthesis of 0D nanomaterials is vast and includes size,7 shape8,9 and composition controlled synthesis39,40 of hetero-structured 0D nanomaterials. Notable chemical synthesis techniques for synthesis of 0D nanomaterials include (co-)precipitation,41,42 sol-gel processes43,44 and thermal decomposition of organic complexes.39 The pregnancy test-kits (gold nanoparticles), antibacterial bandages (silver nanoparticles), several formulations of sun-screen lotions (SiO₂ nanoparticles, or other oxide ceramic nanoparticles) are examples of consumer products that involves chemically synthesized 0D nanomaterials.

Some of the techniques for fabrication of 0D nanomaterial can be extended to synthesis of 1D nanomaterial by varying the synthesis conditions.45 In a later section the thermal decomposition of
organic complexes will be described in details as this technique can also be used for fabrication of 1D and quasi-1D morphologies of several II-VI semiconductor compositions.

1.5 One dimensional nanomaterials

One dimensional nanomaterial has nano-scale sizes along two dimensions and having a rod-like or wire-like appearance. In such nanomaterials, quantum confinement and surface area related nano-scale effects are more pronounced compared to 2D nanomaterials, while at the same time they can be integrated and/or connected into device architectures due to single bulk-like dimension that is absent in 0D nanomaterials. Furthermore, their anisotropic morphology makes it possible to exploit the effects of orientation of an ensemble of such nanowires in addition to size and shape related nano-scale effects. The orientation of the nanowires with respect to the incident optical photons (and its polarization) brings out several novel optoelectronic effects such as polarization dependant absorption of photons and polarized photoluminescence, amongst many others. Due to differences in quantum mechanical parameters of electron and phonon transport (notably, mean free path), it has been theoretically shown that nanowires of certain alloys can be made to have good electronic conduction with decreased thermal conduction, showing good potential for high performance thermoelectric materials.

A number of advanced nano-lithographic techniques notably electron or focused ion beam patterning/writing, X-ray or extreme UV photolithography can be used usually in combination with vapor-phase depositions to obtain nanowire patterns. Typically such nanowires are aligned along the substrates and such techniques are compatible with the planar geometries of contemporary microelectronic devices. These lithography based techniques are usually referred to as ‘top-down’ approach in nanofabrication (excluding direct writing by focused ion beam). In another approach called ‘bottom-up’ involves crystallization of atoms/molecules in a controlled manner (usually diffusion controlled) to obtain size and shape selective fabrication of nanomaterials. In the presence of certain metallic catalysts, vapors of many semiconductor materials crystallize normal to a substrate resulting in vertical, oriented, nanowire-arrays. Several optoelectronic as well as piezoelectric applications have been demonstrated by vertically aligned nanowire arrays of semiconductors that were fabricated by this technique. The commercial potential for these processes are constrained by the

* A special allotrope of carbon known as carbon nanotubes is an important type of 1D nanomaterial that has not been included in this work since they are fundamentally different from traditional materials in terms of growth mechanism and crystalline microstructure.
need for specialized and expensive substrate for proper oriented growth of the nanowires, and also the complexities and cost of such energy intensive systems and processes.

An alternative route for 1D nanomaterials synthesis is by solution chemistry, wherein the bottom up approach is achieved by controlled diffusion of ions/atoms (monomers)* in solution to obtain controlled crystallization.16,52 The advantages of chemical synthesis is the possibility for control of material composition (as alloys and/or heterostructures),46,53 fine control of size and shape,49,54 and most importantly high yield of nanomaterials at relatively lower cost and complexity of processes.10 Several chemical reactions are now known to produce nano-wires mostly for metallic and semiconducting materials, some of which is described in the next section.

1.5.1 Solution chemistry routes for 1D nanomaterials

A straightforward method to control the diffusion of precursors to obtain an anisotropic crystal growth is by physical constraint within a solid template. In such a case, crystallization is forced along nano-scale channels that have been previously fabricated within a solid material.55 This technique works for vapor-phase56 or crystallization from solution,57 in fact even molten materials can be frozen into the shape that is complementary to the nano-channel.58 This technique has been used in combination with electrochemical deposition to obtain several materials including metals, semi-metallic alloys59 as well as semiconductors.60 The main disadvantages of this technique includes, poor quality of the obtained crystals (usually polycrystalline),49 need and complexities of fabricating the template, and commonly encountered need for removing the template after the synthesis of 1D nanomaterial of interest.

Crystal habits of certain materials leads to formation of highly anisotropic crystal structures even in the absence of hard templates. A popular method to fabricate nanowires of noble metals, involves chemical reduction of metal salts with a weak reducing agent, in the presence of amphiphillic surfactant molecules. This technique was referred to earlier as soft-template approach,49 and it was thought that the surfactant molecules self assembled in the form of anisotropic micelles within which the reduction reaction of metallic salts took place. Recent studies have shown that differing crystal habits due to specific types of twinning along the fcc [111] planes, leads to various anisotropic morphologies, including nanowires.61 Such ’template-free’ synthesis of 1D nanomaterials usually

---

* In later sections they will be referred to as ‘monomers’, representing each unit that will eventually take up a lattice position in the crystal usually after undergoing a chemical reaction in the vicinity of the lattice.
involves utilizing specific crystal habits to ensure anisotropic crystal growth. This work deals with aqueous synthesis of ZnO nanowire arrays on a substrate and thermal decomposition of organic precursors in non-polar solvents to obtain colloidal quasi-1D nanotetrapods of CdTe. Although the exact chemical pathways are different for these syntheses, both techniques utilize the anisotropic crystal habits of hexagonal crystals.

Synthesis of ZnO nanowire-arrays
Several II-VI semiconductors (notably ME; M=Cd, Zn and E=S, Se, Te) are known to be stable with hexagonal crystal structures. These semiconductors are partially polar and in the hexagonal structure (wurtzite), the [001] planes terminate with either cations or anions. Thus the cation terminated ends have a partial positive charge and the anion terminated ends have a partial negative charge, which leads to a high surface energy for the polar plane. Non-polar planes along the side faces are more stable, thus in a thermodynamically stable growth process for hexagonal crystals, large facets are usually the non-polar planes causing an inherently anisotropic growth habit for such crystals. This effect is prominent in ZnO where the hexagonal crystal structure is most common. Utilizing such crystal habit, Vayssieres et al., first reported an aqueous chemical bath process for growth of vertically aligned ZnO nanowire-arrays (NWA) on a substrate. As this process is non-epitaxial, such NWAs can be grown on a wide variety of substrates. This process involves growth of ZnO rods on various substrates from an ‘equimolar’ aqueous solution of zinc nitrate and hexamethylenetetramine (HMT) as precursors at temperatures ranging from 55 – 95 °C.

Lowering the thermodynamic barrier by providing nucleation sites by fixing pre-synthesized ZnO nanoparticles on the substrate (seeding), improves the aspect ratio (ratio of length to width) of the obtained rods, and according to some studies, results in better uniformity. Nucleation sites can be introduced by depositing a layer of ZnO particles by sputtering, or spin coating a layer of colloidal ZnO nanoparticles obtained by chemical route. Alternatively, annealing a layer of zinc foil, or drop-casted ethanol solution of zinc acetate results in a dense layer of ZnO and is known to act as a substrate for growth of ZnO nanowires.

The commonly used precursors for the hydrothermal growth process are zinc nitrate (source of Zn ions) and HMT. HMT is a highly water soluble, non-ionic tertiary amine derivative. Variation of the experimental conditions, such as temperature and the concentration of precursors, allows certain degree of control on the growth rate and the morphology of the obtained nanowires. It was suggested
that the main role of hexamine in the growth of ZnO nanostructures in the hydrothermal process is by slowly increasing pH of the chemical bath through decomposition into ammonia.68

In this work, we have studied the role of hexamine during the nanowire growth in a chemical bath. We have also studied the effect of reactant concentrations and the temperature of the chemical bath on the morphology of the grown nanowires. We describe a phenomenological explanation of the epitaxial growth of ZnO nanowires in the chemical bath.

Since the growth of nano-rods or wires occur epitaxially from the seeds, a pre-decided pattern of nanowires on the substrate can be achieved by patterning the deposition of the ZnO seeds, similar to reports of patterned growth of ZnO rods through the vapor phase route.69 However, unlike the vapor phase route, the seeded hydrothermal growth can be achieved on a wide variety of substrates and at much lower temperatures. In this work we have fabricated highly flexible nanofibrous mat of poly-L-lactide (PLLA) by electrospinning as a substrate, followed by growth of radially oriented nanowires (RON) of ZnO by chemical bath deposition. Such hierarchical nanostructured material retains the flexibility and high surface area of the polymeric nanofibrous mat and has the additional functionality of ZnO nanowires.

