Literature Survey

Microheterogeneity is defined as a small variation in the chemical structure or morphology of a molecule/ a composite that does not result in a significant change in properties. Microheterogeneous system refers to a small aggregate system of molecules within the solvent or other surrounding medium and it includes organic and inorganic systems. Surfactants are molecules with two distinctively different parts: hydrophobic and hydrophilic groups and extensively used for organic microheterogeneous system.

An emulsion is a mixture of two or more liquids that are normally immiscible. In an emulsion, one liquid (the dispersed phase) is dispersed in the other (the continuous phase). Two liquids can form different types of emulsions. As an example, oil and water can form, first, an oil-in-water emulsion, wherein the oil is the dispersed phase, and water is the dispersion medium. Second, they can form a water-in-oil emulsion, wherein water is the dispersed phase and oil is the external phase. Multiple emulsions are also possible, including a "water-in-oil-in-water" emulsion and an "oil-in-water-in-oil" emulsion.

Emulsions, being liquids, do not exhibit a static internal structure. The droplets dispersed in the liquid matrix (called the “dispersion medium”) are usually assumed to be statistically distributed. Emulsions usually have internal drop sizes in the range of 0.1 μm and 10 μm and are classical representatives of microheterogeneous systems. The internal droplet phase of water in oil droplets have been used to synthesize particles which are agglomerates of nano particles.

Microemulsions are typical representations of microheterogeneous systems; they have considerable industrial applications, one of them being the synthesis of polymers. They are also used in the process of creating nanoparticles. Microemulsions are dispersion made of water, oil, and surfactant(s) that is thermodynamically stable system with dispersed domain diameter varying approximately from 1 to 100 nm, usually 10 to 50 nm. Microemulsions are clear, thermodynamically stable, isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a cosurfactant. Aqueous phase may contain salt(s) and/or other ingredients, and the "oil" may actually be a complex mixture of different hydrocarbons In contrast to ordinary emulsions, microemulsions form upon simple mixing of the components and do not require the high shear conditions generally used in the formation of ordinary emulsions.

The prime objective of this investigation is the synthesis of nanomaterials in micro heterogeneous media. Semiconducting nanomaterials having very wide application in solar energy harvesting were synthesized and characterized. Synthesis of semiconducting nanomaterials such as titanium dioxide, cadmium selenide etc can be achieved by different routes, each of these routes tend to provide unique morphological characteristic to the materials produced as well as distinct quantum characteristics. In view of these areas being highly investigated from different point of views, a comprehensive review in terms of techniques of synthesis becomes quite arduous. Hence with reference to titanium dioxide and cadmium selenide a brief review of literature is provided that initially discusses synthesis routes and their effect on synthesis of titania nanoparticles and later focuses on the reaction environment and its effect on cadmium selenide synthesis in the later case the effect of route is only briefly touched.

2.1 Routes To Synthesis Of Titanium Dioxide

Titanium dioxide or Titania is obtained either from minerals or from a solution of titanium salts or alkoxides. The most common procedure is based on the hydrolysis of acidic solutions of Ti(IV) salts, gas phase oxidation reactions of the $TiCl_4$ and hydrolysis reactions of titanium alkoxides. Suzuki et al (1969) prepared the same on an industrial scale by the sulphate process or by the chloride process. In the former, the processing is complicated. In the latter, the requirements for equipment and materials are very harsh because of high reaction temperature ($>1400^0$ C) and strong corrosiveness of Cl_2 at high temperature. Nanoparticles of TiO_2 can be prepared by various gas phase and liquid phase methods but mainly by hydrolysis, sol-gel, microemulsion or reverse micelles and hydrothermal synthesis. Synthesis type and conditions influence the transformation behavior of the phases, crystalline structure and morphology.

2.1.1 Hydrolysis Method

Synthesis of titanium dioxide by hydrolysis and precipitation is the simplest of all the methods. Precipitation from solutions includes gel or precipitate formation followed by washing, drying, and thermal treatment. The most common procedures have been based on the hydrolysis of acidic solutions of inorganic Ti(1V) salts. In addition, gas phase oxidation reactions of $TiCl_4$ and hydrolysis reactions of titanium alkoxides have been employed to generate finely divided, high-purity TiO_2 powders. Numerous studies on aqueous solutions of titanium salts have shown that titanium hydrolysis occurs even in highly acidic solutions ($pH<1$) and that boiling the solutions accelerates hydrolysis and consequently, titania precipitates. Compared to other methods, hydrolysis could be carried out at conditions closer to ambient to produce nanoparticles of TiO_2.

Reddy et al. (2001) synthesized fine polycrystalline, nanoparticles of pure anatase titanium dioxide with high surface area using $TiCl_4$ as the starting material. A solution of hydrazine hydrate, H_6N_2O was used as the precipitating agent. The hydrolysis and condensation reactions starts immediately upon mixing, as indicated by the rapid increase in turbidity and the formation of large, visible flocs, which precipitated to the bottom of the reaction vessel. The precipitation product is usually an amorphous hydrous oxide which should be calcined at high temperatures to improve crystalline. D.S. Lee et al. (2002) used the crystalline phases from at different temperatures acid-hydrolysis method in order to prevent high temperature calcinations. Nano-sized TiO_2 crystal could be formed at low temperature with this. Zhang et al. (2008), Qourzal et al. (2006) used titanium tetrachloride as the starting material, as the hydrolysis is more rapid and it is a cheaper raw material comparatively. However, handling of $TiCl_4$ is much difficult as it gives heavy dense fumes when it comes in contact with water and air. Also the hydrolysis should be carried out at very low temperatures as the reaction with water is an exothermic process.

