Chapter 1

Introduction

1.1 Introduction

Tremendous progress has been taken place in the area of nanoscience and nanotechnology nowadays. It is worthy to say that this knowledge is not limited to research work and limited inside the wall of the research laboratory; instead it becomes complete and independent branch of science like chemistry, physics, mathematics etc.

Since a physicist Feynman in the year 1959 said, “There’s plenty of Room at the Bottom.” in his lecture at an American Physical Society meeting at Caltech. This line has actually inspired the development of field of nanotechnology.

Semiconductors are crystalline or amorphous solids with distinct electrical characteristics in between metal and insulator. When synthesized in aqueous or non-aqueous medium with the particle size in the range of 10- 100 nm, they are considered as semiconductor nanocrystals which show properties different than in the bulk form. Semiconductor materials are characterized by their band structures (direct or indirect) and band gap energy (Eg).[1] In direct band gap semiconductor, the top of the valence band and the bottom of the conduction band occur at the same value of momentum, while they are different in case of indirect band gap semiconductor. The band gap energy is the energy required to excite the electrons from the top of the VB to the bottom of CB and it falls within a range between

0 <Eg< 4 eV. Furthermore, if one dimension of a semiconductor is smaller than the Bohr exciton radius of the material, the band structure will be modified and blue shifted to higher energy by the quantum confinement effect. In case of very small particle size (strong confinement regime) quantized energy levels are appeared, which are different from the continuous band of bulk semiconductors. They show characteristics of the discrete molecular semiconductors (Figure 1.1).