**Colloidal CdTe nanotetrapods by thermal decomposition of organic precursors**

Synthesis of colloidal II–VI semiconductor quantum dots (QDs) by solution chemistry are of significant current interest in materials science, owing to their size and morphology-dependent optical,70,71,72 optoelectronic,73,74,75 and photovoltaic properties,76,77 combined with ease of synthesis and processing. As a result, fabrication of simple morphologies such as spheres and rods has been well established over the last decade.9,45,54,78

Thermal decomposition of organic precursors for synthesis of colloidal nanocrystals mainly CdE and ZnE (E=S,Se,Te) composition was pioneered by the Bawendi group.70 Briefly, it involves a rapid injection of cold trioctylphosphine (TOP) solution containing the metal and chalcogenide precursors into hot (>250 °C) trioctylphosphine oxide (TOPO) solvent.70 A rapid nucleation of the CdE nanocrystals is followed by slower growth at a lower temperature. Relatively uniform nanocrystals could be produced by this separation of the nucleation and growth stages in the hot-injection process. In this process, size as well as shape control is primarily achieved by variations in the reaction conditions such as growth time, temperature and monomer concentrations, although choice of precursor complexes are also known to affect the morphology of the obtained nanocrystals. Presently
the most common choice of metal precursor is a salt of the metal with fatty acids or alkylphosphonic acids.54,79

Synthesis of colloidal semiconductor nanocrystals with higher complexity, particularly nanotetrapods (NTP),* has attracted recent attention because of their potential in optoelectronic applications.80 Their unique 3D symmetry allows the possibility of novel alignment of these nanostructures that is difficult to achieve with nanospheres and nanorods.81 There are several reports in the literature describing the syntheses of structures in the past five years, for several II–VI semiconductor compositions, such as ZnO,82,83 CdS,84,85,86 CdTe,78,87,88 and CdSe.89,90,91 In most of the reports, the origin of the tetrapodal morphology is ascribed to the polytypism of such semiconductors, exhibiting both cubic (zinc blende) and hexagonal (wurtzite) crystal structures. The cubic (111) face and the hexagonal (001) face terminates with either only anions or cations, and allows for hexagonal arms to grow epitaxially on the four [111] planes of the cubic core.78,87,92,93 An alternative explanation for the formation of CdTe NTPs is described by Carbone et al.94 wherein a multiple twinned nucleus with hexagonal structure is shown to ‘grow’ into a tetrapodal morphology.

From the very first reports of CdTe NTPs, alkylphosphonic acid has been a common choice of ligand for Cd.87 Recently, Yu et al.93 and Nie et al.95 used fatty acids (oleic acid and myristic acid, respectively) as ligands to obtain CdTe nanocrystals with NTP morphologies. The reaction temperatures chosen in these reports were similar to what is commonly used for syntheses using alkylphosphonic acids as the ligand (typically >250 ºC). Compared to alkylphosphonic acids, fatty acids bind weakly to Cd, so we envisage a much lower temperature requirement for the synthesis of NTPs by choosing oleic acid as the ligand.

Here we describe the synthesis of CdTe tetrapods at significantly lower reaction temperatures, as low as 180 ºC, by using oleic acid as the ligand. We also show a novel formation mechanism for NTP morphologies that is unique to a low temperature synthesis. The lower synthesis temperature, as well as avoiding expensive alkylphosphonic acids, would make this synthetic technique attractive for commercial exploitation of colloidal CdTe NTPs as active materials in photoconductors and solar cells.

* In this work we describe tetrapodal structures in the context of 1D nanomaterials, owing to their geometry of isotropic attachment of four 1D nanocrystals.
1.6 Applications of 1D semiconductor nanomaterials

Considerable research has been devoted to the fabrication of one-dimensional (1D) nanostructures of various materials due to their unique optical and electronic properties.\(^4^9\) Here we will focus on applications arising from photon-electron interactions in 1D nanocrystals of ZnO and CdTe. The main differences between the two semiconductors are the energy of photons required to excite the electrons. Bulk CdTe has a band-gap corresponding to the near-infrared range of wavelengths.\(^8^8\) Thus it will absorb most of the available solar radiation, making them useful in photoelectric applications. Although ZnO is also extensively studied for photovoltaic applications, notably in dye-sensitized solar cells,\(^9^6\) the role of ZnO is usually limited to aiding the conduction of electrons and not photogeneration of carriers. This is mainly due to the high band-gap of ZnO that limits its interaction to photons with ultra-violet range of wavelengths.

ZnO being a wide band-gap material requires high energy photons (>3.1 eV) to excite the valence electrons, implying that the electron-hole pairs that are generated has similar high energies. This energy is found to be high enough to affect certain bonds in organic chemicals. This photochemical property of ZnO is receiving recent attention due to the severe ecological impact of various industrial and agricultural pollutants in water bodies.\(^9^7\) The use of metal oxides as photocatalysts for such applications is attractive mainly due to the relatively simple photo-decomposition process and their capacity to convert a large number of organic pollutant molecules into less harmful compounds.\(^9^8\).

Although TiO\(_2\) (mostly anatase phase) has been extensively studied as effective photocatalyst, recently ZnO has been shown to be more effective than TiO\(_2\).\(^9^9\),\(^1^0^0\),\(^1^0^1\) The ZnO-mediated photocatalysis process under UV and visible light irradiation has been successfully used to decompose organic dye molecules (as a model organic contaminant) for the past few years.\(^1^0^2\),\(^1^0^3\) It is fairly well established that the electron-hole pairs generated in the metal oxide, as a result of photo-excitation, interacts with the solvent to produce chemically reactive free radicals (usually the holes generate OH\(^-\))\(^1^0^4\), which attacks specific bonds of the organic molecule leading to its decomposition.\(^9^8\) Additives like H\(_2\)O\(_2\) and S\(_2\)O\(_8\)^{2-} is known to enhance the photodecomposition of organic molecules by metal oxides.\(^9^8\)

Most of the studies on the use of ZnO nanostructures for photocatalytic decomposition of organic molecules involve colloidal nanoparticles. Commercially available TiO\(_2\) (Degussa P25), a widely studied material in the field of photocatalytic reactions, is also in powder form and is used for photocatalytic decomposition by dispersion in water along with the organic contaminant.\(^1^0^5\) Although
colloidal suspension of nanoparticles has a high surface area, resulting in efficient decomposition of the organic molecule, there is a need for the removal of the metal oxide nanoparticles from the ‘slurry’, which is time consuming and is usually accomplished by centrifugation.98 The need for such expensive additional processing step for removal of the active material from the slurry can be avoided by using the powder as nanoparticulate film on a substrate,106 or arrays of nanowires (NWA) grown on a substrate.107 For a given area of the substrate, oriented NWA have a higher surface area than a nanoparticulate film.

The freedom in choice of substrate for growing ZnO NWAs by chemical bath deposition was demonstrated recently by Baruah et al.108 by using commercially available non-woven polyethylene microfibers as a substrate material. Another approach to maximize the total surface area of interaction between the photo-active ZnO with the organic molecules was shown by Liu et al.109 wherein nanofibrous mat of ZnO was synthesized by electrospinning polymeric blend containing zinc acetate and cellulose acetate, followed by calcination at high temperatures. These ZnO mat structures have shown to outperform nanoparticulate ZnO in photocatalytic decomposition of organic dye molecules, and this is attributed to the porous nature of the nanofibers. In a similar report, Wang et al.110 described the fabrication of TiO$_2$ nanofibers by electrospinning and subsequent calcination of an organometallic Ti-precursor followed by growing of ZnO of various morphologies using chemical bath deposition. In both these studies, electrospinning of organometallic precursors and subsequent calcination was used to obtain fibrous metal oxide nanostructures with a high surface area. The final product is a ceramic material which is not flexible. Photocatalytic decomposition of organic molecules is known to occur at the surface of the metal oxide,97 however increasing the interactive surface area by fabricating ZnO NWA over a very large area, using brittle or rigid substrates, would make the whole material unwieldy and difficult to immerse into the reservoir of ‘contaminated’ water.

In order to overcome these problems, we report the fabrication of highly flexible nanofibrous mat of poly-L-lactide (PLLA) by electrospinning as a substrate, followed by growth of radially oriented nanowires of ZnO on these nanofibers by chemical bath deposition. Such hierarchical nanostructured material retains the flexibility and high surface area of the polymeric nanofibrous mat and has the additional photochemical functionality of ZnO nanowires. As a direct result of the high flexibility of this hierarchical nanostructure, we devised a simple set up for rapid photocatalytic decomposition of organic contaminants in water in a ‘continuous flow’ mode. Our material can be easily scaled up and
the whole photocatalytic water treatment set up can easily be adapted either as a point-of-use system or centralized large-scale water purification system.