2.1.2 Sol-Gel Method

The sol-gel method is a versatile process used in making various ceramic materials. Sols are dispersions of colloidal particles in a liquid. Colloids are solid particles with diameters of 1-100 nm. A gel is an interconnected, rigid network with pores of sub micrometer dimensions and polymeric chains whose average length is greater than a micrometer. The term “gel” embraces a diversity of combinations of substances that can be classified into four categories:

(1) Well-ordered lamellar structures;
(2) Covalent polymeric networks completely disordered;
(3) Polymer networks formed through physical aggregation, predominantly disordered:
(4) Particular disordered structures

The popularity of this method stems from its vast potential of applications, many of which are already in use. Thus the sol-gel process is used for the production of several metal oxides either in pure form or in mixtures. In a typical sol-gel process, a colloidal suspension, or a sol, is formed from the hydrolysis and polymerization reactions of the precursors, which are usually inorganic metal salts or metal organic compounds such as metal alkoxides. Complete polymerization and loss of solvent leads to the transition from the liquid sol into a solid gel phase. A gel may be formed by network growth from an array of discrete colloidal particles or by formation of an interconnected 3-D network by the simultaneous hydrolysis and polycondensation of an organometallic precursor. The overall hydrolysis and condensation reactions of titanium ethoxide are illustrated in Figure 2.1.

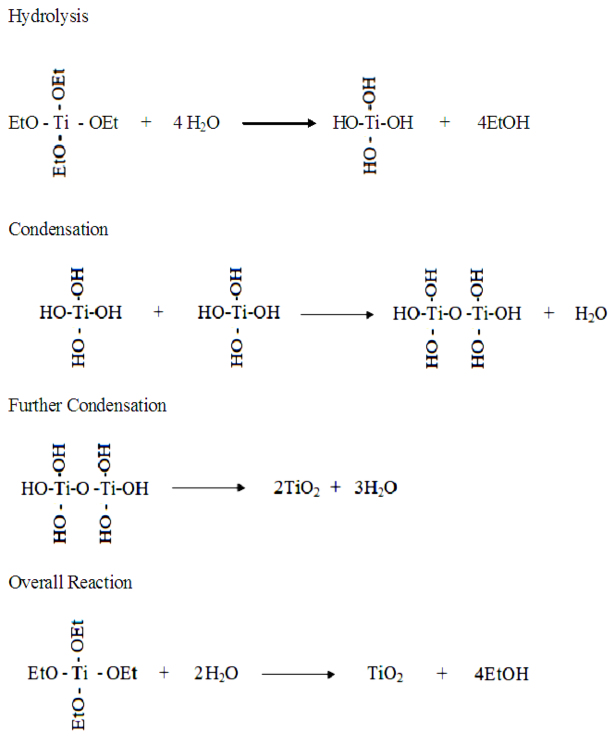

Fig 2.1 Hydrolysis reaction of Titanium Ethoxide

For illustration purposes the hydrolysis and the condensation reactions are shown to proceed to completion in the figure. However, it is understood that OR groups could persist due to incomplete hydrolysis, and the resultant particles being amorphous hydrous titania would also have surface OH groups and not be TiO_2.

Titania can be synthesized via sol-gel process mainly by hydrolysis of titanium alkoxides. Several titanium alkoxides had been tried including isopropoxide by Papoutsi, Ginzberg et al. (1994, 1996), n-butoxide by Wang et al. (1999), and ethoxide by Assmann, Yuan et al. (2004, 2006)have stated to give high surface areas that arise from small particle sizes. Other than the alkoxide precursor, a metal salt precursor like $TiCl_4$ was found to be a good starting material for the preparation of TiO_2 in powder form. Zhu et al. (2000) synthesized nanosized TiO_2 powder with anatase structure by the sol-gel method using $TiCl_4$ ethanol solution as a precursor. Zhu, Zhang et al. (2000) found that the grain size of TiO_2 powder was homogeneous and was about 10nm after the precursor was calcined at 500^0 C for 1 hour.

While the sol-gel process appears to be a simple operation, many variables can influence the quality of the final product. These variables include the choice of solvent, whether acid of base catalysis is employed and use of stabilizing agents. The heat treatment temperature used to crystallize the titania has been shown to be critical in the activity of sol-gel coatings. Marugan et al. (2008) stated that synthesis pH is more important parameter than temperature. They found that neutral aqueous media lead to anatase materials that undergo neither phase transition to rutile nor significant grain growth, whereas the use of acidic conditions favors the formation of rutile.

The sol-gel technique has emerged as one of the most promising new techniques for growing thin films because it has several important advantages. For example, titania thin films prepared in this way can be of high purity and low cost, resulting from the availability of high purity chemicals as raw materials in conjucation with the simplicity of sol-gel processing.

2.1.3 Microemulsion Method

Hubbard et al. defined microemulsion as a thermodynamically stable, optically isotropic solution of two immiscible liquids (i.e water and oil) consisting of micro domains of one or both liquids stabilized by an interfacial film of surfactant. The surfactant molecule generally has a polar (hydrophilic) head group and a long chain (hydrophobic) tail. Such molecules optimize their interactions by residing at the oil/water interface, thereby considerably reducing the interfacial tension. In water-in-oil microemulsions, the aqueous phase is dispersed as micro droplets (typically 10-25 nm in size) surrounded by a mono layer of surfactant molecules in the continuous hydrocarbon phase. The aqueous cores of microemulsions, containing soluble metal salts, are used as micro reactors for the synthesis of nanoparticles. Due to the dynamic nature of the micro droplets, the exchange mechanism involves coalescence and fusion of the droplets upon collision, which then disintegrate into droplets, and this process occurs continuously in microemulsion.

Microemulsions are generally of low viscosity containing oil, water and an amphiphile that brings down the water/oil interfacial tension (IFT), γ, to a very low value. It is accepted that the IFT between oil and water is reduced to a very low value by the presence of an amphiphile, but there are many instances where the amphiphiles do not bring the IFT down to the required very low value and some short chain alcohols or amines need to be added to obtain the required IFT for the formation of a stable microemulsion. Hence in most cases the microemulsions are four component systems including water, oil, surfactant and a short chain substance called a co-surfactant. Aerosol OT (AOT) is an interesting double chain surfactant, which can conveniently form a three component microemulsion system without a co-surfactant.

In the formation of microemulsions, both ionic and nonionic surfactants are used. Co-surfactants are alcohols or amines. Surfactants, particularly nonionic, can form reverse micelles in organic media. But the organic media must not be completely dry. If the medium is completely dry, then reverse micelles do not form. The reverse micelle is somewhat like water-in-oil (W/O) microemulsion. There, the amount of water present is significantly low that satisfies the hydration of the hydrophilic head group. This water is not free, and its properties are different from normal water. If the amount of water present exceeds to that required for hydration of the hydrophilic head group of the amphiphile, then there will be both free and bound water in the water pool of the microemulsion. Maitra et al.(1984) and Majhi et al. (1999) envisaged the presence of three types of water by NMR and calorimetric methods. The distinction between reverse micelle and W/O microemulsion is not sharp (Figure 2.2). Pileni (1993) defined a parameter *w*, which is the mole ration between water and surfactant and suggested that systems with *w*< 10 are reverse micelles; microemulsions require having *w*> 10.

