PREPARATION OF SILICA NANOPARTICLES USING MICROEMULSION TECHNIQUES

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology

In

Chemical Engineering

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2008

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CERTIFICATE

This is to certify that the thesis entitled,
"PREPARATION OF SILICA NANOPARTICLES USING MICROEMULSION TECHNIQUES"

Submitted by Mr. Bikash Ranjan Mallick & Mr. V Ganesh Aditya

In partial fulfillments for the requirements for the award of
Bachelor of Technology Degree in Chemical Engineering
At National Institute of Technology, Rourkela is
An authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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ACKNOWLEDGEMENT

I would like to make my deepest appreciation and gratitude to Prof. Santanu Paria for His invaluable guidance, constructive criticism and encouragement during the course of this project.

We would like to thank Prof. R. K. Singh for being a uniformly excellent advisor. He was always open minded, helpful and provided us with a strong broad idea.

I would like to express my gratitude to Shri Rakesh Pattnaik for helping us in characterizing the samples under the SEM.

Grateful acknowledgement is made to all the staff and faculty members of Chemical Engineering Department, National Institute of Technology, Rourkela for their consistent encouragement.

I would also like to extend my sincere thanks to all my fellow students (UG, PG and Research) for their time, invaluable suggestions and help. In spite of the numerous citations above, the author accepts full responsibility for the contents that follow.

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ABSTRACT

Silica nanoparticles have been prepared in this work using water in oil (W/O) emulsion system at room temperature that employs a water-soluble amine as catalyst and tetraethylorthosilicate (TEOS) as the silica source. The pH value of the aqueous phase and the water: surfactant ratio were found to be the key factors contributing to the formation and final size of stable and regular spherical silica particles. When the pH value of the aqueous phase was controlled between 8 and 9, silica particles could be synthesized. The shell thickness of the hollow particles as and when prepared was found to increase with the length of the hydrocarbon tail of the amine catalyst. The viscosity of the external oil phase determined the shape regularity of the spherical silica hollow particles. The kinetics of the formation of silica hollow particles was believed to be based on the difference between the hydrolysis rate and the condensation rate of TEOS, which can be adjusted by the pH value of the aqueous phase. After treating the core-shell particles with concentric nitric acid, the hollow silica spheres were obtained correspondingly. The particles were characterized by Scanning electron Microscope (SEM), Optical Microscope and UV Spectrophotometer. The study shows that through further processing, advanced materials could be prepared; and that the hollow silica spheres could be potentially used as a novel class of catalyst supports.

***Keywords*:** Scanning electron microscopy(SEM); Colloids; Nanoparticles; Silica; Silicates; R Ratio; Solution chemistry;

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Chapter 1

GENERAL INTRODUCTION

Nanotechnology has emerged as a promising vehicle for an emerging scientific and technological revolution. Richard Feynman, in his seminal 1959 lecture, proposed a variety of potential nanomachines, which could be engineered to a higher level of functional efficiency than currently available manufactured devices by exploiting changes in the behavior of matter at the nanometer length scale. In order to realize this goal, scientists and engineers have to devise strategies to synthesize specified functional nanoparticles, and then learn how to incorporate them into devices in which they might function individually or in cooperation with other nanoparticles or devices. This "bottom up" approach of "nanoparticle design" followed by "device assembly from nanoparticles" is widely accepted as a promising route to nanotechnological applications, separate from a more traditional "top down" approach followed in semiconductor and electronics research. In recent years, "bottom up" nanotechnology has led to promising innovations in fields such as biotechnology, electronics and catalysis. This approach also could potentially address the ever-present need to miniaturize components, especially in the electronics industry.

Today it is widely accepted that reduction in size to a molecular level (nanometer scale) cannot be achieved with conventional "top down" methods (e.g. photolithography, etching etc). Thus, nanoparticle-based (or "single-molecule" based) device development is emerging as a fundamental requirement in realizing the goals of nanotechnology. Single-molecule devices can be faster, more precise, and more efficient in energy utilization than devices made of bulk materials. Numerous molecules having electronic properties have hence been identified and reported [1]. Single molecule logic gates and circuits have been theorized and detailed molecular designs have been put forward for actualization and incorporation in solid state electronics. Biotechnology is also stressing the need for nanoscale devices for a variety of applications, notably in DNA sequencing and biosensing.

The nanometer scale of these structural features offers unique engineering challenges. First, there is little quantitative understanding of the processes governing the controlled synthesis of important synthetic nanoscale materials like nanotubes, nanowires and nanodots which could be used as components of such devices. However, knowledge of these processes is essential for rational design of nanodevices, since fine control over dimensions, structure, and composition is key to

producing nanomaterials suitable for incorporation in devices. Additionally, the properties of any nanoscale system are controlled by "molecular" physics and confinement effects as opposed to "bulk" physics, and it is well known that the functional properties of nanomaterials are usually very different from the corresponding bulk materials. Once the synthesis-structure-size-shape-property relations of a nanoparticle are accurately determined, one can begin to rationally address the next set of problems such as manipulation of the nanoparticle and direction to a specific location in a device, and connection of the device to a larger system or collection of devices.

1.1 NANOPARTICLES

Nanoparticles can be defined as materials and systems whose structures and components exhibit novel and significantly improved physical, chemical and biological properties, phenomena and processes due to their nanoscale size i.e. in a range of 1-100nm. Nanotechnologies have become one of the promising research areas which might bring a significant progress into material and device development. At present, there is a wide spectrum of technological approaches capable of producing nanoparticles and simple nanostructures, however, none of them can be considered as an ideal and generally acceptable tool.

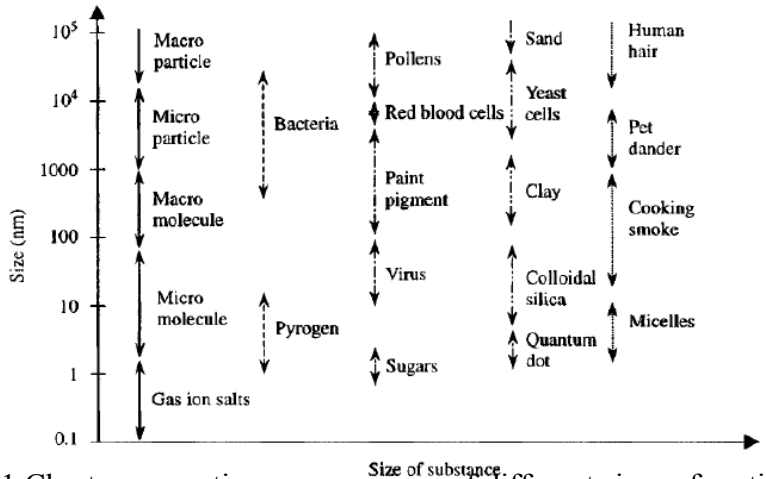


Fig 1.1 Chart representing a comparison of different sizes of particles[2]

In addition to surface microscopy, scanning probe microscopes (SPM) find their application in fabrication of nanostructures and nanodevices as well as they represent a technique for the serial processing of surfaces, they have been exclusively used for

applications in laboratory-scale experiments on building the nanostructures and verification of their fundamental properties.