The relatively low energy level of the photo-generated electron hole pairs of CdTe limits its applicability in photochemistry. Nevertheless they have high mobility\textsuperscript{111} and can interact with a wide range of photon energies, suggesting potential in photoelectric and photovoltaic applications.\textsuperscript{88} Theoretical studies have shown the suitability of CdTe nanotetrapods as circuit elements.\textsuperscript{112} Thus CdTe nanocrystals, especially CdTe NTPs, show good potential as photovoltaic materials. There are several reports in the literature describing the photoconductivity of an ensemble of CdTe nanocrystals either as drop-casted films\textsuperscript{113,114} or embedded within conducting polymers, between transparent electrodes.\textsuperscript{115} A more direct evaluation of the optoelectronic properties of this promising nanomaterial is difficult due to its extremely small size. There are a few reports describing the measurement of electrical and mechanical properties of individual CdTe tetrapods and nanorods,\textsuperscript{116,117,118} although Trudeau et al.\textsuperscript{117} also noticed alloying of the electrode metal (Pd) into the CdTe nanocrystal during the deposition causing artefacts in the measurements. However, there is no direct data available in the literature on the optoelectronic properties of individual NTPs. Such evaluations can enhance the understanding of the underlying physics and also help in designing better photoconductor or photovoltaic systems that consists of an ensemble of such nanocrystals. We also report here probably the first artefact-free direct evaluation of photoconductivity of CdTe nanotetrapods by employing gold electrodes with a gap of 30 nm that was fabricated in-house.

In this thesis, we have studied the solution chemistry based synthesis of ZnO nanowires and CdTe nanotetrapods. For both the syntheses, we have developed a novel formation mechanism that describes the anisotropic growth of the nanomaterial. In order to enhance the applicability of ZnO nanowires in photocatalytic water treatment, we have developed a novel hierarchical nanomaterial consisting of polymer nanofibers that was used as a flexible and high surface area substrate for the growth of radially oriented ZnO nanowires, and employed it in a ‘continuous flow’ photocatalytic water-treatment system. We also describe a low temperature synthesis of CdTe nanotetrapods and performed one of the first ‘artefact-free’ measurements of its photoconduction employing nano-gap gold electrodes.
2. Experimental

2.1 Materials and Synthesis

2.1.1 Aligned nanowire arrays of ZnO

Vertically aligned nanowire array (NWA) of ZnO was prepared by a two step process consisting of deposition of a uniform and dense layer of ZnO on the desired substrate to act as seeds, followed by subsequent immersion of the substrate into a chemical bath for the growth of NWA of ZnO.

**Deposition of seed layer:** Two different techniques were used for the deposition of seed layer, depending on the temperature sensitivity of the substrate; (i) for Si or glass substrate, 5 mM ethanol solution of zinc acetate (Aldrich 98%) was prepared and drop-casted on a clean Si Wafer and heated to 300 °C on a hot plate; (ii) For poly-L-lactide nanofibrous substrates, suspension of homogenous ZnO nanoparticles was prepared based on a method described by Bahnemann *et al.* In brief, it involved preparation of a 1 mM zinc acetate [Zn(CH$_3$COO)$_2$, Aldrich, 99% purity] solution in 80 mL of 2-propanol [(CH$_3$)$_2$CHOH, Aldrich, 99.5% purity] under vigorous stirring at ~50 °C, followed by dilution to a total volume of 920 mL and cooling in an ice bath. To this solution, an 80 mL aliquot of 20 mM sodium hydroxide [NaOH, Merck, 99% purity] solution in 2-propanol was added under continuous stirring and the mixture was immersed in a pre-heated water bath at 50 °C for 2 h. The transparent colloidal solution was stored at room temperature and is stable for months, under ambient conditions.

**Growth of ZnO NWA:** The coated substrate was placed in an oven at 95 °C for 12 h (or vacuum dried at 60 °C for the same duration for polymeric substrates), for proper fixation. The substrate was then placed in chemical bath containing equimolar solution, with concentrations depending the experiment (20 mM, 1 mM, or 0.5 mM zinc nitrate hexahydrate [Zn(NO$_3$)$_2$·6H$_2$O, Aldrich, 99% purity] and hexamine [C$_6$H$_{12}$N$_4$, Sigma, 99% purity]. The growth process was carried out in at various temperatures (60 – 95 °C) for up to 24 h. The growth temperature, time were systematically varied.

**Preparation of nanofibrous poly-L-lactide substrates:** Poly-L-lactide (Aldrich, Mw = 100000) nanofibers were fabricated by electrospinning technique. The polymer was dissolved in chloroform (7 wt %) and stirred for 2 h. Then it was loaded into a syringe with a stainless steel needle (0.8 mm in diameter) and the needle was connected to the anode of voltage supply (Brandenburg). A collector covered with aluminum foil was connected to the cathode of voltage supply. A voltage of 10 kV was applied between the needle and the collector. The syringe containing the polymer solution was
attached to a syringe pump (Cole-Parmer) in a horizontal mount. The distance from the tip of the needle to the collector is 10 cm and the flow rate is 1 mL/h. The nanofibers were obtained in the form of a non-woven mat with dimensions following that of the aluminum foil cathode (typically 10 × 10 cm).

**Synthesis of PLLA-ZnO hierarchical nanostructure:** The PLLA nanofibers were immersed for 30 minutes into a colloidal ZnO suspension that was prepared based on a method described by Bahnemann *et al.* and then allowed to dry. This ‘seeded’ nanofibers was immersed into a mixed aqueous solution of 20 mM each of Zn(NO₃)₂ and hexamine and heated to 75 °C for 6 hours. The hierarchical nanostructure consisting of PLLA nanofibers with radially aligned nanowires (RON) of ZnO was washed with de-ionized water and then dried in a vacuum oven for 1 hour.

### 2.1.2 Colloidal CdTe nanotetrapods

Colloidal CdTe nanotetrapods were fabricated by a hot-injection process that is based on hot injection process for quantum dots, developed by Bawendi and co-workers.70

**Stock solutions for injections:** 0.642 g CdO powder (99.9% Fluka) was added to 13 mL of 1-octadecene (ODE; 90% Aldrich) and 7 mL of oleic acid (90% Aldrich), in a three-necked flask and heated at 160 °C with nitrogen flow for 1 h, to obtain cadmium oleate (Cd-oleate). After cooling down to room temperature the solution was stored in a nitrogen environment. 0.638 g Te powder (100 mesh 99.8% Aldrich) was added to 8.5 mL of trioctylphosphine (TOP; 90% Aldrich) and 11.5 mL of ODE and heated at 200 °C with nitrogen flow for 1 h, to obtain trioctylphosphine telluride (TOP-Te). After cooling down to room temperature the solution was stored in a nitrogen environment. Both stock solutions can be stored for about two weeks, and the container has to be periodically purged with N₂.

**Synthesis of CdTe nanotetrapods:** In a typical synthesis, 4 mL of ODE was added to a three-necked flask with a magnetic stirrer bar and heated to 180 °C with nitrogen flow. At this temperature, a mixture of 0.4 mL each of Cd-oleate and TOP-Te solutions was quickly injected into the hot solvent. The reaction vessel was immediately taken out of the heating mantle and allowed to cool to room temperature (~10 min). CdTe NTPs were precipitated from the reaction mixture by adding 40 mL of ethanol and collected as sediment after centrifugation. The sediment was re-dispersed in hexane for preparation of transmission electron microscopy (TEM) samples and for ultraviolet–visible (UV–Vis) spectroscopy. Variations from the typical synthesis include different injection temperatures, and cooling sequences.
Synthesis of CdSe nanotetrapods: 4 mL of ODE was added to a three-necked flask with a magnetic stirrer bar and heated to 180 °C with nitrogen flow. At this temperature, a mixture of 1.2 mL of Cd-oleate solution and 0.4 mL of trioctylphosphine selenide (TOP-Se) was quickly injected into the hot solvent ([Cd]:[Se] = 3:1). The reaction was maintained at this temperature for 5 min and then taken out of the heating mantle and allowed to cool to room temperature (~10 min). CdSe nanocrystals were precipitated from the reaction mixture by adding 40 mL of ethanol and collected as sediment after centrifugation. The sediment was redispersed in hexane for preparation of TEM samples.

2.2 Methods of Characterization

2.2.1 Characterization

Transmission electron microscopy: TEM samples were prepared by drop-casting a dilute suspension of the nanomaterials onto a carbon-coated copper grid and dried in ambient conditions. Typically the dispersion medium was hexane for colloidal NTPs and ethanol for ZnO samples. TEM analysis was done with a JEOL FEG-JEM-2100F operated at 200 kV.