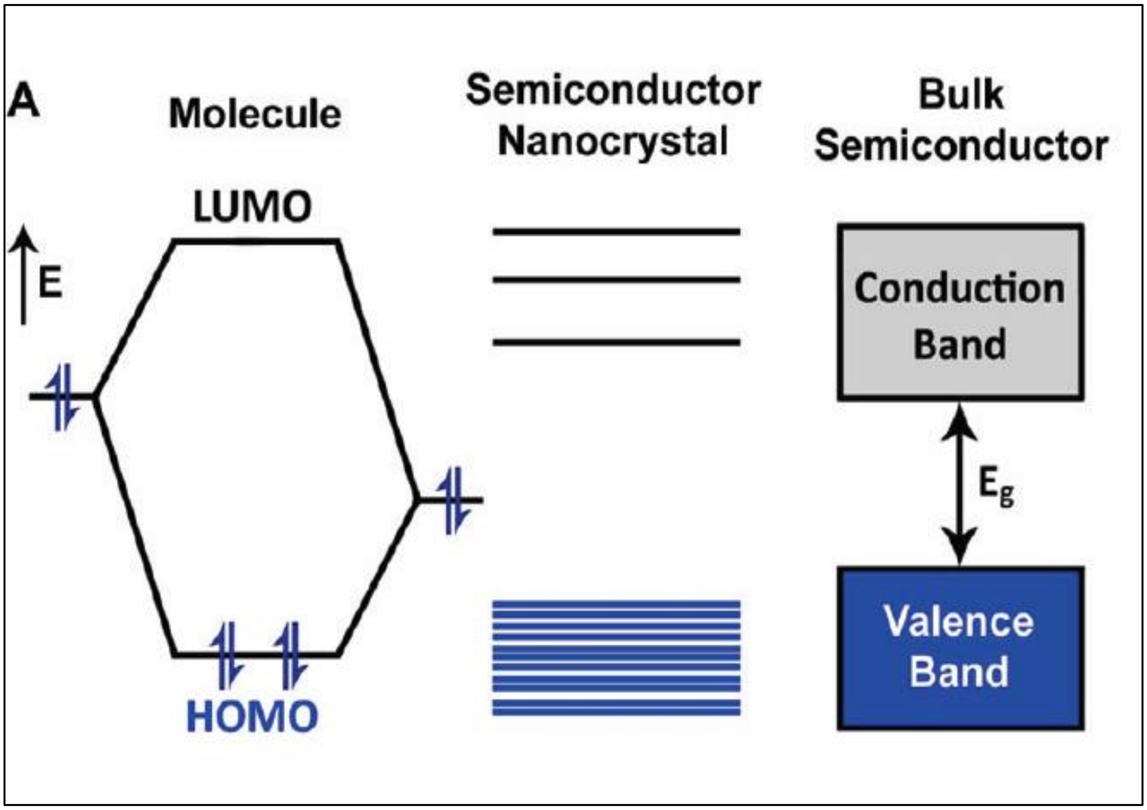


Figure 1.1.Electronic energy states of different types of semiconductor materials.

The quantum size effect opens up possibilities for the fine-tuning of the band structures and the optical and electrical properties of semiconductor NCs by controlling their sizes. Apart from the size-effect, the physical and chemical properties of semiconductor NCs are highly dependent on their compositions, shapes, structures, and surface chemistry, which have enabled semiconductor NCs to be used as active materials in various applications and fields.[6-9]

1.2 Synthesis of Nanoparticles

Earlier nanomaterials were synthesized by applying the principles of colloidal chemistry such as arrested precipitation, reverse micelle, etc. One of the methods is synthesis and growth of nanoparticles inside the cavity having predefined dimensions and shapes present in the micellelar systems, proteins or carbohydrates (eg. cyclodextrins). This method is called the nanocavity route. Another method is to separate the nucleation and growth steps by controlling the precursor concentrations, reaction temperature, concentration of capping ligand etc. The method is called the bulk solution route.

The comparision between these two routes are given below in Table 1.1.

Table 1.1: Comparison between Nanocavity Route and Bulk solution Route [2]

Nanocavity Route	Bulk solution Route
• To grow nanocrystals inside a designated nanocavity or template	• To control the size of nanocrystals by kinetically hindering the nucleation and growth of crystals by varying reaction conditions, such as precursor concentrations, temperature, ligand concentrations etc.
• Yields nanocrystals within a ligand nanocavity and the resulting nanocrystals are thus coated with a monolayer of ligands or embedded inside a large molecule, such as a dendrimer.	• The nanocrystals are often coated by the ligands provided in the solutions.
• From a crystallization point of view, these two routes are significantly different.	

Nanocavity Route	Bulk solution Route
• Nucleation takes place in each preformed cavity, and the nucleus/nuclei formed inside each nanocavity should grow to a single particle.	• Nucleation occurs in a bulk solution and all nuclei will chemically communicate with each other.
• As a result, polycrystalline particles may be common in this route.	• The size of the resulting nanocrystals is largely determined by the thermodynamics and kinetics of the entire system
• In addition, the final size of the crystal should roughly be determined by the size of the nanocavity.	

- Unfortunately, size and shape control of nanocavities in solution is also a challenging issue. Certain sized and shaped ligand cavities, such as reverse micelles, microemulsions etc., can only be formed under quite strict conditions.

- Those conditions might not be ideal for the growth of single crystalline nanocrystals in the cavities.
- For example, high temperatures in a reverse micelle solution may completely destroy the desired nanostructures formed by ligands resulting into low quality semiconductor nanocrystals.

The bulk solution route was also limited to

- **Low temperatures and**
- **Aqueous solutions**

The quality of the nanocrystals produced was deteriorated than those produced by the nanocavity route.

However, this route is dominated by

- **Crystallization processes alone**
- It is simple compared to the nanocavity route and easy to optimize

1.3 Organometallic Approach:

The success of the organometallic approaches in the early1990s has led to most research efforts being directed towards this route.

In this approach in coordinating solvents, invented in the early 1990s by Steigerwald et al. and developed to a practical level by Murray et al. are regarded as having been the first major breakthrough that yielded CdSe nanocrystals.