1.2 MICROEMULSIONS

A microemulsion is a thermodynamically stable dispersion of two immiscible fluids; the system is stabilized by added surfactant Different types of microemulsion are known, such as water-in-oil (w/o), oil-in-water (o/w), water-in-sc-CO_2 (w/sc- CO_2). A "water-in oil" microemulsion is formed when water is dispersed in a hydrocarbon based continuous phase, and is normally located towards the oil apex of a water/oil/surfactant triangular phase diagram

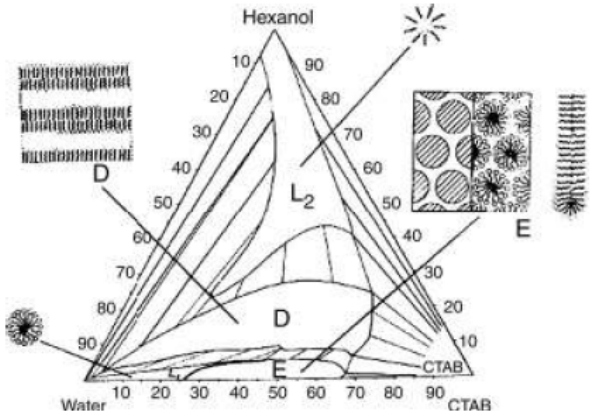


Fig 1.2 Phase diagram for CTAB/1-hexanol/water systems[3]

In this region, thermodynamically driven surfactant self-assembly generates aggregates known as reverse or inverted micelles (L_2 phase on Fig. 1) spherical reverse micelles, which minimize surface energy are the most common form. Added polar or ionic components will become compartmentalized into the central cores of these reversed micelles, hence affording fine dispersion of inorganic materials in oil. It is important to recognise that these systems are dynamic — micelles frequently collide via random Brownian motion and coalesce to form dimers, which may exchange contents then break apart again [4,5]. Clearly, any inorganic reagents encapsulated inside the micelles will become mixed. This exchange process is fundamental to nanoparticle synthesis inside reversed micellar 'templates', allowing different reactants solubilized in separate micellar solutions to react upon mixing. Micelles in these systems can be described as "nanoreactors", providing a suitable environment for controlled nucleation and growth. In addition, at the latter stages of

growth, steric stabilisation provided by the surfactant layer prevents the nanoparticles from aggregating.

1.3 METHODS OF PREPARATION

Generally, nanostructures with hollow interior are commonly prepared by coating the surfaces of colloidal particles (e.g., silica bead, silver or gold colloids, and polymer latexes) with thin layers of the desired materials (or its precursor), followed by selective removal of the colloidal templates through wet chemical etching or calcinations. It was reported that some inorganic hollow spheres had been prepared by different methods, involving the synthesis of intact inorganic shells around sacrificial templates and in situ templates. The main disadvantage using pyrolysis is that costly equipment is required. In addition, precipitation method has been successfully employed. However, this method was affected by many factors, such as precipitation agent, pH, and temperature and solution concentration; hence the process is difficult to control.

Most of the work involving nanoparticle preparation using microemulsions has focused on forming nanoparticles through a reaction carried out by mixing two identical microemulsions each containing one of the reactants forming the nanoparticle. For rapid reactions, the mixing of two microemulsions technique is limited by the solubilizate exchange dynamics. Slow solubilizate exchange dynamics contributes to simultaneous nucleation and aggregation, which in turn results in large particles with wide size distribution. Intermicellar exchange of solubilizate is achieved through a Brownian motion of the reverse micelles, surfactant layer opening upon coalescence, diffusion of the solubilizate molecules, and finally decalescence to reverse micelles. In one approach of forming nanoparticles aimed at minimizing the role of the surfactant surface layer opening by means of a direct reaction with the surfactant counter ion in a single microemulsion. Another involved the direct formation of nuclei of the nanoparticles while accommodating the aqueous solution of the added reactant into the water pools of the reverse micelles due to the presence of the counter ion in each reverse micelle.

1.4 ORGANIZATION OF PROJECT REPORT

Preliminary introduction about nanoparticles, hollow silica spheres, types and properties of micro-emulsion, various methods of preparation and organization of project report is discussed in chapter 1. Chapter 2 provides a detailed discussion of literature on the mechanism & techniques of reaction, effects of important parameters on the final results. The main objective of the present work, which is based on the literature survey on preparation of silica nanoparticles, is presented towards the end of chapter 2. In chapter 3, the various techniques used in the present work such as materials used, preparation of micro-emulsion, preparation of nanoparticles are described in detail. Chapter 4 describes the results and characterization of the particles formed in the solution. Finally, conclusions of project work are given in Chapter 5.

Chapter 2

LITERATURE REVIEW

There are many methods proposed by many works to prepare hollow nanoparticles. Among them most popular, significant, and cost effective methods are core – shell templating method, solvothermal method, sol – gel method, self assembly, and last but not least is microemulsion method.

Many technologies have been explored to fabricate nanostructures and nanomaterials. These technical approaches can be grouped in several ways. One way is to group them According to the growth media:[6]

1. Vapor phase growth, including laser reaction pyrolysis for nanoparticle synthesis and atomic layer deposition (ALD) for thin film deposition.
2. Liquid phase growth, including colloidal processing for the formation of nanoparticle and self assembly of monolayers.
3. Solid phase formation, including phase segregation to make metallic particles in glass matrix and two-photon induced polymerization for the fabrication of three dimensional photonic crystal.
4. Hybrid growth, including vapor-liquid-solid (VLS) growth of nanowires.

Another way is to group the techniques according to the form of products:

1. Nanoparticles by means of colloidal processing, flame combustion and phase segregation.
2. Nanorods or nanowires by template-based electroplating, solution-liquid-solid growth (SLS) and spontaneous anisotropic growth.
3. Thin films by molecular beam epitaxy (MBE) and atomic layer deposition.
4. Nanostructured bulk materials, for example, photonic band gap crystals by self assembly of nanosized particles.