Scanning electron microscopy: SEM imaging was done without any post-fabrication treatment in cases samples that were grown on Si wafer. For the case of ZnO NWAs grown on glass substrate, to minimize the effect of charging from insulators under the electron beam, the samples were coated with a thin layer of gold by sputtering. The imaging was done using LEO 1550, and Zeiss FEGSEM Ultra 55.

X-ray diffraction: Vertical ZnO NWAs on Si and glass substrates were analyzed with Siemens D5000 X-ray diffractogram (using Cu-kα line) for studying the crystalline microstructure of the ZnO.

Fourier transform infrared spectroscopy: FTIR spectroscopy was performed using a Perkin Elmer Spectrum-One, in the attenuated total reflectance (ATR) mode, by placing a drop of the sample on the crystal window. The consumption of hexamine was monitored by collecting samples for FTIR spectroscopy from a 0.1 M solution of zinc nitrate and hexamine that was placed in an oven at 60 °C for upto five hours.

UV-Vis spectroscopy: All the spectroscopy analysis was done using Cary 100 Bio UV–Vis spectrometer (dual beam) with a pair of quartz cuvettes as ‘sample’ and ‘reference’. The reference cuvette contained the solvent(s) only and sample contained the analyte in addition to the same solvent(s).
For studying the reaction kinetics, the consumption of TOP-Te (one of the precursors) was followed by spectroscopic methods. Rapid quenching of the reaction (within 2–10 s) was done by quickly injecting a large volume of ODE. To the rapidly quenched reaction mixture, 3 mL of hexane and 20 mL of ethanol was sequentially added and then centrifuged at 10 000 rpm to sediment the nanocrystals. The supernatant was collected and added to a quartz cuvette and its UV-Vis absorption spectrum was recorded. The absorption at 300 nm was noted and compared with a calibration curve prepared beforehand with known concentrations of TOP-Te.

2.2.2 Continuous flow photocatalytic treatment of aqueous organic molecules
The PLLA-ZnO hierarchical nanostructured material so prepared was inserted into a glass tube. This column was connected to a 50 mL glass bottle (reservoir) and a quartz flow cell, via a peristaltic pump. The flow cell was inserted into a UV-Vis spectrophotometer (Cary 100 Bio), to monitor the changes in absorption spectra in real time. The solution was pumped at a flow rate of 5 mL/minute. Typically, 20 mL water solution of the organic compound (5 ppm) was added to the ‘reservoir’ and allowed to run through the PLLA-ZnO hierarchical nanostructure for 30 minutes before illumination with a 100 W mercury vapor lamp.

2.2.3 Continuous flow treatment of water contaminated with Escherichia coli
A suspension of E. coli was added into a diluted nutrient broth solution and 20 mL of this was placed in the reservoir used for photocatalysis, as described above. The solution in the reservoir was flowed through the photocatalytic column for 90 minutes and every 30 minutes, a 1 mL sample was withdrawn from the reservoir, and centrifuged at 2000 rpm. The sediment from the centrifugation was collected and spread on a nutrient agar plate and incubated overnight at 37 °C. The approximate number of viable bacteria was determined by counting the individual colonies visible on the corresponding agar plate after overnight incubation.

2.2.4 Nanogap electrodes
The nanoelectrodes that were used for the photoconductivity measurements were fabricated as described in the literature. In brief, a pattern of 2 μm × 200 nm was made on a Si wafer with a thermally grown 1 μm thick SiO₂ layer by electron beam lithography (EBL) using an FEI XL30 ESEM. After developing the EBL pattern, resistive evaporation was used to deposit a 5–10 nm layer of chromium as an adhesion layer followed by an 80–120 nm layer of gold. Photolithography was then used to pattern 100 μm × 100 μm × 300 nm gold contact pads at the two ends of the line. A gap of 25–
30 nm was cut in the EBL line with a focused ion beam (FIB) using Ga⁺ ions in a FEI Strata 235 dual-beam FIB at an acceleration voltage of 30 kV. Electrical resistance across the fabricated nanogap electrodes was typically 1000–1500 TΩ. Electrical characterization was carried out in ambient conditions with Agilent B1500A semiconductor parameter analyzer probe station. The probe station was fixed on a solid table for the mechanic stability of system and placed inside a custom-made thick aluminium box to shield the measurements from external electrical noise and light sources.

2.2.5 Trapping of CdTe nanotetrapods between the nanogap electrodes

The nanogap electrodes were placed in a probe station and 6 μL of diluted colloidal suspension of CdTe NTPs in octane was dropped onto the gap in the electrodes. An alternating voltage of 2.2 V_{RMS} at a frequency of 1 MHz was applied across the nanogap for 60 s and the dielectrophoretic force due to presence of the non-uniform electrical field drew the nanocrystals towards the area of greatest electric field strength. A series resistance of 10 MΩ was used to limit the current flowing through the circuit. After trapping, the liquid drop was evaporated from the substrate using nitrogen flow and the electrodes were rinsed with de-ionized water.
3. Results and discussions

3.1 Aligned ZnO NWAs

3.1.1 Structural characterization

In general, the most commonly observed morphology of ZnO is needle-like or rod-like structures attributed to the inherent anisotropy of the hexagonal lattice with an axial c/a ratio of 1.602. Theoretical calculations predict that the surface energies of the non-polar surfaces of ZnO are small, while the cleavage energy of the polar surface is predicted to be two times larger than the non-polar surfaces. During a hydrothermal growth in the presence of ZnO seeds, the highest growth rate is along <002> direction. This form would minimize the total surface energy since the total surface area of the [002] facets would be limited to the tips and hence very low. Nevertheless, it is reported that upon prolonging the growth period, the nanowires grow laterally reducing the overall aspect ratio. In order to achieve a desired aspect ratio, the composition of the chemical bath in which the growth takes place, and also the quality of the seed layer becomes important.

SEM analysis of a Si wafer on which the seed layer was deposited, showed a dense layer of fairly uniform nanoparticles of 10–15 nm Figure 4a. X-ray diffraction (XRD) analysis of the colloidal particles, after repeatedly dropping aliquots of the colloidal solution on a (111) Si wafer and drying, shows fairly equal dominance of [100], [002], [101], and [102] crystallographic planes, as shown in Figure 4b. Due to the fine size of the nanoparticles, the XRD pattern had a very low signal to noise.
ratio, which is common for nanosized particles. These particles were found to consist of 2–3 crystallites agglomerated, of average size of ~5.4 nm determined from [100] peak employing the Debye-Scherrer formula. Figure 4c shows high resolution TEM (HRTEM) analysis of a part of the seed layer that was scraped from the surface of the wafer. We can clearly see that average crystallite size obtained from XRD analysis was overestimated, probably due to high noise in the diffractogram.

It is reported that a high density of nanowire growth is important to obtain aligned and oriented growth. We tested this by using a diluted suspension of colloidal ZnO nanoparticles for preparing the seed layer on a Si substrate. In another substrate we prepared ZnO seeds by drop casting an ethanol solution of zinc acetate followed by annealing at 300 °C, which results in a dense layer of ZnO. From Figure 5a we can see that using a dense seed layer results in high density of nanowire growth, leading to highly oriented NWAs compared to more or less random growth of ZnO nanowires in the case of substrate with well dispersed seeds (Figure 5b).

Due to the highly aligned orientation of the ZnO NWA, the XRD diffraction pattern obtained from the substrate shown in Figure 5a showed a dominance of [002] planes as shown in Figure 6a. The XRD pattern matched with hexagonal ZnO crystal

Figure 5. Effect of seed layer density, where (a) high density of seeds leads to growth aligned nanowires, compared to (b) disperse seeds leading to randomly oriented nanowires.

Figure 6. Crystalline nanowires of wurtzite ZnO shown by (a) XRD (matching with JCPDS Card: 36-1451), and corroborated with (b) TEM and (c) HRTEM analysis.
structure (JCPDS Card: 36-1451). HRTEM images taken from a single nanowire corroborates the XRD analysis regarding the crystalline nature of the nanowires in the array (Figure 6c).

Figure 7a shows the X-ray diffractogram from the ZnO nanoparticle coated substrate placed in the growth solution of an equimolar solution of 1mM hexamine and zinc nitrate, for 0, 1, 3, and 5 h of growth at 95 °C. The anisotropic growth is evident from the steady rise of the diffraction peak from [002] planes of hexagonal crystal while the diffraction peaks from other crystallographic planes remain unchanged during the one hour to five hour growth period. In a recent report it was suggested that the role of hexamine in the chemical bath is primarily to provide \( \text{OH}^- \) ions while undergoing slow thermal decomposition into formaldehyde and ammonia.  