The term organometallic refers to the fact that the precursors for the formation of nanocrystals are organometallic compounds, such as $Cd(CH_3)_2$, $Zn(CH_3)_2$, $S(TMS)_2$, $P(TMS)_3$, etc.

The most successful system for organometallic approaches is CdSe Nanocrystals. The typical reaction protocol is as follows.

- 4g TOPO (trioctylphosphineoxide) was heated to 360 $^{\circ}$C with Ar flow
- 2.4 ml cold stock solution (Se:$Cd(CH_3)_2$: tri-butylphosphine = 2 : 5 : 100 by mass, made in a glovebox) was quickly (< 0.1 s) injected into the rapidly stirred, hot TOPO solution.
- The temperature was lowered to 300 $^{\circ}$C by the injection.
- At various time intervals, aliquots of the reaction mixture were removed and dissolved in toluene for monitoring of the reaction by UV-vis.
- Upon the desired size being reached, the reaction mixture was allowed to cool to room temperature and methanol was added to precipitate the nanocrystals from other components.

- After centrifugation, decanting, and drying under Ar, CdSe nanocrystals coated with TOPO were obtained in powder form, which were soluble in non-polar solvents.

In contrast to the nanocrystals reported in earlier works, the CdSe nanocrystals grown by organometallic approaches are highly crystalline.

The **drawbacks** of the organometallic approaches is

- **Extreme toxicity** of $Cd(CH_3)_2$, i.e. substantial equipment is required for their handling eg. A glove box.
- Owing to this limitation, access to the only kind of high quality yet expensive semiconductor nanocrystals has been **limited** to a dozen of groups in the world.

This has motivated scientists in the field to explore other ways to synthesize high quality nanocrystals. Among those, the so-called alternative routes or greener approaches are the most widely adopted.

A new strategy for the synthesis of nanostructures which will simultaneously simplify and improve the nanostructures by using

- **Relatively safe reagents**
- **At relatively low temperatures**
- **Yielding structures of better quality**

- **A soft Nanochemistry is the demand of the days.**

These new syntheses allow for

(i) Production of multi-gram quantities of nanostructures in a single laboratory-scale reaction

(ii) Recycling of unused precursors

(iii) Use of far higher concentrations (which reduces the consumption of solvents)

(iv) Remarkably different growth kinetic with unexpected consequences on the product's morphology and size.

This strategy is based on the use of **heterogeneous reaction environments.**

In the case of hot injection techniques

- **The nucleation is arrested by the sudden decrease in temperature following the injection.**
- **This is the strategy to halt nucleation and to prevent it from consuming most of the available precursors, lead to a fast aggregation and ripening process.**
- **Upon reaching an appropriate temperature the previously formed nuclei grow all at the same time.**