In most of the preparation methods, it's very difficult to control size and shape of the particle except microemulsion method, in which we need to control one thing and that, will control everything for particle synthesis.

2.1 **TEMPLATE METHOD**

In the template formation technique the basic formation principle involves the template cores to be sacrificed by either dissolution or calcination at high temperature in order to achieve hollow spheres, while the osmotic pressure will usually deteriorate the shell integrity resulting in perforation or fracture. Alternatively, soft template cores for example emulsion droplets, gas bubbles, quasireverse emulsions, are used to synthesize hollow spheres.

The cores can be easily removed by evaporating liquids at elevated temperature. However, composition of the coating materials is rather restricted, and the weak liquid cores are easily deformed and coalesced during synthesis. To avoid using core templates, hollow spheres such as polyelectrolyte capsules, viral capsids, vesicles have been recently used as templates to synthesize composite hollow spheres. During the template synthesis using viral capsids, materials usually grow in the cavity rather than within the shell. It is not easy to form composite shells. The hollow spheres such as polyelectrolyte capsules, viral capsids, vesicles have been recently used as templates to synthesize composite hollow spheres. During the template synthesis using viral capsids, materials usually grow in the cavity rather than within the shell. Polymeric gels are such interesting materials with tunable chemistry and physical environment, which can be used as templates to induce favorable growth of materials with varied composition through specific interactions. When LBL assisted polyelectrolyte gel hollow spheres are used to prepare composite hollow spheres, ionic cross-linking nature within the shell significantly sacrifices the functional groups such as proton ions.

In this method, first of all, a core is prepared by using inorganic or organic material. Then using Si or Ag a shell is formed around the core by layer by layer deposition or by using something other procedure. Then core part is removed by treating core – shell particle with acid at suitable concentration or by calcinating the core – shell particle, which produce a hollow shell particle. The main disadvantages in this case, are, we have to choose an appropriate cell particle, on which shell can be formed, and which could be easily removed after formation of the particle. Secondly, we have to maintain most suitable acid or other solvent to dissolve cell.

Given below are some examples of template method:

2.1.1 PREPARATION OF HOLLOW NANOPARTICLES AS A TEMPLATE UNDER SONICATION

Cyclodextrins (CDs), torus-shaped cyclic oligosaccharides consisting of six or more 1, 4-linked D-glucopyrannose units, are usually used to fabricate some new structured materials. Some modified CDs could form nanospheres by the aggregation among the interaction of molecules. 2-Hydroxypropyl- β-cyclodextrin (2-HP-β-CD) is one kind of derivatives of CDs and has been widely applied to design new pharmic carrier system because of its very good solubility in water [7]. Now is used their complex structure and valence state results in to from various stoichiometries. CuS shows metallic conductivity and transforms at 1.6 K into a superconductor. The photoelectric properties of the copper sulfide can be used as the quantum dots in photoelectron transformation devices.

Sonication is act of applying energy to agitate particles in a simple, for various purposes. It can used to speed dissolution, by breaking intermolecular bonds. It's specially useful when its not possible to stir samples [7].High-intensity ultrasound is induce for the fabrication of copper sulfide hollow nanospheres in water solution containing $Cu(CH_3\text{- }COO)_2$, thiourea and 2-HP-β-CD. At the end of the reaction, a great amount of black precipitates occurred. The sonication was conducted without cooling so that a temperature of about 330 K was reached at the end of the reaction. After cooling to room temperature, the precipitates were centrifuged, washed with distilled water and dried in air at room temperature.

Without 2-HP-β-CD, the prepared products were aggregation composed of CuS nanoparticles. With 2-HP-β-CD adding into the solution, the products were semi-hollow spherical structures. When 2-HP-β-CD was added into the solution, the product changed to be uniform CuS hollow spheres with average size of 30 nm. Thus with increase in quantity the size of the sphere also increases.

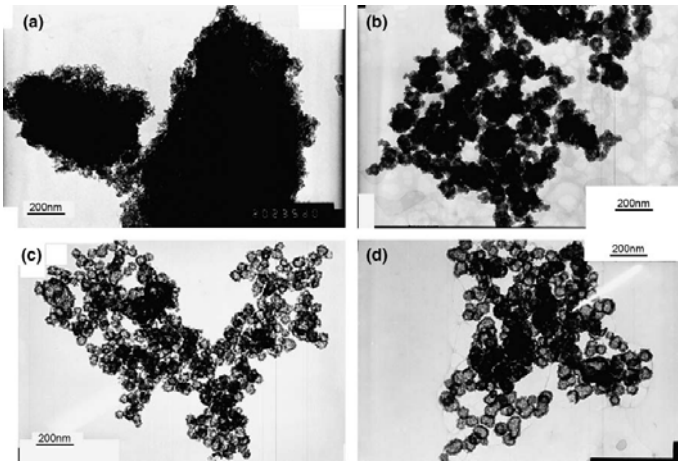


Fig 2.1.1 TEM images of CuS samples prepared under different conditions: (a) without 2-HP-b-CD (b) 2 g 2-HP-b-CD (c) 4 g 2-HP-b-CD (d) 8 g 2-HP-b-CD[8]

The Cu ions would be absorbed by the 2-HP-β-CD to form the Cu–HP-b-CD complex. When the mixture solution is exposed under ultrasound, the 2-HP-β-CD molecules would cross-link with each other through the hydroxyls and hydroxypropyls. Due to the special structure of the 2-HP-β-CD, the cross-link of the particles inclined to form the sphere-like structure. Therefore the higher concentration of 2-HP-β-CD led to bigger spheres. In the initial stage, the Cu ions would be absorbed on 2-HP-β-CD molecules to form a homogenous complex spheres. As shown in the Figure 2.1.2, the cup-like part of the 2-HP-β-CD model would appear on the surface of the spheres.