FTIR spectra collected in the ATR mode of a mixture of 0.1 M hexamine and zinc nitrate (the concentration was intentionally kept higher than typical concentrations of the reactants used for the nanowire growth reported here, to circumvent the problem with sensitivity of the ATR measurements) at 65 °C for different periods of time were compared (Figure 7b). The spectra were recorded using the attenuated total reflectance (ATR) mode, since the solvent was water. A peak due to the stretching vibrations of C–N bonds in tertiary amines of hexamine at ~1012 cm\(^{-1}\) was observed in the vibrational spectra. No noticeable degradation of this tertiary amine could be observed even upon heating the mixture for up to 5 h under conditions similar to that of the chemical bath. We have observed anisotropic growth of ZnO nanowires within 5 h, (X-Ray diffractogram of Figure 7a). Under slow thermal decomposition of hexamine into formaldehyde and ammonia, the vibrations of C–N bond in the infra-red spectra was
expected to reduce over time upon continued heating. The FTIR spectra of the mixture heated for 1 h, was almost identical to the spectra recorded after heating for 5 h indicating no changes in the tertiary amine structure (Figure. 7b).

Extending the growth period to 24 h at 95 °C typically yielded uniform nanowires of ~30 nm diameter with lengths well exceeding 5 μm, leading to an aspect ratio of over 150 (Figure. 8a). No significant lateral growth could be observed even after extended periods of growth, though there was evidence of a few nanowires fusing into larger structures, along the non-polar facets. Similar observation of side planes of two or more nanowires fusing to form a single structure with a lower aspect ratio have been reported by others upon prolonging the hydrothermal growth period.65 Figure 8b shows several nanowires bundled together, which might be the initial stages of the formation of lower aspect ratio micro-rods.

In a phenomenological perspective, ZnO crystal exhibits partial polar characteristics, and in a typical hexagonal structure the (001) plane is the basal polar plane. One end of the basal polar plane terminates with partially positive Zn lattice points and the other end terminates in partially negative oxygen lattice points.62 It is believed that, in the chemical bath, hexamine being a non-polar chelating agent would preferentially attach to the non-polar facets of the nano-wires, thereby exposing only the (002) plane for epitaxial growth. Thus a preferential growth along the <002> direction is made possible.

There is a recent report on a reversible reduction of the aspect ratio of ZnO nanorods by introducing acidic anions in the growth medium to cap the polar plane,64,122 wherein citrate anions probably cap the (001) which terminates with charged Zn$^{δ+}$. This shows the dependence of the morphology of the ZnO nanowires on the ionic content of the chemical bath, a clear demonstration of the versatility of the hydrothermal growth process, which can be studied further for controlled nanowire growths.
3.1.2 Hierarchical nanostructures

Subsequently, we employed flexible nanofibrous mat of poly-L-lactide (PLLA) was obtained by electrospinning, as a substrate for deposition of radially oriented nanowires (RON) of ZnO. The dimension of the PLLA nanofibrous mat typically follows the dimension of the cathode plate, and in this work our cathode plate had a dimension of 10 cm × 10 cm. In the obtained nanofibrous mat, the individual fibers are randomly oriented and from SEM images we estimated the average diameter of the PLLA fibers to be ~200 nm (Figure 9a).

Since the polymeric nanofibers cannot be heated above 90 °C we provided the initial nucleation sites for the growth of ZnO nanowires by depositing pre-synthesized colloidal ZnO nanoparticles. The subsequent growth of the RON of ZnO was performed under the same conditions as in the case of Si wafer substrate, and the typical growth time was limited to ~6 hours. SEM analysis of the nanofibers after ZnO deposition showed a hierarchical 3D nanostructure consisting of polymeric nanofibers which were densely covered by radially oriented ZnO nanowires (Figure 9b). A schematic representation of the hierarchical 3D nanostructure is shown in Figure 9b (Inset). As expected, the morphology of the ZnO nanorods was similar to those obtained directly on the Si wafer.

The high specific surface area of polymeric nanofibers obtained by electrospinning is fairly well documented. From BET measurement, we found that a typical nanofibrous mat had a total...
surface area equivalent to square Si/glass substrate with 75 cm side length. Since BET measurement is optimized for powder samples, and attaining similar compaction with a polymeric nanofibrous mat is difficult, our BET measurement has underestimated the true surface area. Our PLLA-ZnO hierarchical nanostructure was found to retain the high flexibility of the original PLLA nanofibrous mat, and it was possible to insert it into a glass tube (diameter ~1 cm) to form an ‘active-filter’. **Figure 10** shows a photograph of the final material as prepared (Inset) and after insertion into the glass tube showing the flexibility and compactness of this polymer fiber-ZnO hierarchical nanostructured material. The significance of the improved flexibility is explained in the next section where we utilize this hierarchical nanostructure for photocatalytic applications.

### 3.1.3 Photocatalytic Effects

Using the hierarchical nanostructure we then used a ‘continuous flow’ photocatalysis set up to evaluate the performance in water purification applications. An aqueous solution of organic compounds to be decomposed was passed through the glass tube containing the PLLA-ZnO nanofibers using a peristaltic pump. The glass tube was illuminated by a 100 W mercury vapor lamp (as UV light source) and the photocatalytic decomposition of the organic molecules was monitored by ultraviolet-visible (UV-Vis) spectroscopy (see Experimental Section). A schematic representation of the set up is shown in **Figure 11a**. For all the experiments, flow rate was maintained at 5 mL per minute, and the reservoir contained 20 mL of aqueous solution of organic molecules. We initially selected methylene blue as the organic molecule to be studied.

When we passed a solution of methylene blue (5 ppm) through the glass tube containing the polymer/ZnO nanostructure we obtained ~90% decomposition within 80 minutes (**Figure 11b**). In order to evaluate the stability of the NWA, we washed the hierarchical nanostructure by passing de-ionized water through the glass tube for 2 hours and then used a fresh solution of methylene blue and
performed the experiment again. We repeated this three times, and obtained almost identical
decomposition rates for the three cycles (Figure 11b). This indicates that the entire PLLA-ZnO
hierarchical nanostructure is structurally and chemically stable.

Two types of control experiments were studied, in the first; we passed the dye solution through the
glass tube which contained only PLLA nanofibers with no RON of ZnO. In this case we observed that
under illumination there was up to a maximum of 10% decomposition of methylene blue, which was
probably due to direct photo-bleaching under UV-illumination. In the second control experiment, we
passed dye solution through the glass tube containing the hierarchical polymer/ZnO
nanostructure but this time with the illumination turned off. The glass tube was placed within a box
to keep out ambient light. In this case we observed no decomposition at all for 80 minutes. These
control experiments clearly show that photocatalysis in the presence of ZnO
nanostructures is the main cause of decomposition of methylene blue in the solution. This method of
‘continuous flow’ photocatalytic decomposition of
organic compounds in water is simple and
effective as there is no need for separation of the
photo-chemically active material from the
reservoir, and the purified water can be collected
from the reservoir directly.

In a following study, we tested the
photocatalytic decomposition of two widely used
and extremely toxic organic compounds,
monocrotophos (MCP; organophosphate
insecticide) and diphenylamine (DPA; antioxidant for fruit storage). In one experiment, the reservoir
was filled with aqueous solution of MCP (5ppm) and passed through the glass tube containing the
hierarchical polymer/ZnO nanostructure under UV-illumination. The UV-absorption spectrum of the

![Figure 12. (a) UV absorption spectra of aqueous solution of MCP, taken every 5 minutes (for 125 minutes) during continuous flow photocatalytic decomposition. ▼ marks peak position that was monitored to follow the decomposition. *Inset* shows percent decomposition over time. (b) UV absorption spectra of a mixture of MCP and DPA taken every 5 minutes (for over 100 minutes) during photocatalytic decomposition. The symbols (▼ for MCP, ◆ for DPA) indicate the peak absorption for the corresponding molecules. *Inset* shows the percent decomposition, ○ for MCP and ◼ for DPA. The absorption data for MCP may have interference from the absorption of DPA.](image)
solution was recorded every 5 minutes and we observed a rapid decrease in the absorption peak at 215 nm, corresponding to the photocatalytic decomposition of MCP (Figure 12a). We also performed two control experiments (i) with no UV-illumination and (ii) with no RON of ZnO (data are not shown) and found negligible decrease in the absorption intensity at 215 nm in both the cases.

In another experiment, to simulate a realistic situation, aqueous solution of MCP and DPA (5 ppm each) was passed through the glass tube containing the hierarchical PLLA/ZnO nanostructure, under UV illumination and the UV absorption spectrum was recorded every 5 minutes (Figure 12b). In this case, we observed a rapid decrease in absorption peaks at ~200 nm and 232 nm (for DPA) and 215 nm (for MCP). This demonstrates that simultaneous photocatalytic decomposition of more than one organic contaminant is possible using the hierarchical PLLA/ZnO nanostructures.