Reverse micelle systems (or water-in-oil microemulsions) have been used as micro reactors to synthesize ultrafine particles with a narrow distribution of particle size by controlling the growth process. Boutonnet et al. (1982) used microemulsions to obtain ultrafine monodispersed metal particles of Pt, Pd, Rh and Ir by reducing corresponding salts in the aqueous droplets of water-in-oil microemulsions with hydrazine or hydrazine or hydrogen gas. Curri et al. (2000) showed if instead two microemulsions containing salts of, e.g. $Cd(NO_3)_2$ and Na_2S are used, water insoluble compounds such as CdS can be prepared as nanoparticles. Joselevich, Arriagada et al. (1994) generated ultrafine TiO_2 particles in water-in-oil microemulsions. Chhabra et al. (1995) synthesized TiO_2 nanoparticles using water-in-oil microemulsions composed of Triton X-100, cyclohexane and hexanol and studied the effect of the calcination temperature on the phase and particle size of TiO_2 particles. Nanosized TiO_2 particles have also been prepared by microemulsions-mediated processing.

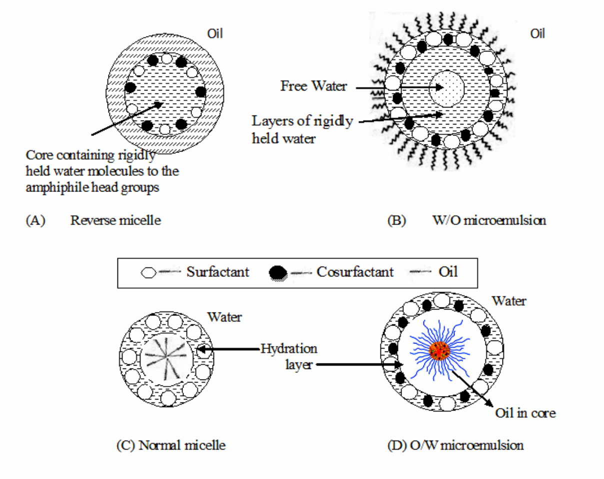

Fig 2.2 Pictorial representation of microemulsion and reverse micelles

TiO_2 colloidal suspensions or films are usually made by hydrolysis of alkoxide precursors in an aqueous acidic environment. Reverse micelles provide a greater control to both the size and size-polydispersity and the shape of TiO_2 mesoporous films with the method of reverse micelles usually involves three stages:

1) Hydrolysis of an alkoxide in a reverse micellar environment and formation of a gel by inorganic polymerization;

2) Deposition of a composite inorganic/organic film on a solid substrate;
3) Heating of the film up to 450^0 C to burn out all organic content and obtain the final mesoporous structure.

The three materials made during the three above stages i.e., the gel, the composite film and the TiO_2 film are very interesting physiochemical systems by themselves. The variants of each system affect the properties of the system that follows, providing control for the final product.

Microemulsions represent complex phase behavior and the chemical structure of the co-surfactant and the characteristics of surfactant have a pivotal role to play on their phase behaviors. Many surfactants have been tried and compared as well. While Chhabra et al.(1995), Papoutsi et al. (1994), Andersson et al. (2002) used Triton X-100 and Stathatos et al. (1997) used AOT, Papoutsi et al. (1994) used sodium dodecyl benzene sulfonate (SDS) and Zang et al. (2003) used NP-5 (Igepal C0-520) have also been tried.

Stathatos et al. (1997) have prepared reverse micellar solutions using the two well-known surfactant, Triton X-100 and AOT. These choices were made because they provide well-characterized reverse-micellar systems, because one of them is ionic and the other nonionic and because, they produce TiO_2 films with differently sized and shaped particles but with the same remarkable mono dispersity and reproducibility. AOT (bis (2-ethylhexyl) sulfosuccinate sodium salt) is a well-known double-chain surfactant, soluble in several organic solvents, that gives reverse micelles in the presence of water. Triton X-100 (poly (oxyethylene) (1,1,3,3-tetramethyl-butyl) phenyl ether) is a nonionic surfactant that forms non-spherical micelles in cyclohexane, both dry and swollen. Solutions based on AOT gave elongated particles with a very high degree of orientation. Low hydrolysis rates are observed with Triton X-100 compared to AOT as water is consumed for hydration of polar groups and hardly available for alkoxide hydrolysis.

The microemulsion process has the advantage of obtaining nanosized particles without serious agglomeration. Andersson et al. (2002) developed a new hydrothermal microemulsion process in order to prevent grain growth of the nanoparticles using an acid as another aqueous phase. Wen et al. (2008) modified this work using a base as a precipitating agent. They investigated a microemulsion process combined with hydrothermal techniques for synthesizing anatase-type Titania. Chung et al. (2008) prepared nanosized TiO_2 powders by employing this hydrothermal microemulsion process.

2.1.3.1 Factors influencing the formation of reverse micelles

The advantage with the microemulsion route is that the size of the particles can be varied with the ratio of surfactant to water. The sizes of the water droplets in the reverse microemulsions are approximately of the same size as the produced particles. The microemulsion formation is a spontaneous process which is controlled by the nature of amphiphile, oil and the temperature. The mechanical agitation, heating, or even the order of component addition may affect micro emulsification. The complex structured fluid may contain various aggregation patterns and morphologies known as microstructures.

Pure rutile and anatase nanoparticles can be obtained at appropriate acid concentrations. Zhang et al. (2002) investigated the influence of various reaction conditions, such as concentration and type of acid, water, content, H_2O/Ti molar ratio, and reaction time, on the formation, crystal phase, morphology, and size of the TiO_2 particles.