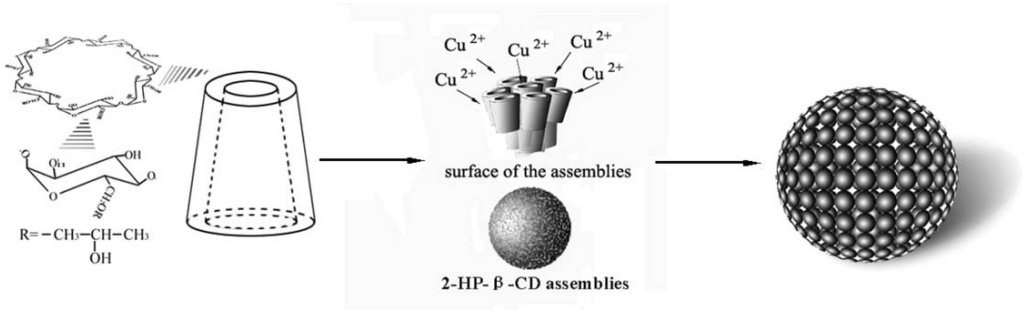


Fig 2.1.2 the possible mechanism for formation of hollow spherical assemblies[8].

Hence parts of the Cu ions would be exposed on the surface of the spheres equably. In the presence of sonication, the S ions could be released slowly into the solution and first reacted with the Cu ions on the surface of the complex spheres giving rise to the

CuS nuclei. Due to the strong adsorption ability of 2-HP-β-CD, the nuclei could also be adsorbed on their surface. With time increasing, the nuclei would grow up until the particles become stable. At the end of reaction, the process led to hollow spherical structure with one-layer shell.

2.1.2 PREPARATION OF HOLLOW NANOPARTICLE THROUGH A SELF-TEMPLATING SOLID GAS INTERFACE REACTION

In this method same material is being used for both reactant and templates for hollow nanosphere formation. Aluminum nanoparticles were synthesized by hydrogen plasma metal reaction. An aluminum ingot was melted and evaporated by arc in a 1:1 mixture of argon and hydrogen[9]. The evaporated Al condensed into nanoparticles when leaving the hot plasma area and were transported into a filter for collection by circulate pumping. The Al nanoparticles were passivated with a mixture of argon and air to prevent the particles from burning before removing from the collector. The synthesis of nanosized AlN hollow spheres was carried out in a horizontal quartz tube furnace. Al nanoparticles were loaded in a ceramic boat which was placed in the center of the tube furnace. The system was first evacuated to 0.6 Pa and then flushed with 99.99% Ar three times to remove oxygen and moisture. The system was then filled with Ar to 1 atm and was heated to 1000°C at 20 C/min under a constant Ar flow of 100 standard cubic centimeters per second (sccm). When the furnace temperature reached 1000°C, the gas flow was switched to a mixture of 25 sccm Ar and 25 sccm NH_3 (99.99%). The system was maintained in that condition for 3 h before it was allowed to cool down to room temperature in a pure argon flow. The powder in the ceramic boat turned from black to gray. Thus hollow nano particle is prepared.

When the AlN layer is formed at the surface of each Al nanoparticle through the interface reaction, the Al and N atom have to pass through the AlN layer by solid-state diffusion to meet each other to form AlN. Aluminum was established to be the dominant diffusion species in the Al–N diffusion couple. Therefore, there will be a net outward matter flux and an inward vacancy flux for compensation due to the outward diffusion rate of Al is much faster than the inward diffusion rate of N. The vacancies

accumulate at the center of the nanoparticle, leading to the void formation. The vacancy involved diffusion mechanism is known as the Kirkendall effect which was first proposed by Kirkendall [10] .This effect has been known to cause void formation for a long time. Kirkendall effect usually involves the self-templating effect of one precursor. No additional template agents are needed, which makes this approach an economic way to obtain hollow structures.

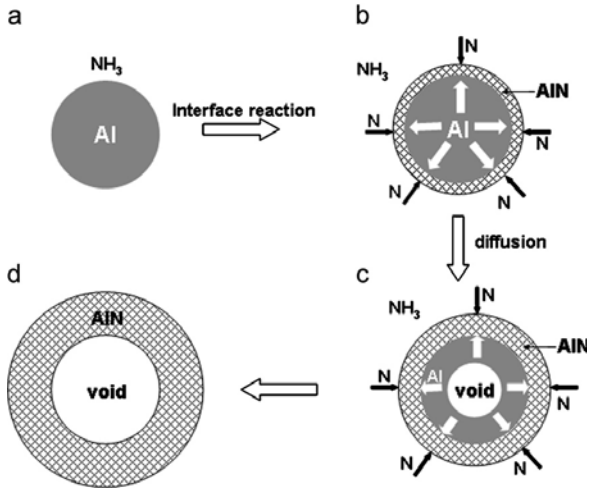


Fig 2.1.3 schematic illustration of the formation process of Nanosized AlN hollow spheres[9]

A schematic illustration of the formation process of nanosized AlN hollow spheres through interface reaction is shown in Figure 2.1.3. Aluminum and nitrogen atoms diffuse across the AlN layer to continue the reaction and thicken the AlN shell. But the outward Al diffusion is much faster, leading to the void formation in the central area. The Al core is gradually consumed and a spherical shell is formed, with its cavity size close to that of the Al precursor nanoparticle. Thus nanosized AlN hollow spheres with cavity diameter from 15 to 100nm and wall thickness from 5 to 15 nm were produced by a simple heat treatment of aluminum nanoparticles in ammonia.

2.1.3 PREPARATION OF MONODISPERSED HOLLOW SPHERE

Usually in all the sacrificial templating method, seed growth and core separation are done in two different processes. But in this method both work are done through one mechanism simultaneously. Here monodisperse hollow Ag and Ag/Au submicrometer spheres have been synthesized by a facile colloidal templating method. The silver

nanoparticle seeds are synthesized on the silica colloids surface through the electroless plating approach to avoid the complex surface functionalization, and the subsequent seeding growth and dissolving silica core are carried out simultaneously. The prepared hollow spheres remain mostly the fine monodispersity and spheric shape of the silica core, and can self-assemble directly into ordered structure.