In both the spectral series of Figure 6, although the spectral curve becomes almost flat at the end of the experiment, the decrease in absorption intensity was found to saturate at ~50% of its initial value. From reports in the literature describing use of TiO₂ nanoparticles for photocatalytic decomposition of MCP, we find that it is common to have saturation at ~50% decomposition in the absence of additives in the ‘slurry’.¹²⁵ We are currently investigating methods to improve the decomposition percentage by testing the effects of various additives into the reservoir to aid the photocatalytic decomposition.

Since UV-irradiation is a well known sterilization technique and furthermore ZnO in the presence of UV light is also known to have enhanced antibacterial effect,¹²⁶,¹²⁷ we tested the effectiveness of the water treatment system for microbial decontamination of water, by passing an aqueous suspension of *Escherichia coli* through the glass tube containing the hierarchical polymer/ZnO nanostructure under UV-illumination. We passed the ‘contaminated’ water through the glass tube for 90 minutes and collected 1 mL samples every 30 minutes (see Experimental Section). We found that at the start of the experiment, there were ~325 viable bacteria in the sample. Number of viable bacteria in the sample decreased to 1, 0 and 0 after 30, 60 and 90 minutes of treatment respectively (Figure 13). This

![Figure 13. Incubated culture media containing samples after various times of treatment, showing 325 viable bacteria in the original sample, which decreased to 1 and 0 after 30 and 60 minutes of treatment.](image)
clearly shows the multi-functionality of our water treatment system with PLLA/ZnO hierarchical nanostructure as the active material, allowing for rapid decontamination of toxic organic contaminants as well as bacteria from ‘contaminated’ water. 

Since the site of photocatalytic decomposition is physically separate from the reservoir containing contaminated/infected water, the need for removal of the photocatalytic material is avoided. Thus the photocatalytic water treatment system described here can be easily modified for point-of-use applications. We are currently investigating the efficiency of photocatalytic decomposition under solar irradiation, which will further enhance the applicability of the material and the system described here. Since the scale up of the fabrication of polymeric nanofibers, as well as the chemical bath deposition of ZnO nanorods is straightforward, larger scale water purification systems with this material is envisaged.

3.2 Colloidal nanotetrapods of CdTe

ZnO is almost exclusively exhibits hexagonal crystal structure. However, in case of all CdE (E=S, Se, Te) polytypism is common, wherein both cubic and hexagonal crystal phase is known to be stable. Unlike the case of crystal growth of ZnO, morphology of CdE nanocrystals also depends on the crystal phase of the seeds (or nuclei, in a ‘one-pot’ synthesis). Growth of seed crystals is inherently rod-shaped if the seeds have hexagonal crystal structure, and this is similar to the case of ZnO NWAs described in the previous section. However, if the initial nuclei (or seeds) have a cubic crystal structure and if the conditions for growth of seeds favor a hexagonal crystal structure, then the resultant nanocrystals have a novel tetrapodal morphology. The traditional explanation for the origin of tetrapodal morphology is that the four [111] faces (enclosing a tetrahedron) of the cubic crystal terminates with only cations or anions and have very similar lattice parameters, allowing for an epitaxial growth of four wurtzite crystals growing along the <002> directions.

There are a large number of reports describing isotropic core-shell nanocrystals, wherein irrespective of the crystal structure of the core (seeds) nanocrystal, the shell growth is isotropic resulting in a more-or less spherical final hetero-nanocrystal. Importantly, in all those reports the secondary growth of the shell is performed in a deliberately slow and controlled manner, either by slow addition of the precursors for shell growth (drop wise, over a few hours), or in discreet injections.

---

to allow for monolayer-by-monomer growth. If the same amounts of precursor complexes are added suddenly, the shell formation is invariably irregular, and quite often either rod-shaped or tetrapodal.

Another factor favoring anisotropic growth (rod-like or tetrapodal morphologies) in CdE nanocrystals is a fast release of metal and chalcogen monomers from their corresponding complexes during the growth stage of the nuclei,\textsuperscript{78,93} and this is important to maintain the growth of the nanocrystals in the diffusion-limited regime.\textsuperscript{54} It was also suggested in the early reports of synthesis of tetrapodal nanocrystals that alkylphosphonic acids play an additional role of selective capping of non-polar side plans of the hexagonal crystal.\textsuperscript{87} As a result of this, in the reports describing tetrapodal CdE nanocrystals, the most common ligands for the Cd-complex are alkylphosphonic acids, which are known to strongly bind to Cd. Therefore, probably to maintain a fast release (by thermal decomposition) of the monomers, almost all reports describing tetrapodal CdE nanocrystal involves temperatures in the range of 250 °C or higher.

### 3.2.1 Effect of temperature

Since it is known that oleic acid bonds weakly to Cd,\textsuperscript{93} when compared to alkylphosphonic acids (a commonly chosen complexing agent for Cd for synthesis of NTPs), we expected a lower reaction temperature would be sufficient to release Cd monomers from the Cd-oleate complex to form anisotropic CdTe nanocrystals. To confirm this, we carried out two syntheses at reaction temperatures of 180 °C and 250 °C. A typical synthesis involved heating 4 mL of 1-octadecene (ODE), which is a non-coordinating solvent, to the desired temperature followed by rapid injection of a mixture of pre-synthesized Cd-oleate and trioctylphosphine telluride (TOP-Te) in 1:1 ratio. In both cases we observed a rapid color change of the reaction medium from pale yellow (of TOP-Te) to red and finally dark brown within seconds. In the case of 180 °C, we noted that the color change was perceptibly slower. To compare the kinetics of reactions performed at 180 °C and 250 °C, we evaluated the temporal decrease in TOP-Te concentration within the first 10 s by UV–Vis spectroscopy. We found that TOP-Te decomposed much faster at 250 °C and its concentration decreases by ~60% within 10 s, compared to 30% decomposition at 180 °C for the same time (Figure. 14a). The most rapid drop in the molar concentration of TOP-Te, [TOPTe], is recorded within the first two seconds, indicating rapid nucleation. For reactions at both 180 °C and 250 °C, a much slower subsequent drop in [TOP-Te] is recorded indicating growth of the nanocrystals. It is reported for a similar reaction that Cd-oleate and TOP-Se reacts with each other forming CdSe,\textsuperscript{79} implying that the kinetics of nucleation (precipitation of thus formed CdSe) is different from the diffusion-limited growth involving approach of monomers
(after decomposition of their complexes) to the vicinity of a nucleus. We found that \( \ln[\text{TOPTe}] \) decreased linearly with reaction time from 2 to 10 s (Figure 14b) confirming that the decomposition of TOP-Te during the growth stage of the nanocrystals for both reaction temperatures is a first order reaction.

By fitting the data points in Figure 14b to the rate equation \( \ln[\text{TOP-Te}] = kt + \ln[\text{TOP-Te}]_0 \), we obtained the decomposition rate constant \( k \) during the growth stage of the nanocrystals for both the temperatures. It is notable that the intercepts of both curves are much lower than the actual \( \ln[\text{TOP-Te}]_0 \) because during nucleation, the consumption of TOP-Te is not a first-order reaction. At 250 °C the calculated rate constant \( k \) was 0.0336 s\(^{-1}\), and was 2.3 times more than the rate constant at 180 °C. Based on this observation and the temperature dependence of kinetics of this class of reactions in general, we expect the thermal decomposition of Cd-oleate also to be faster for the reaction at 250 °C. Thus at 250 °C, monomers are released rapidly allowing a diffusion-limited growth of nuclei into branched and elongated nanocrystals as described previously in the literature.\(^{54}\) In contrast, in the case of the reaction performed at 180 °C, within the first 10 s only 30% of the TOP-Te is consumed, and the release of Te monomers during the growth stage is also slower. The slow release of monomers after the nucleation stage will in turn, impede the growth of nuclei. It is possible that this slow decomposition of the monomers becomes the rate limiting factor during the growth of the nuclei (reaction limited growth regime\(^{128}\)) in the reaction carried out at 180 °C.