2.1.3.2 Influence of pH and concentration

The pH of the reaction medium has a significant effect on the crystal structure of obtained TiO_2 nanoparticles. In general, the titanium alkoxides hydrolyze rapidly in water and amorphous titanium dioxide hydrate is obtained. Wu, Long et al. (1999) found that in order to obtain a crystalline product, hydrothermal treatment or calcination is usually necessary. In the presence of acid, however the hydrolysis of titanium alkoxides is inhibited to a certain degree, depending on the acidity of the aqueous phase. At high acidity, the hydrolysis of the titanium alkoxides may become very slow, which is favorable for the ordered arrangement of TiO_2 molecules and the crystalline phase may be allowed to from, even at ambient temperature. Rubio et al. (1997) discovered that depending on the exact pH, both rutile and anatase can be formed through different condensation routes. It has been reported that the concentration of $TiCl_4$, which is directly related to the acidity of the reaction medium, significantly influences the crystallization of rutile under hydrothermal conditions.

In the work of Wu and co-workers (1999, 2002), nanoparticles of rutile or anatase were prepared through microemulsion-mediated hydrothermal (MMH) and hydrothermal methods in the presence of hydrochloric or nitric acid. It was found that the concentration of the acid plays a dominant role in the hydrolysis and polycondensation of titanium (IV) n-butoxide and higher HCl concentration favors rutile crystallization. Dongbai et al.(2002) studied the influence of pH on the crystal structure of TiO_2 nanoparticles synthesized by the hydrolysis of titanium tetrabutoxide in the presence of acids in NP -5 (Igepal CO-520) – cyclohexane. The TEM micrographs and electron diffraction patterns provide direct information about the size, morphology and crystalline structure of the TiO_2 particles obtained at different acidities.

2.1.3.3 Influence of H_2O/Ti ratio

Brinker et al. (1990) studied the influence of H_2O/Ti ratio, h value by keeping w value (water to surfactant ratio), acid concentration and reaction time as constant. When h is less than 6, which is lower than the coordination number of the Ti(IV) ions, the amount of the water in the water pools of the reverse micelle system is not sufficient to completely hydrolyze the alkoxide and hence, the process of crystallization is hindered, so only spherical amorphous TiO_2particles can be obtained. On increasing h to greater than 10, the product changes from amorphous to crystalline rutile. The size of the primary particles is barely influenced by the h value, but the morphology of the particles changes with increasing h.

2.1.3.4 Influence of water content and temperature

Zbu and Schelly (1992) studied the reverse Micelles of Triton -100 in Cyclohexane and the effects of temperature, water content and salinity on the aggregation behavior. The monomer concentration is reduced by the addition of water but increased by raising the temperature. Around room temperature (at 30^0 C), the aggregation number goes through a maximum with increasing water content. Wet TX-100 reverse micelles are larger than the dry ones, and the saline aggregates are in between in size. The hydrodynamic diameter generally increases with water content, but not monotonically. However, the size of all aggregates is reduced by increasing temperature.

2.1.3.5 Effect of nature of acid

Brinker (1990) found that the concentration of the acid plays a dominant role in the hydrolysis and polycondensation of titanium alkoxides and higher acid concentration favors rutile crystallization. Zhang et al. (2002) observed the irregular and amorphous product when the concentration of hydrochloric acid in the aqueous phase of the reverse micelle system was below 2 M. When the acid concentration was increased to 2 M, the TiO_2 particles formed were found to be of a mixed crystal phase consisting of rutile and anatase. Pure rutile phase was formed when the acid concentration was raised to 2.5 M. When the acid concentration was further increased to 4M, only amorphous TiO_2 particles were obtained.

2.1.4 Hydrothermal Method

The term hydrothermal usually refers to any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions to dissolve and recrystallize (recover) materials that are relatively insoluble under ordinary conditions. Byrappa et al. (1992) defines hydrothermal synthesis as any heterogeneous reaction in an aqueous media carried out above the room temperature and at pressure greater than 1atm. Yoshimura et al.(1994) proposed the following definition: reactions occurring under the conditions of high-temperature-high-pressure ($>100^0$ C, >1 atm) in aqueous solutions in a closed system. Roy et al. (1994) declares that hydrothermal synthesis involves water as a catalyst and occasionally as a component of solid phases in the synthesis at elevated temperatures ($>100^0$C) and pressure (greater than a few atmospheres).

Hydrothermal synthesis is normally conducted in steel pressure vessels called autoclaves with or without Teflon liners under controlled temperature and/or pressure with the reaction in aqueous solutions. The temperature can be elevated above the boiling point of water, reaching the pressure of vapor saturation. The temperature and the amount of solution added to the autoclave largely determine the internal pressure produced. It is a method that is widely used for the production of small particles in the ceramics industry.

The synthesis of TiO_2 is usually carried out in small autoclaves of the Morey type, provided with Teflon liners. The conditions selected for the synthesis of TiO_2

particles are: T ¼ <200 C, P < 100 bars. Such pressure temperature conditions facilitate the use of autoclaves of simple design provided with Teflon liners. The use of Teflon liners helps to obtain pure and homogeneous TiO_2 particles. Though the experimental temperature is low w150° C, TiO_2 particles with a high degree of crystallinity and desired size and shape could be achieved through a systematic understanding of the hydrothermal chemistry of the media. Here it is appropriate to mention that the size of the titania particles is the most critical factor for the performance of material with photocatalytic activity, and the monodispersed nanoparticles are the most suitable ones. It has been shown that the particle size is a crucial factor in the dynamics of the electron/hole recombination process, which offsets the benefits from the ultra high surface area of nanocrystalline TiO_2.

While TiO_2 can be prepared by various methods, the hydrothermal method has many advantages when compared with other:

(1) A Highly homogenous crystalline product can be obtained directly at relatively lower reaction temperature (ingeneral< 250^0 C). Hence the sintering process, which results in a transformation from the amorphous phase to the crystal phase, can be avoided. It favors a decrease in agglomeration between particles.

(2) From a change in hydrothermal conditions (such as temperature, pH, reactant concentration and molar ratio, additive, etc.), crystalline products with different composition, structure and morphology could be formed. It offers the uniform composition and control over the shape and size of the particles.

(3) The purity of product prepared in appropriate conditions could be high owing to re-crystallization in hydrothermal solution.