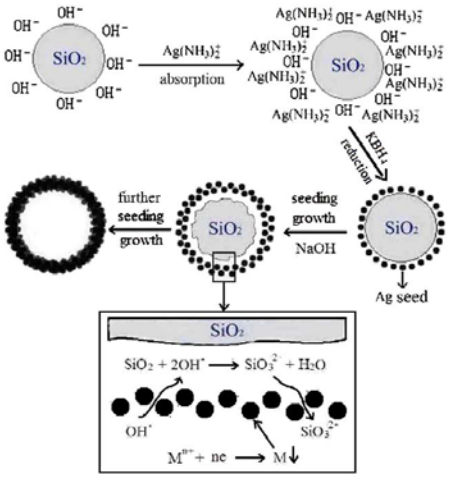


Fig 2.1.4 Fabrication procedure of hollow spheres[10]

Fig 2.1.4 shows the preparation procedure of the monodisperse hollow Ag and Ag/Au spheres[10]. First of all, silica colloids were dispersed in ethanol containing PVP(polyvinylpyrrolidone), then $[Ag(NH_3)_2]^+$ (0.1 M) ions solution was added quickly under stirring at room temperature, and the complex $[Ag(NH_3)_2]^+$ ions were absorbed by the negatively charged Si–OH groups on the surface of the silica colloids. Then, the colloids were washed with ethanol by centrifugation and ultrasonic dispersion to remove the excessive $[Ag(NH_3)_2]^+$ ions, and dispersed in ethanol. Then, KBH_4 solution was added quickly to reduce the $[Ag(NH_3)_2]^+$ ions, and the surface of the colloids was covered uniformly with silver nanoparticles. Then, after sometime the colloids were washed with distilled water to remove the excessive KBH_4. Silica colloids after seeding were added into aqueous ethanol in which the ethanol–water volume ratio is 1:1. Then, 10% HCHO diluted with distilled water was added dropwise to grow the silver nanoparticles. During the seeding growth procedure, with increasing the shell thickness, the silica core is dissolved gradually:

$$SiO_2 + 2OH^- \rightarrow SiO_3^{2-} + H_2O$$

The shell made of silver nanoparticles on the surface of the silica colloids after surface seeding is incomplete, both OH^- and SiO_3^{2-} can diffuse across this shell until the silica core has been completely consumed. Controlling the amount HCHO, monodisperse hollow Ag spheres with controllable shell thickness can be obtained.

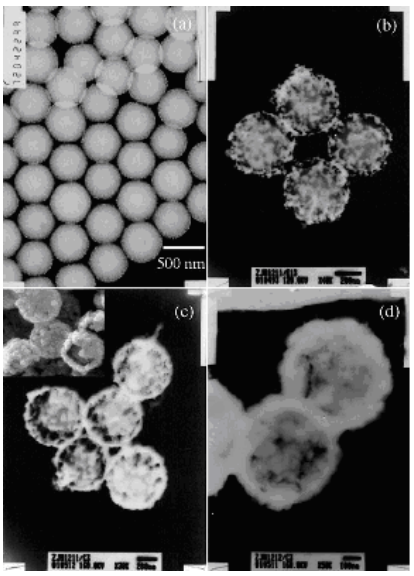


Fig 2.1.5 TEM images of the composite spheres: a) silica colloids after seeding b) to d)silica colloids after seeding and seeding growth, the shell thickness and the corrosion degree of the silica core increase from b to d[10].

Fig 2.1.5 shows the typical TEM images of the composite spheres at different stages of the fabrication process of hollow silver spheres. In this case, the complex $[Ag(NH_3)_2]+$ rather than silver ions as the precursor of the silver nanoparticles because the reduction of the former is more controllable and uniform, PVP is exploited to protect the silica colloids from aggregation due to the charge neutralization during the absorption process of the complex $[Ag(NH_3)_2]+$, and the ‘‘rapid’’ reducing agents-KBH_4 is used to assure the seeds size is very small. By controlling the seeding growth speed and the dissolving speed of the silica core, the spheric shape and mono-dispersity of the silica colloids are preserved mostly throughout the seeding growth process.

During seeding growth process, the role of $C_6H_5O_7Na_3.2H_2O$ is to slow down the reduction speed through the coordination between citrate and silver ions and work as stabilizer to protect the colloids from aggregation; NaOH is used to dissolve gradually

the silica core; 10% HCHO solution is added dropwise to control the reaction speed and the reduction amount of silver ions, and increase the silver shell thickness. The initial concentration of NaOH in the seeding growth solution is crucial for the formation of hollow silver spheres. So by using this method, its possible to prepare hollow nanaoparticle, by simultaneous seed formation and core breaking without using any foreign surfactant.

2.2 HYDROTHERMAL METHOD

For preparing nanoparticle with hollow structure different materials are used. Among them ZnO is an important one, because it can be used in photelectrode, solar cells, and nanolasers, because of its wide band gap and large excitation binding energy of 60 meV. Different nanostructures including nanowires, nanorods, nanotubes, nanoribbons, nanoneedles, nanocables, tetrapods, comb-like structures can be prepared from ZnO and these new structures have a wide application in different areas. Here in this case hydrothermal method is used for preparation of ZnO nanoparticles in which temperature and pH has significant role.

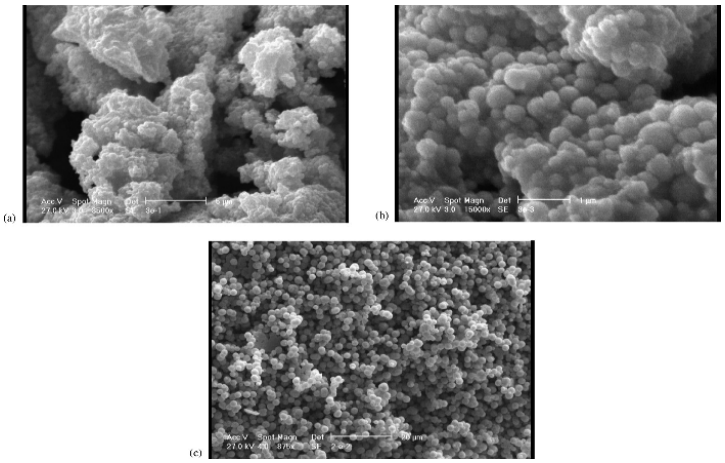


Fig 2.2.1 SEM images of ZnO samples prepared with same experimental condition (initial pH 9 and final pH 10) at 100 ◦C: (a) ZnO under conventional stirring, and (b, c) hydrothermal treatment in autoclave[11]

For synthesis of ZnO nanostructures, zinc acetate was slowly added to an aqueous solution of triethanolamine to reach the desirable pH referred to as the initial pH.

Then, potassium hydroxide was added to the solution pH to a certain value referred to as the final pH. The resultant solution was heated at certain temperature (100°c), from which ZnO hollow particles are prepared.