### 3.2.2 Growth mechanism

We then carried out a reaction for longer times at 180 °C. To monitor the morphology evolution of the nanocrystals, we continued the reaction at 180 (±5) °C, extracted samples with a syringe after 60 s, 120 s, 300 s, and 600 s and quenched them by adding into hexane (at room temperature). After 600 s we
took the reactor out of the heating mantle and allowed the remaining reaction mixture to cool to room temperature for ~10 min. We found very few nanocrystals with NTP morphology in the intermediate samples even after 600 s of continued reaction. The nanocrystals had no defined morphology and the average sizes did not change significantly during this time and were determined to be 5 (±0.9) nm, 5.2 (±1.2) nm, and 5.2 (±1.0) nm for sample quenched after 120 s, 300 s, and 600 s respectively. However, the sample collected after cooling contained nanocrystals with tetrapod morphology (Figure 15). In another experiment, we took the reactor out of the heating mantle immediately after injection of the precursors. In this case also we obtained CdTe nanocrystals with tetrapod-like morphology. These observations indicated that the evolution of CdTe nanocrystals into NTP morphology occurred mainly during the cooling. This cannot be explained by the conventional mechanism for NTP formation based on a homogenous nucleation of cores with cubic crystals (zinc blende) and subsequent diffusion-limited growth of four arms with hexagonal (wurtzite) crystal structure.\(^{87}\) We found no precedent for this observation in the literature, which was presumably because almost all reports of CdTe NTPs involve synthesis in a weakly coordinating solvent TOPO (notable exceptions include the work of Yu et al.\(^{93}\)), and reaction temperatures employed are much higher.

![Figure 15](image)

**Figure 15.** Growth mechanism at 180 °C (a), (b) and (c) during continued heating there is no tetrapodal nanocrystals present, but (d) after slow cooling to room temperature distinctly tetrapodal nanocrystals are obtained; (e) schematic representation of the proposed growth mechanism at 180 °C

Since the growth of nanocrystals and Ostwald ripening are concurrent processes, when the former is slowed down, the latter emerges. During the growth of the nanocrystals at 180 °C, the slow release of monomers causes Ostwald ripening to overtake the reaction-limited growth of the nanocrystals resulting in more isotropic structures (irregular and more importantly, non-tetrapodal morphologies).
Furthermore, our reaction medium is mainly non-coordinating and the ligand for capping the nanocrystals is the excess oleic acid present in the Cd-oleate injection solution. The low ligand concentration also enhances the Ostwald ripening of the nanocrystals during the growth stage in the reaction at 180 °C. In this scenario, prolonging the reaction would result in continued re-dissolution of any nanocrystals with complex morphologies and thus explain the near absence of NTPs, and the irregular morphologies of the obtained nanocrystals even after continued reaction for 600 s at 180 °C. On the other hand, cooling down the system lowers the solubility of the dissolved CdTe in the reaction medium leading to fast re-crystallization onto available nanocrystals.

Recently, Carbone et al. showed that rapid crystallization promotes twinning defects and growth of multiple twinned CdTe wurtzite nuclei also lead to formation of tetrapodal morphologies. Similarly we suggest that during the reaction at 180 °C, fast re-crystallization leads to the formation of NTPs during the cooling stage as observed in Figure. 15d.

This evolution sequence of tetrapodal morphology is unique to our reaction at 180 °C, where the nanocrystal growth rate is limited by the slow release of monomers, and is summarized by a schematic representation in Figure. 15. When we performed the same reaction at the higher temperature of 250 °C and quenched sample aliquots after 60 s, 300 s, and 600 s after injection of precursors, we obtained colloidal particles with almost exclusively NTP morphology in all the samples (two examples shown in Figure. 16). Therefore, at 250 °C the CdTe nuclei exhibit a diffusion-limited growth regime to grow into NTP morphologies and this is consistent with the conventional understanding of the formation of elongated structures of CdE nanocrystals. This effect is summarized in the schematic shown in Figure. 16.

* Cd-oleate injection solution contains oleic acid in the ratio [Cd]:[oleic acid] = 1:4. A recent study has shown that 2 moles of oleic acid is consumed in the formation of 1 mole of CdSe. Assuming a similar mechanism for CdTe formation, in our reaction [Cd]:[ligand] is 1:2.
For the reaction carried out at 180 ºC, we tried to suppress Ostwald ripening by replacing ODE with trioctylphosphine oxide (a weak coordinating solvent), but no indications of nucleation (no color change in the reaction medium) were observed even 10 min after injection of the precursors. In another experiment, we used a mixed solvent consisting of 2 mL oleic acid (excessive ligand to suppress Ostwald ripening) and 2 mL ODE. In this case, after injection of Cd and Te precursor solutions into the reaction medium at 180 ºC we took the reactor out of the heating mantle immediately. TEM analysis of the obtained nanocrystals clearly showed tetrapodal morphology ([Figure 17a](#)) that was qualitatively better than the nanocrystals obtained using only ODE as the reaction medium ([Figure. 15d](#)). It has been reported that the synthesis of CdSe nanocrystals with NTP morphologies is inherently difficult due to the instability of the zinc blende crystal phase at temperatures >250 ºC.91 Since the reaction temperature for our synthesis of CdTe NTPs is 180 ºC, we carried out a similar reaction, replacing the TOP-Te precursor solution with TOP-Se solution. The resultant nanocrystals clearly showed a tetrapodal morphology ([Figure. 17b](#)) thus showing the versatility of this reaction scheme.

In comparison to other reports in the literature describing the synthesis of CdE NTPs where a combination of an expensive ligand (alkylphosphonic acid) and a weakly coordinating solvent (trioctylphosphine oxide) is consistently used, our reaction medium consists of a relatively inexpensive ligand (oleic acid) and a non-coordinating solvent. Thus, we could reduce the reaction temperature almost by half and still obtain a qualitatively similar final product.

### 3.2.3 Photoconduction measurements of CdTe nanotetrapods

We also performed preliminary photocurrent measurements of the CdTe NTPs. From a drop of dilute octane suspension, we trapped a few colloidal CdTe NTPs between gold electrodes with a 30 nm ‘nanogap’ using dielectrophoresis.32 We prepared three separate devices and performed current–voltage ($I–V$) measurements across the nanogap electrodes with an applied voltage ranging from –3 to +3 V. We then compared the effect of illumination with a 20 W halogen lamp on the $I–V$ response of...
CdTe NTPs. A list of calculated average resistance values, from the measured $I-V$ curves for three devices, at bias voltages of 1 V and 2.5 V, is shown in Table 1.

<table>
<thead>
<tr>
<th>Device</th>
<th>1 V</th>
<th>2.5 V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dark $R$ (Ω)</td>
<td>Light $R$ (Ω)</td>
</tr>
<tr>
<td>Device 1</td>
<td>5.911×10^-15</td>
<td>4.542×10^-15</td>
</tr>
<tr>
<td>Device 2</td>
<td>1.838×10^-15</td>
<td>5.503×10^-14</td>
</tr>
<tr>
<td>Device 3</td>
<td>3.244×10^-15</td>
<td>2.303×10^-14</td>
</tr>
</tbody>
</table>

**Figure 18** shows the $I-V$ measurements for device 1. From the $I-V$ measurements performed under dark conditions we observed current levels in order of 1–2 fA and a non-linear increase in current at voltages >2.5 V, up to a maximum of ~25 fA (**Figure. 18a**). The non-linear increase in current at higher voltages could be attributed to the tunnel barrier that is formed at the junction consisting of gold/oleic acid/semiconductor interfaces.

For the same device, in the $I-V$ measurements performed under the white light illumination (25 µE m^-2 s^-1), the current was significantly higher and was typically in the range of a few pA (**Figure. 18b**). The current in this case was also non-linear but rapidly increasing even at lower voltages (>1 V). The absorption onset wavelength of bulk CdTe is 820 nm. Though the CdTe NTPs will have a slightly higher bandgap, photons from our white light illumination source had sufficient energy to excite the electrons to the conduction band resulting in enhanced current levels as seen in the $I-V$ measurements (**Figure. 18b**).

For all devices, the current measured under illumination was enhanced by a factor of 10–300 as compared to the current measured under dark conditions at 2.5 V. A clear enhancement of current under illumination can be observed at even lower voltages, i.e. 1 V (see Table 1). The variation in
current levels listed in Table 1 is typical for such nanogap-electrode based devices and it depends on
the number of trapped nanocrystals as well as on the atomic scale variation in the metal/oleic acid/NTP
junction between different devices. In a control experiment, we performed a similar ‘trapping’
experiment with a dilute solution of oleic acid and trioctylphosphine in octane and measured its $I–V$
response under dark and illuminated conditions. We found no illumination-dependent changes in the
current measured across the nanogap.

Photoconductivity measurements performed by others on spin-coated thin films of CdTe
nanocrystals also show 8–10 times enhancement of current levels under illumination. In another
work, Klevkov et al. showed a two-order of magnitude decrease in resistivity of CdTe
nanocrystalline films. In both these reports, although a decrease in resistance due to illumination was
observed, the measured current levels are much higher compared to our results, due to the larger
number of nanocrystals contributing to the conduction.