(4) The equipment and processing required are simple, and the control of reaction conditions is easier etc. So the hydrothermal synthesis is a good method for the preparation of oxide ceramic fine powders. The hydrothermal technique has been found to be one of the best techniques to prepare TiO_2 particles of desired size and shape with homogeneity in composition and a high degree of crystallinity.

Many groups have used the hydrothermal method to prepare TiO_2 nanoparticles from different precursors. Cheng et al.(1995) and Gao et al. (2003) used $TiCl_4$ as the precursor to synthesize uniform nanosize rutile and anatase particles. They made an attempt to discuss the influence of preparation conditions like concentration of $TiCl_4$ solution, pH in reaction medium, temperature, time and mineralizer on the formation, morphology, phase and a particle size of the TiO_2 products from coordination chemistry. X-ray diffraction revealed this TiO_2 to be anatase or rutile depending on the various process conditions and the average crystal size less than 8nm were observed.

Hydrothermal treatment for a microemulsion process had also been tried. Andersson et al. (2002) and Lu et al. (2008) had come up with a new microemulsion process combined with hydrothermal technique to overcome the difficulties involved in the general microemulsion process. In order to prevent grain growth of the nanoparticles, a new hydrothermal microemulsion process had been developed in their study. The former used tetra butyl titanate and the latter used titanium tetrachloride as the aqueous phase of the microemulsion. Andersson et al. (2002) found that if hydrochloric acid was used, the rutile structure formed, and if nitric acid was used, anatase formed. Lu and co-workers observed that the cryst size of the prepared TiO_2 powders increased with increasing pH value. The crystal size of TiO_2 powders was 6nm at pH 4. When the pH value was increased to 7, the crystallite size enlarged to 17nm.

Research on the mechanism of hydrothermal reaction has seldom been reported. The main reason could be that the related thermodynamic data under hydrothermal conditions are much scarcer and usually limited to the Gibbs energies at 398.15. Lencka and Rimanlo (1993) made a beneficial attempt; they studied “Thermodynamics modeling of hydrothermal synthesis of ceramic powders” and obtained some interesting results. But on the other hand, they also indicated the thermodynamic data used were most accurate at low and moderate temperatures and lose accuracy above ca. 473 K. SO far the knowledge and experimental data for ions in hydrothermal systems, especially more complex ions such as Ti^{4+}, $TiOH^{3+}$, $Ti(OH)_2{}^{2+}$, $Ti(OH)^{3+}$, etc., are less well known. These caused difficulty for the research on the mechanisms of hydrothermal reaction.

2.1.4.1 Influence of Hydrothermal conditions

Titanium dioxide prepared by the hydrothermal method can have different crystal structures and various morphologies, depending on the hydrothermal conditions. It could be concerned with the composition and structure of Ti(IV) complex ion in hydrothermal solution. The hydrothermal treatment conditions can be used to control the physical properties of the crystallined anatase powder, which in turn control the subsequent phase-change properties of the anatase/rutile phase change. The morphology and particle size of the powders depends on the hydrothermal conditions such as the concentration of precursor solution, pH in reaction medium, temperature, time and mineralizer etc.

2.1.4.2 Effect of pH & Concentration in reaction medium

The pH in the reaction medium had a significant effect on the phase of TiO_2 products. A very low pH indicates high acidity of the reaction medium which favors the formulation of rutile phase. Lu et al. (2008) found that the particle size of TiO_2 powders increased with an increase in the pH value of the microemulsion solution. The prepared powders had a large aspect ratio. This kind of morphology is considered to facilitate the crystal growth along a specific direction, thereby resulting in an increase in the crystal size.

2.1.4.3 Effect of temperature

Gao et al. (2003) studied the effects of hydrothermal conditions on the properties of TiO_2nano-crystals. They found that the specific surface area of the products decreases with the raising of the hydrothermal temperature and phase-pure rutile nanoparticles with specific surface area in the range of 56.5-202.2 m^2/g are obtained by the hydrothermal treatment of the $TiCl_4$ solution. The particle size of powders derived from a fixed concentration of $TiCl_4$ solution increases with the raising of the hydrothermal temperature. Accordingly, the specific surface area and the area-to-volume ratio decline with increasing temperature. The trend that non agglomerated particles formed at higher temperatures (such as 393 and 423 K) is also seen in the TEM micrographs.

2.2 Synthesis Of Cadmium Selenide (CdSe)

The synthesis of semiconductor nanoparticles has experienced an enormous development in the past two decades. CdSe, in particular, has been the subject of much basic research into the electronic and optical properties of quantum dots. The amount of literature dealing with this topic is too voluminous to review within the context of this thesis. Hence, initially we focus on the type of reaction systems considered to prepare the nanocrystals and the results of the effects of experimental parameters on the nanocrystals. Thereafter we focus on some key investigations that attempts to understand and eventually model the growth kinetics of CdSe nanocrystals.

2.2.1 Organic-based Systems

The most successful preparations that realize high quality nanocrystals with narrow size distributions entail the pyrolysis of organometallic precursors in hot coordinating solvents. Murray et al. (1993) pioneered this strategy by injecting cadmium and selenium precursors into a hot (300°C) solution of tri-n-octylphosphine oxide (TOPO) and maintaining growth at 230-260°C. The TOPO served multiple crucial roles by acting as the reaction medium, controlling the growth process, stabilizing the colloidal dispersion, and passivating the nanocrystal’s surface. This strategy produced TOPO capped CdSe nanocrystals with a tunable size range from 1.2 – 11.5 nm. The average size and the size distribution were dependent on the growth temperature, and growth appeared consistent with Ostwald ripening. They observed that as the size distribution sharpens, the reaction temperature must increase to maintain steady growth. Conversely, they add, if the size distribution broadens, the necessary temperature for slow steady growth decreases.

Adding a solvent, such as a primary amine, to TOPO has allowed researchers to overcome some of the disadvantages inherent in TOPO alone. Hines et al. (1998) found primary amines to provide superior passivation to bare nanocrystals, such as ZnSe, as they may provide higher capping density and boost the quantum efficiency. Furthermore, they allow for a higher reaction rate than TOPO, and monodispersity can be achieved quickly and maintained throughout the reaction. Knowing this, Talapin et al. (2001) tried to improve upon the original TOPO synthesis by introducing HDA (hexadecylamine). Exceptionally monodisperse samples (fwhm = 27-31 nm) were obtained, thus, the need for post preparative size-selective precipitation was eliminated. The alkylamines effectively passivated the bare CdSe nanocrystals allowing them to reproducibly reach quantum yields of 40-50%. The nature of the amines was found to be an important parameter in their system for growing nanocrystals with high quantum efficiency.