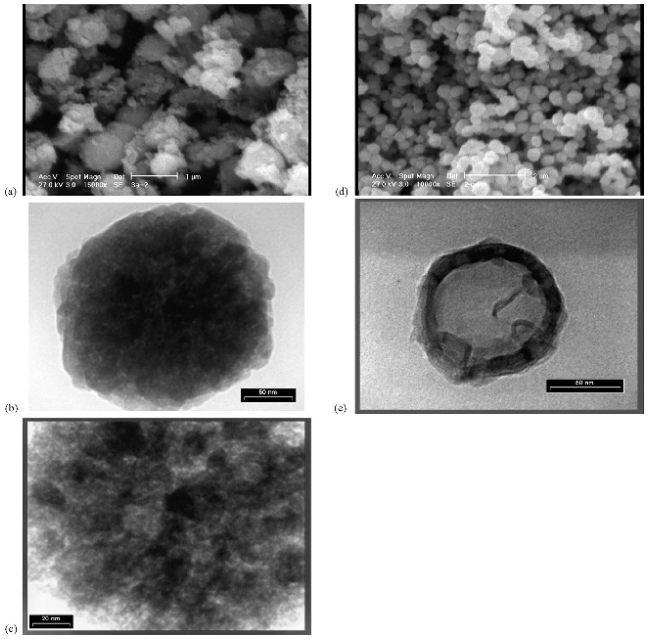


Fig. 2.2.2 (a) SEM and (b, c) TEM images of the sample prepared with pH 8 and similarly (d) SEM and (e) TEM images of the sample prepared with pH 9.[11]

As seen in Figure 2.2.1, conventional stirring results in the formation of highly agglomerated nanoparticles, while uniform nanospheres are formed during hydrothermal synthesis. Since the formation of ZnO nanostructures is due to the decomposition of amine-based zinc complex in basic media, the solution pH during the formation and decomposition of the zinc complex has an important influence on the morphology of ZnO nanostructures. For typical zinc complex formed at pH 8, decomposition at pH 10 results in the formation of ZnO nanoparticles consisted of tinier nanocrystals (Fig. 2.2.2a–c). Since the decomposition pH controls the rate of ZnO formation it just affects the size but not the shape of nanostructures. For higher pH (as the difference between the initial and final PHS is higher), just the nucleation rate increases to avoid continuous growth of the particles to achieve larger sizes. Whereas the initial pH affects the nature of the zinc complex generated, and generation of zinc complex at pH 9 leads to the formation of hollow nanospheres (Fig. 2.2.2 d and e).

2.3 SOLVOTHERMAL METHOD

Many methods can effectively fabricate hollow spheres, for instance, liquid droplets. Colloidal templating, coordination polymer, and self-assembly processes. Generally, these methods require additional template materials or surfactants. To simplify preparation procedure, solvothemal method is very simple. In this method, a solution is prepared by using required reactants, and then the product is heated and dried to get hollow particles.

For example to synthesize potassium nickel fluoride ($KNiF_3$) hollow $NiCl_2 \cdot 6H_2O$ was dissolved in ethanol[13], then KF aqueous solution was added in, the solution turned turbid immediately after adding KF, indicating sediment formation. The mixture was filled in a Teflon-lined autoclave and was maintained at 110°C and then cooled to room temperature naturally. The product was filtered and washed with absolute ethanol and distilled water several times, until pistachio precipitate is collected. Finally product was dried in a vacuum box.

In the present synthetic process, the composition and morphology of the product are greatly affected by the proportion of reactants. The reaction process may be formulated as follows: in ethanol solution, K^+ ions and Cl^- ions firstly form KCl spherical precipitate

$$K^+ + Cl^- \rightarrow KCl, \quad (1)$$

Where the KCl formed absorbs the F^- ions and Ni^{2+} ions on its surface. Then, these ions react with KCl to form KNiF3 nanoparticles under ethanol thermal conditions

$$Ni^{2+} + 3F^- + KCl \rightarrow KNiF_3 + Cl^-, \quad (2)$$

If the molar ratio between initial materials KF and $NiCl_2$ is less than 1, unreacted Cl^- ions (in reaction (1)) block the proceeding of reaction (2). Some Ni^2+ ions and F^- ions will form NiF_2 precipitate, resulting in the final product is mixture of NiF_2 and $KNiF_3$. However, when the molar ratio between initial materials KF and $NiCl_2$ is relatively high (e.g., larger than only few hollow spheres, along with a mass of irregular nanocrystals with different size and dispersivity are obtained. The absence of hollow spheres in the final product may be due to the fact that large amounts of K^+ ions exist

in solution, which directly react with F^- ions and $Ni^{2}+$ ions to form $KNiF_3$ nanocrystals, so that reaction (2) cannot effectively carry out on the surface of KCl spherical precipitate. Anyway, the appropriate molar ratio between initial materials KF and $NiCl_2$ is 2–3.

Temperature has a very great effect on the morphology of product in solvothermal process. The optimum reaction temperature is about 110◦C. When the temperature is too low (such as 70 ◦C), the reaction velocity will be much slower, and the yield of $KNiF_3$ hollow spheres will decrease, too. When the temperature is higher than 160 ◦C, no hollow spheres can be formed.

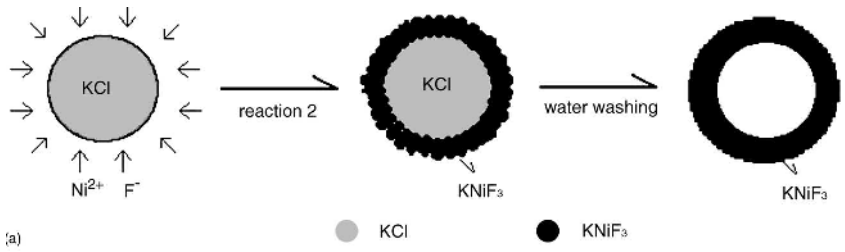


Fig 2.3.1 Illustration of the possible growth mechanism for $KNiF_3$ hollow spheres [12]

2.4 OIL IN WATER EMULSION METHOD

A microemulsion is a thermodynamically stable dispersion of two immiscible fluids; the system is stabilised by added surfactant Different types of microemulsion are known, such as water-in-oil (w/o)[14], oil-in-water (o/w)[15], water-in-sc-CO_2[16] (w/sc-CO_2). A "water-in-oil" microemulsion is formed when water is dispersed in a hydrocarbon based continuous phase, and is normally located towards the oil apex of a water/oil/surfactant triangular phase diagram (Refer Fig. 1.2).