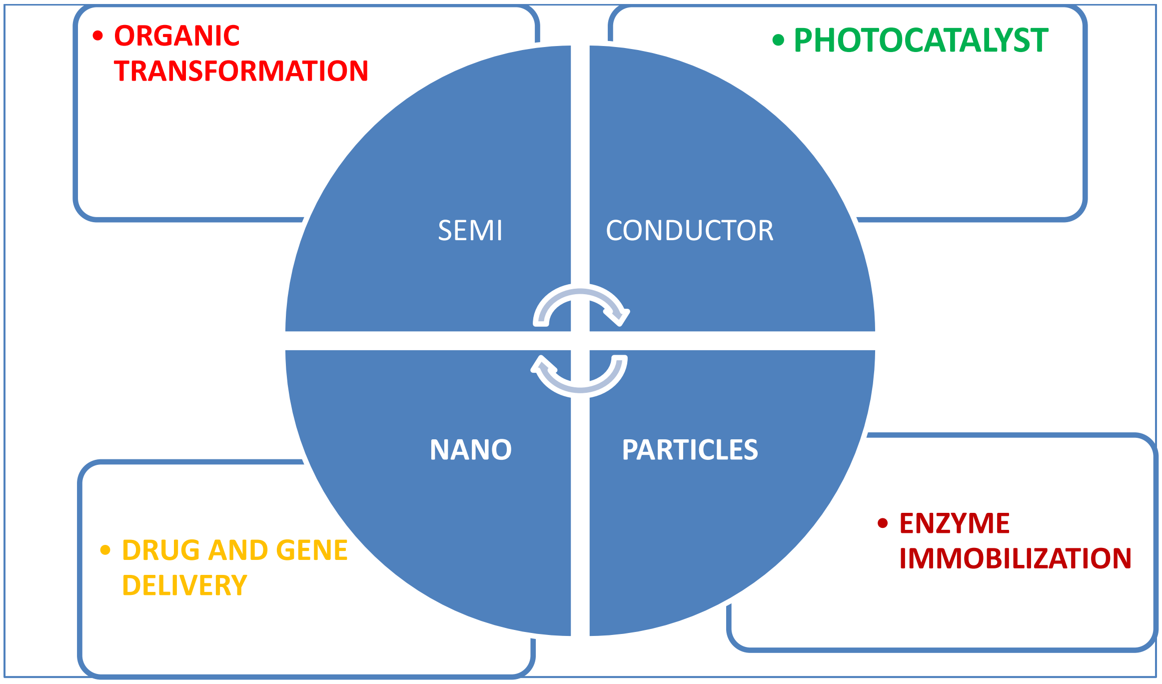
- **The large supersaturation left after injection leads to a uniform growth of all nuclei at very similar rates.**

  This decreases the size dispersion.

This phase is called focusing, widely regarded as the main reason for the remarkable success of hot injection (or decomposition) techniques in obtaining colloidal products with low polydispersity (approx. 4–6%).

For the work reported in this thesis, we have adopted the green chemistry approach using water as a reaction medium. We have synthesized semiconductor nanoparticles most them of are from the II-VI class. We have also reported the change in properties (in term of photocatalytic efficiency) of the synthesized nanoparticles by doping transition metal ions (e.g. Ni^{2+}).

The research area covered under this study can be described as:


• ORGANIC TRANSFORMATION
• PHOTOCATALYST
SEMI
CONDUCTOR
NANO
PARTICLES
• DRUG AND GENE DELIVERY
• ENZYME IMMOBILIZATION

References

[1] J. Chang and E. R. Waclawik, *RSC Adv.*, 2014, **23505**, 4.

[2] X.Peng and J. Thessing, *Stru Bond*, 2005, **79**,118.

[3] L. E. Brus, *J. Chem. Phys.*, 1983, **5566,** 79.

[4] L. Brus, *J. Chem. Phys.*, 1986, **2555**, 90.

[5] M. G. Bawendi, M. L. Steigerwald and L. E. Brus, *Annu.Rev. Phys. Chem.*, 1990, **477**, 41.

[6] M. L. Steigerwald and L. E. Brus, *Acc. Chem. Res.*, 1990, **183**, 23.

[7] D. J. Norris and M. G. Bawendi, *Phys. Rev. B*: *Condens. Matter Mater.Phys.*, 1996, **16338**, 53.

[8] J. Y. Kim, O. Voznyy, D. Zhitomirsky and E. H. Sargent, *Adv. Mater.*, 2013, **4986**, 25.

[9] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim and H. Yan, *Adv. Mater.*, 2003, **353**, 15.

[10] D. Koziej, A. Lauria and M. Niederberger, *Adv. Mater.*, 2014, **235,** 26.

[11] M.R.Gao, Y.-F. Xu, J. Jiang and S.H. Yu, *Chem. Soc. Rev.*, 2013, **2986**, 42.

[12] A.P. Alivisatos, *Science, 1996*, **933**,271.

[13] X. Peng, *ChemEur J*, 2002, **334**, 8

[14] X. Peng, L. Manna, W. D. Yang, J. Wickham, E. Scher, A. Kadavanich and A.P. Alivisatos, *Nature*, 2000, **59**, 404.