Alternatives to TOPO have been used due to TOPO's inherent hazards. For example, Qu et al. (2001) used a one-pot approach to produce CdSe nanocrystals in a fatty acid solvent, namely, stearic acid at a growth temperature set between 200°C and 320°C. Fatty acids are much less expensive and more environmentally friendly. This solvent system yielded nanocrystals in a broad size range (2 to >25 nm). They observed extremely fast reaction rates, compared with the traditional TOPO method, and stated that this solvent was ideal for synthesizing larger nanoparticles (>4 nm). The system did luminesce well with a quantum yield QY = 20-30%. The QY did tend to decrease with an increase in particle size.

Dickerson et al. (2005) also noticed rapid growth of CdSe nanoparticles in a reaction mixture comprised of 95% stearic acid, achieving a maximum QY of about 26% at a temperature of 255°C. Nanoparticles synthesized in dodecylamine obtained a maximum QY of 28% at a reaction temperature of 195°C. In general, the evolution of the QY and emission peak width (fwhm) correlated more consistently with the emission wavelength than with temperature. Furthermore, the nanoparticle radius was virtually unaffected by the initial Cd:Se ratio. They also observed that higher selenium levels led to the formation of more initial nuclei.

The advancement of TOPO-based preparations has served as the benchmark for the widespread success of producing CdSe nanocrystals. Early applications of CdSe are based on this strategy, such as the fabrication of a light-emitting diode and a single electron transistor. But the success has, in the recent years, been tempered by the need to maintain environmental benignity. As such, researchers have been motivated to develop alternative synthetic methods for the well-studied model system. Peng et al.(2002), in particular, discussed the drawbacks to using the organometallic synthetic approach in a hot coordinating solvent such as TOPO, citing toxic and hazardous conditions, expensive chemicals and sophisticated equipment.

Additionally, this approach is not easily controllable or reproducible, and only preparation of cadmium chalcogenides has been successfully developed.

2.2.2 Aqueous-based Systems

Another method commonly used to prepare nanocrystals uses an aqueous medium. Aqueous synthetic approaches are in general, simpler, less expensive, more reproducible, and scalable. Moreover, water-soluble materials are required for biological applications. Murray et al. (1993), Talapin et al. (2001), Qu et al. (2001), Mattoussi et al. (2000), Chan et al. (1998), Pellegrino et al. (2004), Wu et al.(2002) tried to prepare the nanocrystals in organic media, and then manipulate the surface through ligand exchange or application of a polymer shell to make it water-soluble. But these methods require more chemical processing. Researchers have investigated various types of precursors, stabilizers, heating technologies and other experimental parameters in attempts to further develop the aqueous-based method.

Zhang et al. (2000) produced cubic-structured nanocrystalline CdSe, with an average size of 5 nm, in an aqueous solution at room temperature. The reaction took place in an excess volume of alkaline selenium solution. This was done to prevent dilution of the selenium source so that selenium ion would not precipitate. A cadmium complex rather than cadmium ion served as the cadmium source; the complex proved to be more stable, greatly reducing the byproduct of cadmium hydroxide. A TEM image showed spherical but slightly agglomerated particles.

Xu et al.(2001) produced CdSe quantum dots in an aqueous solution using a gelatine stabilizer at room temperature. They observed quenched photoluminescence, suggesting inadequate passivation or overall low crystallinity. Li et al. (2005) realized highly photo luminescent CdSe nanocrystals from room temperature aqueous synthesis, followed by a low temperature chemical etching process. Prior to etching, the nanoparticles showed no photoluminescence. The etching process served to eliminate surface defects, thereby increasing the quantum efficiency to as high as 50%. Furthermore, they observed narrower size-distributions post-etching, with fwhm values as low as 30 nm, in addition to smaller size nanoparticles.

Sondi et al. (2004) synthesized CdSe nanoparticles in the presence of aminodextran (Amdex) in an aqueous solution at room temperature. The Amdex served as a growth stabilizer and capping agent. They produced CdSe nanocrystals with quantum yields of 15-16%. They observed wider particle distribution in the presence of Amdex compared with CdSe prepared in the conventional TOPO method. They attribute this to the wide molecular weight distribution of the polymer itself.

Water alone cannot provide a ligand suitable for stabilizing and/or passivating the nanocrystal surface. Therefore, judicious effort must be taken to provide a ligand or capping agent that is soluble and can withstand the reaction conditions. The above examples describe a variety of capping agents that served the researcher’s purpose. Gaponik et al. (2002), Herron et al. (1993) used thiols in aqueous solutions, however, in their effort for producing cadmium telluride, and CdS-core clusters.

Rogach et al. (1999) extended the use of thiols to CdSe nanocrystal synthesis. They prepared CdSe in higher temperature aqueous-solutions using various thiols as a stabilizer. One preparation involved refluxing the solution for different lengths of times, resulting in larger nanoparticles at longer times. They noticed that, during the heating of the solution, particle growth proceeded about 5 times faster in the presence of thioacid-stabilized CdSe compared with thioalcohol-stabilized CdSe. As a result, thioacid-stabilized CdSe nanocrystals were larger (2.1-3.2 nm) than thioalcohol-stabilized samples (1.4-2.2 nm). The CdSe samples prepared showed a quantum yield of less than 0.1%.

Deng et al. (2006) also synthesized citrate-stabilized CdSe nanoparticles in water at 75°C. They incorporated a photoactivation procedure by exposing the nanoparticles to ambient light for a few days, hypothesizing that this would eliminate topological surface defects. They noticed a trend of increased QY with prolonged exposure to ambient light, reporting a final QY of 4%. They also reported a decrease in the nanoparticle size with an increase in the pH, further noticing that nanoparticles prepared in a pH = 9.1 displayed stronger luminescence properties than those prepared at pH = 8 and 10. They investigated the effects of the initial Cd:Se molar ratio on the nanoparticle properties, and found that the photoluminescence intensity increased as the ratio increased from 2 to 10. Also, the fwhm narrowed to 37 nm as the molar ratio increased.