Spherical reverse micelles, which minimise surface energy, are the most common form. Added polar or ionic components will become compartmentalised into the central cores of these reversed micelles, hence affording fine dispersion of inorganic materials in oil. It is important to recognise that these systems are dynamic — micelles frequently collide via random Brownian motion and coalesce to form dimers, which may exchange contents then break apart again. Clearly, any inorganic reagents encapsulated inside the micelles will become mixed This exchange process is

fundamental to nanoparticle synthesis inside reversed micellar ‘templates', allowing different reactants solubilized in separate micellar solutions to react upon mixing. Micelles in these systems can be described as “nanoreactors”, providing a suitable environment for controlled nucleation and growth. In addition, at the latter stages of growth, steric stabilisation provided by the surfactant layer prevents the nanoparticles from aggregating.

2.4.1 EMULSION–SOLVENT EVAPORATION METHOD TO PREPARE MICROPOROUS POLYMERIC HEMI – CELLS

There are many methods used to prepare hollow nanoparticles like emulsion-solvent evaporation systems, phase separation, emulsion polymerization, and spinning disk atomization. The most widely used route for manufacture still remains the emulsion-solvent evaporation technique. In this method, by controlling the solvent evaporation rate, particles can be modified to be into different shapes and sizes. [17]

Polycaprolactone hemi-shells were prepared by using an O/W technique. PCL was fully dissolved in Dichloromethane (DCM) (oil phase). $NaHCO_3$ was then stirred into the oil phase with a porogen: PCL ratio of 2:1 by weight. Polyvinyl alcohol (PVA) was dissolved in deionized water (water phase). The O/W emulsion was prepared by using a homogenizer.

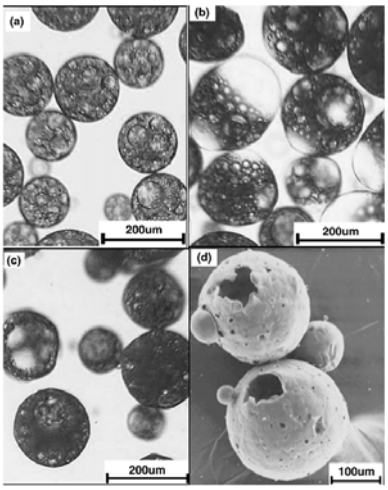


Fig. 2.4.1 Time varied morphological changes in the stages of hemi-shell development[17]

The emulsion was solvent evaporated while constantly stirring. Glacial acetic acid was added to increase CO_2 gas evolution by the reaction (3) as given below. After solvent evaporation was completed, the hemi-shells were isolated using filtration, washed three times with deionised water and then left to dry.

$$NaHCO_3 + CH_3COOH \rightarrow CH_3COONa + H_2O + CO_2\uparrow \quad (3)$$

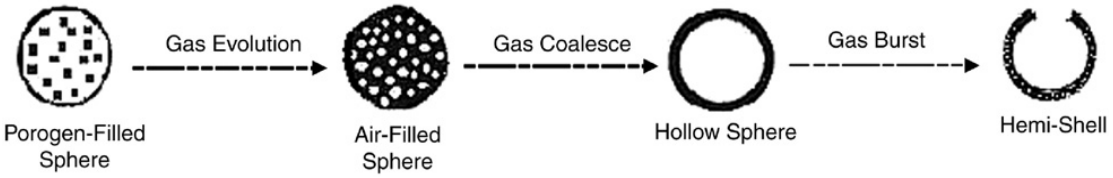


Fig 2.4.2 Schematic illustration of hemi-shell formation.

After solvent-evaporation the porogen dissolved forming small CO2 gas bubbles which were entrapped within the polymeric micro-spheres. These bubbles gradually coalesced forming larger bubbles. It's believed that these gas bubbles once fully coalesced2), eventually burst thus creating an internal cavity with an externally micro-porous shell. Acid addition also increased the gas formation thus creating more porosity. Coalescence of smaller bubbles to form larger bubbles can be attributed to the change in Laplace pressure

$$P_{inside} - P_{outside} = 2\,\sigma / r$$

Where P_{inside} and $P_{outside}$ are the internal and external pressure, respectively on the bubble, r is the bubble radius and σ is the surface tension.. The gas evolution from porogen dissolution leads to a highly porous micro-particle at the onset, which finally develops into a hollow concavity with a micro-porous shell.

2.4.2 PREPARATION OF HOLLOW MICROCAPSULE BY IMMOBILIZATION METHOD

Entrapment provides a method for immobilization, and it can control the release of active ingredients, sustain the effectiveness of ingredients, permit liquids to be handled as solids, protect reactive components until the time of use, allow the safe handling of toxic materials, and overcome product incompatibilities. For this we need a porous particle in nanometer or micrometer size which can hold material.

The success in the synthesis of hollow microcapsule is in controlling the polymerization speed. The addition of inorganic metal salts, such as $NiCl_2$ lowered the reaction rate in comparison with that without inorganic metal salts cores, and different inorganic metal salts presented different reaction rates till the completion of interfacial polymerization. [18] The urea group could be produced by the reaction between water and toluene 2,4-diisocyanate (abbreviated as 2,4-TDI) occurring at the oil–water interface, and unstable $–NCOOH_2$ was prepared and could be easily changed to $–NH_2$ group by the release of CO_2.TheresultantTDI-basedwater-borneamin produced urea, i.e., –NHCONH– by the reaction with another 2,4-TDI. This subsequent reaction produced a polymer wall membrane onto the emulsion globules. Following this, the sample was washed and heated, the water inside the microcapsule was vaporized and thus the formation of hollowmicrocapsule with $NiCl_2$ dotted in the interior surface. Fig 2.4.3 gives the complete process diagrammatically.

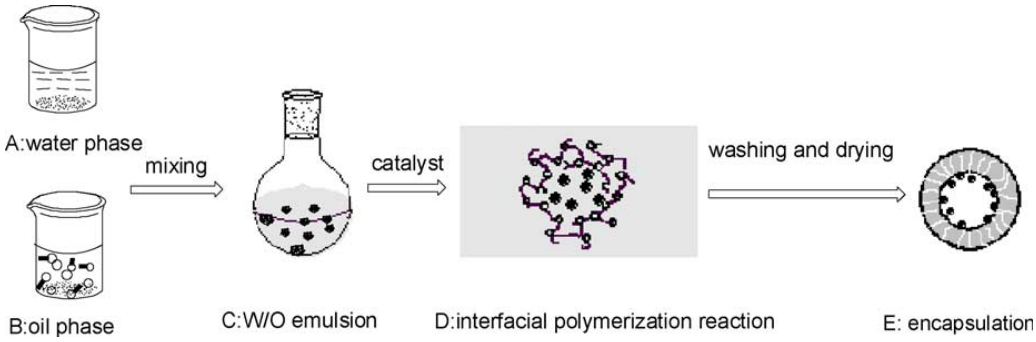


Fig 2.4.3 Schematic illustration of forming hollow microcapsule with $NiCl_2$ dotted in the interior surface[18]