Recently, Hu et al. employed static electric fields
and obtained hundreds of CdSe and CdTe nanorods
between 100 nm gap electrodes. In our trapping
experiments, the length of the arms of the CdTe NTPs
[~15 nm; Figure. 19 (Inset)] and the gap between the
electrodes (~30 nm) would make it difficult to
accommodate such large numbers of NTPs, due to steric
considerations. Using SEM imaging we observed some
contrast between the nanogap electrodes, which could be
attributed to the trapped NTPs (Figure. 19). Nevertheless
more work is needed to quantify the
number and positioning of these NTPs within the
nanogap electrodes. From previous trapping experiments
on other nanoparticles, we typically observe fewer than
10 nanoparticles between the electrodes under similar trapping conditions. The preliminary
optoelectronic measurements reported here are intended only to validate this novel technique, using
pre-fabricated nanoelectrodes, for optoelectronic characterization potentially down to the level of
single NTPs.

Figure 19. SEM image of the CdTe nanocrystals
between the gold Nanogap electrodes. Inset shows
tem image of a single NTP used for the trapping
experiments. Below possible schematic
arrangement of NTPs between the electrodes.
Another reported method for measuring the electronic transport of such nanocrystals involves the thermal deposition of metallic contacts on individual nanocrystals.\textsuperscript{117} The method is reported to introduce artefacts into the measurements due to diffusion of the metal into the CdTe nanocrystal.\textsuperscript{117} This makes our ‘direct and artefact-free’ evaluation of the photoelectric properties of CdTe NTPs described here unique and significant, particularly since CdTe nanocrystals are widely reported to be active materials in future photoconductors and solar cells. We are currently performing a thorough investigation of the photoelectric properties with respect to different morphologies and material architectures, which will be described in detail elsewhere.
4. Summary and Conclusions

In this work we have studied two different syntheses based on solution chemistry to obtain 1D nanomaterials of II-VI semiconductors, namely ZnO and CdTe. Although the chemical pathways for the two syntheses are very different, the anisotropic growth has common phenomenological origin, which is based on the anisotropic crystal growth habits of the wurtzite phase (hexagonal crystal structure).

We have studied the synthesis of vertically aligned ZnO nanowire arrays, by a chemical bath process on various substrates. The synthesis involves epitaxial growth of ZnO seed-layer on a substrate in a chemical bath containing an aqueous solution of zinc nitrate and hexamine. We have also extended this synthesis to obtain hierarchical nanostructure, which consists of flexible polymeric nanofibers of poly-L-lactide (PLLA) acting as a substrate for the radially oriented growth of ZnO nanowires. We find that this hierarchical PLLA-ZnO nanostructure has a good potential for applications of ZnO pertaining to water purification by photocatalytic reactions occurring at the surface of ZnO. The combination of high surface area and flexibility of the nanofibrous ‘substrate’ with the photocatalytic functionality of ZnO nanowires enabled the proof-of-principle demonstration of a ‘continuous-flow’ water treatment system that could effectively degrade single and combination of known organic pollutants in water, as well as render common waterborne bacteria non-viable. Our hierarchical PLLA-ZnO nanostructures can be easily scaled up and the whole photocatalytic water treatment set up can easily be adapted either as a point-of-use system or centralized large-scale water purification system.

We have studied another class of reaction that is commonly used for size controlled synthesis of colloidal quantum dots, which can be modified to obtain anisotropic nanocrystals mainly for CdE (E=S, Se, Te). The mechanism of formation of anisotropic nanocrystals is very similar to the synthesis of ZnO nanowires, wherein the inherently anisotropic crystal growth habit of the wurtzite phase results in rod-shaped or tetrapodal nanocrystals. However, the precursor chemicals, chemical pathways and even the size scale are different compared to the ZnO nanowires. Anisotropic growth process in this case is typically self-seeded, and the morphology of the final nanocrystal depends on the crystal phase of the nuclei. In this work we find that by choosing a fatty acid, oleic acid (instead of alkylphosphonic acids) it is possible to synthesize CdTe and CdSe nanotetrapods at much lower temperatures (~180 ºC) than what is commonly reported in the literature, and the formation mechanism is significantly different in our low-temperature reaction compared to the traditional understanding. Since CdTe, especially with nanotetrapodal morphologies, is a promising material for futuristic photovoltaic devices we expect that
our low temperature synthesis will afford cost-effectiveness due to lower temperature requirements and also use of inexpensive chemicals.

The preliminary photoconduction measurements with CdTe nanotetrapods using gold ‘nanogap’ electrodes fabricated in-house, and showed up to 100 times enhancement in current levels in the $I–V$ measurements under illumination with a white light source. We expect that such direct and artefact-free measurements which can potentially to evaluate single nanocrystal photo-electric properties will provide valuable insights to the underlying physical phenomenon of photo-excitation, as well as help design better solar cells using such CdTe nanocrystals.
5. Future work

The photocatalytic degradation process of organic chemicals in water by ZnO nanomaterials is known to be enhanced by the presence of certain noble metals. Presently we are investigating the effect of the presence of gold nanostructures deposited on ZnO on the efficiency of photocatalytic process. We have some preliminary results indicating that the rate of the degradation process is enhanced. Another area of study would be introduction of additional functionalities that would remove heavy metals dissolved in water. Some studies earlier studies within our group have demonstrated the possibility using specific phases of iron oxide nanoparticles. In combination with such functionality, the water treatment mechanism developed in this work can become truly multifunctional and complete, addressing all major pollutants in water.

Colloidal nanotetrapods of CdTe developed in this work are known to be an effective photo-active component for photovoltaic applications. Recent studies have shown the effectiveness of heterostructured architectures which have nanoscale interfaces between materials that have a staggered alignment of conduction and valence band levels. Such materials can have been shown to spatially trap and separate the photo-generated electrons and holes. This will greatly enhance their lifetimes and diffusion lengths, allowing the design of very efficient solar cells, as well as other optoelectronic devices such as quantum dot lasers. Future work in this field will focus on development of simple syntheses for such heterostructured materials and evaluation of their photoelectric properties using our nanogap electrodes. We have currently developed a synthesis method for colloidal heterostructured quantum dots consisting of CdSe/CdS interface and are currently evaluating its potential as an optical gain medium. The next logical step is to evaluate the photo-current response.

The photoconduction measurements described in this work were performed on nanogap electrodes that were fabricated on Si wafers. Owing to the small sizes of the NTPs, and other complications, it is difficult to use topology evaluation tools such as SEMs to visualize the NTPs. We are currently developing the technique for electrode fabrication of electron transparent membranes so that the trapped nanocrystals can be visualized in order to estimate their numbers and geometry of attachment to the electrodes. This information is valuable to gain a deeper understanding of the photoconduction mechanism as well as physics of photo-excitation of valence electrons.
Acknowledgement

I would like to thank my supervisors, Prof. Mamoun Muhammed and Assoc. Prof. Muhammet S. Toprak for their valuable guidance and patience without which much of this work would not have been possible. The resourcefulness and leadership of Prof. Mamoun went a long way in establishing new partnerships that turned out to be valuable for this work. The fruitful collaborations, discussions and guidance from Prof. Klaus Leifer, Jafri, and the group are also gratefully acknowledged. Thanks are also due to Prof. J. Dutta who was my guide and supervisor during the initial stages of my scientific career and his unique style of solving problems will always remain an inspiration for me.

Thanks are also due to several members of the Division of Functional Materials whose direct collaboration has been invaluable, namely Dr. Jian Qin, Dr. Shanghua Li, Dr. A. Uheida. I would also like to thank the assistance received, direct and indirect, by several M. Sc. students which led to major parts of this work, namely V. K. Guduru, and Kabir. I sincerely hope that they have also benefited from the time spent on working in the lab with me.

Instructions received from Wubeshet and Hans on using the transmission electron microscope, and also assistance in scanning electron microscopy from Mazhar and Mohsin were very significant and insightful, and are gratefully acknowledged.

I would like to thank the people involved in writing, following up and maintenance of several current E.U. projects, including NanoEar, which funded most of my research. The time spent during my research would not have been as smooth without the discussions, chatting, and the general companionship received from all members of the Division of Functional Materials. Many thanks to Andrea, Carmen, Xiaodi, Ma, Sverker, Fei, Robina, Mazhar, Roody, Yichen, Jafri, et al. for their valuable friendship.

Last but not the least I would like to thank my loving wife whose unconditional love and support I hope I have not taken for granted during the early days when I spent more time in the lab than at home. Thanks are also due to my parents whose support and encouragement was and still is very valuable to me.
References


121  http://www.sigmaaldrich.com/spectra/rair/RAIR005128.PDF: Product information from supplier; accessed on 2010-03-17.