Most recently, Gao et al. (2007) prepared CdSe nanocrystals in water, and then fabricated an LED by redispersing the as-prepared nanocrystals in a surfactant to transfer them to an organic solvent. They noticed that by changing the molar ratio of cadmium and selenium and the reflux time, different size nanocrystals were obtained. The average size obtained was just under 10 nm. Of interest were two characteristics of the integrity of the nanocrystal. The photoluminescence spectra showed weak emission, but electroluminescence spectra displayed strong emission. Basically, the electron transport inside the crystal was quite good as it served to act as an electron carrier while a polymer acted as an electron hole. By applying a voltage between the two entities, an exciton was formed. These results provide more substantive proof that the promise of CdSe can be realized as a device component when fabricated in an aqueous medium.

Zhang, Liu et al. (2003, 2003) reported that aqueous-based reactions above the boiling point (130-180°C) for synthesis of various semiconductor nanocrystals such as CdTe and CdSe. As-prepared CdTe nanocrystals prepared by Zhang et al. evolved from 2 to 4 nm within 2 hours of growth. They exhibited a QY of 30% without any post-preparative treatment. Liu et al. (2003) prepared polymer-capped CdS nanoparticles with an average diameter of 8 nm and an fwhm of ~42 nm. Qian et al. (2005) prepared alloyed CdSe-CdS nanocrystals at a reaction temperature of 140°C for 1 hour. Because of the CdS shell, the QY measured at 25%. They found that after a short heating time (less than 1 hour) the QY measured <0.1%. The prolonging of the heating time allowed the CdS shell to mature on the CdSe surface. The fwhm was about 28 nm. They note that their method of heating, microwave irradiation, greatly accelerated the growth compared with conventional aqueous synthesis. Other hydrothermal methods have produced semiconductor nanocrystals as reported by Rajamathi et al. (2002).

Chen et al. (2000) reported a simple method for the preparation of crystalline and water soluble CdS and CdSe nanorods via arrested precipitation from their respective inorganic ions in a micellar solution. All reactions were performed under ambient conditions. *Two separate precursors microemlusion prepared in CTAB micellar solution. After careful mixing under sonication, CdSe/CdSnanorods precipitates with significant colour change at lower part of solution. The solution exhibited optically clear colors ranging from yellow to orange (for CdS samples) or orange to dark red (for CdSe samples).* They reported that nanorods exhibited zinc-blende structure for CdSe and wurtzite structure for CdS. Their results indicated that the shape transition of CTAB micelles may occur from rod to sphere (or vice versa) depending on the aliphatic hydrocarbons (cyclohexane) added. In this case, cyclohexane molecules may incorporate into bilayers and subsequently induce the morphologic changes of bilayer vesicles.

Chen et al. (2005) reported that single crystal CdSe nanorods with diameters in the range of 40-60nm and aspect ratios of 5-8 were successfully synthesized at 180°C for 10 hour through a facile surfactant-assisted hydrothermal method, using Na2SeO3 as a high-quality soluble selenium source. Through varying the concentration of surfactant (CTAB), the morphologies changed from dendrite-like nanostructures to nanorods, short nanorods, and nanoparticles. The surfactant plays a vital role in the synthesis of nanorods through effectively restraining the agglomeration and favouring the formation of 1-D nanostructure.

Xi et al. (2007) synthesized hexagonal CdSe nanorods using novel *microemulsion* method at moderate temperature. They found that using surfactant (AOT) and hydrazine hydrate, it is possible to control the morphology of the CdSe nanoparticles. The hydrazine hydrate acts as both a reducing agent and a templating agent that favors the formation of the rodlike structure. Experimental procedure indicated that the reaction completed in 6 hr under N2 environment resulting deep dark red precipitates of CdSe nanoparticles. They reported influence of mole ratio of Water to AOT and hydrazine hydrate to AOT on as-prepared CdSe morphologies.

Williams et al. (2007) reported feasibility of CdSe nanoparticles synthesis in high-temperature water. The base-case experimental conditions (T=200°C, Cd/Se molar ratio = 8:1, and a reaction time = 1.5 min) produced nanoparticles that exhibited quantum confinement behavior. The quantum yield was 1.5%, but it was easily increased to approximately 7% by adding a CdS shell. The mean particle size increased with increasing reaction time, temperature, stabilizer concentration, and Cd/Se ratio. The mean particle size decreased with increasing pH. They suggested that hydrothermal synthesis method may provide new opportunities to engineer nanoparticle production systems.

Further to earlier work, Xi et al. (2008) synthesized one-dimensional wurtzite CdSe nanoparticles with a diameter of 43±6 nm and an aspect ratio of 3.7±0.6 through a novel *reverse micelle assisted hydrothermal method* at a relatively low temperature.

This method combines the advantages of the hydrothermal method's ability to achieve good crystallinity with the well-controlled growth *offered by the reverse micelle method*. The morphology of the nanoparticles can be controlled by the amount of AOT, hydrazine hydrate and reaction temperature. It was proposed that AOT controls the length while hydrazine hydrate controls the diameter of the growing nanocrystals.

2.2.3 Growth Kinetics

One important aspect of Murray's work (1993) with TOPO involved a temporally discrete nucleation event followed by relatively rapid growth from the monomers in the solution. This permits a controlled growth of the nanocrystals. The challenge then is to understand the mechanisms behind the nucleation and growth. Researchers have just recently begun to study and understand the kinetic behavior of CdSe growth under a variety of reaction conditions.

Bullen et al. (2004) investigated the effects of temperature and an oleic acid stabilizer on the growth kinetics of CdSe nanocrystals in octadecene, a non-coordinating solvent. They observed increasing oleic acid concentrations led to lower nuclei concentrations, smaller nuclei size and larger final particle size. They also observed that at higher temperatures, particles nucleated with smaller radii than those present at lower temperatures. This, according to them, indicated that the nucleation is faster as temperature increases and that growth kinetics are less strongly dependent on temperature. Consequently, higher temperatures produced more nuclei.

Peng et al. (1998) discussed the focusing of size distributions and its effect on nanocrystal growth. After growing CdSe nanocrystals in TOPO at 200°C, they observed an initial large size distribution (~20%) for particles with an average diameter of 2.1 nm, and two distinct kinetic regimes. During the first 22 minutes, the size increased rapidly and the initial size distribution of particles began to narrow to ~7.7% (average diameter of 3.3 nm). The nanocrystals then grew more slowly and the size distribution broadened to about 10.6% (average diameter of 3.9 nm). The reason for this broadening was the occurrence of Ostwald ripening. Upon a second injection of precursor, the size distribution began to narrow and decreased to 8.7%. They later emphasized the importance of maintaining a high enough precursor concentration so that the system does not experience Ostwald ripening which could lead to broader size distributions.

Qu et al. (2004) introduced an in situ method for the study of the nucleation and growth kinetics of CdSe nanocrystals. Their observations suggest that the growth process can be divided into four stages. The first stage is the nucleation where the total number of particles increases as a result of nuclei forming. The second stage shows a significant drop in the concentration of the particles, and a narrowing of the size distribution. They contend that the decrease of the particle concentration could not be seen ex situ. A third stage, the stable stage exhibited equilibrium between the monomers and the particles in solution. The monomer concentration was close to the solubility of the particles in solution, so little to no growth was occurring. The fourth stage is Ostwald ripening, and thus a broadening of the size distribution occurs.

It is apparent that Ostwald ripening, although regarded as the primary means of growth in earlier research, is not easily controllable, and, because of recent insights in kinetic behavior, can possibly be avoided. Peng et al, (1998) above, provides one example of a solution to prevent Ostwald ripening from occurring. More important, however, is determining where, in the kinetic regime, growth is at its optimum. This understanding is crucial for the control of the growth process. It can also serve as a conceptual framework for developing large-scale systems that can produce uniform particles under optimum conditions.

Dushkin et al. (2000) supplied a comprehensive study of the kinetics of CdSe nanocrystal growth in a hot amphiphile (TOPO) matrix. They solved kinetic equations, based on classical theory, to derive analytical expressions for the mean radius and variance of the size distribution. They considered the growth to be a two-stage process in order to describe the time variation of nanoparticle size. During the first stage, called reaction-limited growth, they noticed the size of the initial nuclei rapidly increased and caused an exhaustion of reactants at the nanoparticle surface. The growth also favored a size focusing or narrowing of the size distribution. Further development of the nanocrystal followed classic diffusion-limited growth. The size distribution began to broaden at this time, however, increasing in proportion to the average particle size. Their theoretical model was in good agreement with their experimental observations. They conclude that the reaction-limited growth is important to obtain well-defined nanocrystals of high quality. Good, precise control of the nucleation process is the key to reproducible uniform nanoparticles, but, unfortunately, how to control this process is still unknown.

Dickerson et al. (2005, 2005) saw the need for developing analytical expressions that would yield the activation energy for CdSe growth in a given reaction solvent. Citing the need for eventual commercialization as a reason for measuring activation energies, they developed expressions based on synthesis time, temperature and reactant concentration. Their model yielded activation energies for nanocrystals prepared in TOPO and stearic acid.

2.3 Conclusions

Loryuenyong et al. (2012) prepared TiO_2 nanoparticles by a sol-gel process, employing titanium(IV) tetraisopropoxide as starting precursor and ethanol/ isopropanol as an alcoholic solvent. The synthesized mesoporous TiO_2 was calcined at 300-700^0 C. It was found that pore collapsing, crystallite growth, and anatase-rutile phase transformation occurred with an increase in calcination temperatures. The use of isopropanol solvent was likely to inhibit the anatase-rutile transformation through the control of hydrolysis rate. The photocatalytic property of TiO_2 consisting predominantly of anatase crystallites improved the degradationof methyleneblue under UVC light. Compared to ethanol, enhanced photocatalytic activity was obtained with isopropanol solvent through the thermal stability of anatase phase. The sol-gel method is a versatile method for the synthesis of the doped nanomaterial with very high surface area to volume ration. The incorporation of a metal ion in the sol during the gelation stage allows cations to be uniformly incorporated into the host lattice. Thus, metal ions such as Ca_2^+, Sr_2^+, Ba_2^+, Cu_2^+, Fe_3^+, V_5^+, Cr_3^+, Mn_2^+, Pt_4^+, Co_2^+, Ni_2^+, Pb_2^+, W_6^+, Zn_2^+, Au_3^+, Zr_3^+, La_3^+, Ag^+ and Eu_3^+ were introduced into TiO_2 powders and films by this method, and the photocatalytic activity was improved to varying extent.

Cong et al.(2006), synthesized nitrogen-doped nanocrystalline TiO_2 by microemulsion-hydrothermal process under nitric or hydrochloric acid environment. This did not require high calcinations temperature and thus averted the agglomeration and sintering of the TiO_2 particles. The photocatalytic activity for the decomposition of rhodamine B by TiO_2 was greatly improved as compared with the undoped samples under visible light irradiation.

Desorsola et al.(2009) adopted water-in-oil microemulsions to produce ultrafine and nanometric particles. The synthesis of TiO_2 nanoparticles has been carried out from a $TiCl_4$ solution emulsified into the oil phase. Precipitation of spherical and ultrafine particles occurred due to the high instability of Ti precursor and the interaction among nanodroplets.

Namin et al.(2008), reported TiO_2 nanoparticles prepared by precipitation of $TiCl_4$ aqueous solution with ammonium hydroxide as precipitation agent. In their report, freshly prepared TiO_2 gel was allowed to crystallize under refluxing and stirring condition for 6 h over 90^0 C and oven dried over-night in temperature above 100^0 C.

Wang et. Al (2011) prepared $TiO_2 – Al_2O_3$ supports with high specific surface area and large pore diameter using ultrasound-assisted precipaitation. Ultrasound could produce the strong chemical and mechanical effects, which was beneficial to inhibit the agglomeration of the nanoparticles. Using anhydrous ethanol to replace the water in the as-prepared support could hinder the particles agglomeration and then increased the specific surface area and the pore diameter significantly. Adding CTAB in the as-prepared support before calcinations could enlarge the pore volume greatly.

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