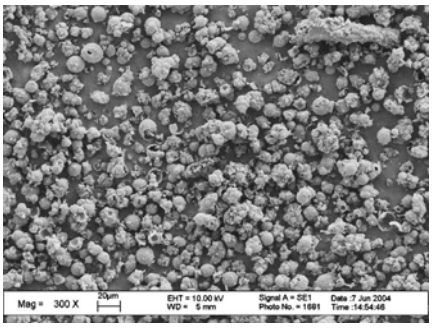


Fig. 2.4.4 the obtained polyurea microcapsule with encapsulated $NiCl_2$[18]

2.4.3 PREPARATION OF HETEROGENEOUS COMPOSITE PARTICLE WITH HOLLOW STRUCTURE

In this preparation method, micrometer-sized hollow silica particles were synthesized by sol–gel reaction in water-in-oil (W/O) emulsion as the viscosity of water droplets in W/O emulsion was controlled with polyethylene glycol (PEG) or polyvinylpyrrolidone (PVP).

First of all, to prepare MPTMS (used as a chemical protocol)-functionalized silica particles with hollow structure, W/O emulsion was prepared as follows. An external oil phase was prepared by dissolving HPC (hydroxypropyl cellulose as a stabilizer of emulsion structure) in *n*-decyl alcohol (used as an oil phase in emulsion) then kept for sometime to dissolve HPC completely. Then sorbitan mono-oleate, a low-HLB surfactant, was added into the oil phase. HPC and sorbitan mono-oleate , added into the external oil phase, increased the stability of the W/O emulsion structure. The internal water phase was prepared by adding NH_4OH as a catalyst into the water. As a final step of the preparation of W/O emulsion, the water phase was added into the external oil phase. The weight ratio of water phase to oil phase in the emulsion was kept at 1:9. To disperse the water phase into the oil phase, agitation was performed using the magnetic stirrer. [19]

The sol–gel reaction for the formation of silica particles was initiated by adding TEOS into W/O emulsion. After sometime reaction, MPTMS was added into the reaction system in order to obtain silica particles with hollow structure and terminal thiol groups at the surface of silica. The molar ratio of water to TEOS and MPTMS was 10 and 50, respectively. Sample was prepared in the experimental beaker and kept for about for a day with soft agitation, using small magnetic stirrer. After the reaction was completed, the sample was centrifuged to obtain hollow nanoparticle. In order to remove the un-reacted materials such as polymer, *n*-decyl alcohol, and surfactant, the precipitates were washed with absolute ethanol two times. Then, these particles were dried in an incubator.

To prepare silver shells on the hollow silica surface modified with thiol group, polyol process was employed Silver nanoparticles were deposited on the silica surface as follows: dry hollow silica particles functionalized with thiol group was dispersed ethylene glycol. After completely dispersion PVP was added into the mixture. In order to completely dissolve the PVP without a distortion of polymer chain, the mixture was softly stirred with magnetic stirrer for 1 day. And then $AgNO_3$ was dissolved in the mixture. After all additives were completely dissolved the mixture solution was heated with reflux.

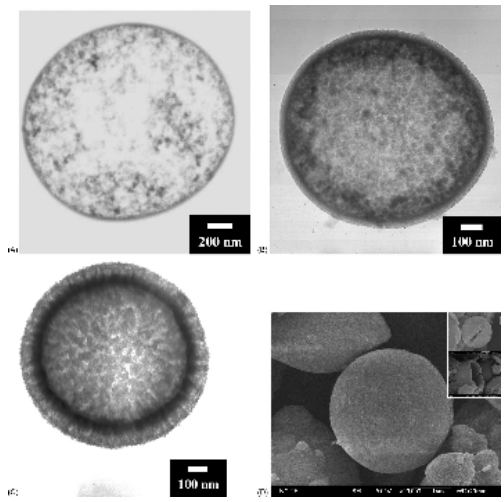


Fig. 2.4.5 TEM images of hollow silica spheres functionalized with MPTMS at (A) 3.5 h, (B) 12 h, and (C) 24 h reaction time and (D) FE-SEM image of the same sample with TEM image (C). [19]

It is well known that thiol groups attach to silver ions by the cleavage of an S–H bond and the spontaneous formation of an S–Ag bond. As a result of unique behavior of thiol groups containing sulfur atom, chemicals containing thiol groups have been widely used as chemical protocols to make various metal–polymer and metal–metal oxide composites. In addition, compounds containing sulfur, including metal sulfide such as cadmium sulfide, are known as an excellent “adsorbent” for metal ions. Therefore, the introduction of thiol groups by adding TEOS and MPTMS by stages is very important, because they were used as a chemical protocol to deposit silver nanoparticles on the silica surface. The reaction system is W/O emulsion in which water including the ammonium hydroxide as a catalyst is dispersed in *n*-decanol as a form of droplet. TEOS and MPTMS molecules as silica sources are dissolved into the continuous phase, *n*-

decanol, because they are initially hydrophobic. When they are contacted with the interface of water droplets containing ammonium hydroxide, sol–gel reaction of TEOS and MPTMS molecules takes place. As a result, surface-modified hollow particles can be synthesized by control of hydrolysis and condensation of TEOS and MPTMS at the interface between water and *n*-decanol.

To coat hollow silica spheres with silver nanoparticles, polyol process was employed as a reduction method for silver ions. The preparation steps of silver shell can be explained as follows. At the first stage of the reaction, MPTMS-functionalized hollow silica particles and PVP are dissolved into the ethylene glycol. After completely dissolution of PVP, $AgNO_3$ is added into the system. In this stage, some silver ions are bonded with thiol groups of the silica surface by the cleavage of an S–H bond and the spontaneous formation of an S–Ag bond. In the second in the second stage, Ag+ ions are reduced to Ag0 metal state by ethylene glycol and PVP, and silver nuclei are formed and immobilized on the surface of the MPTMS-functionalized hollow silica particles. Finally, silver nanoparticles are formed on the silica surface by growth of nuclei as the thermal energy is supplied to the system by heating at a given temperature.

Thus Hollow silica particles were synthesized through the sol–gel reaction by adding the TEOS and MPTMS by stages into the W/O emulsion.

2.4.5 PREPARATION OF CORE – SHELL SILICA PARTICLE THROUGH MICROEMULSION METHOD

The core-shell structures formation is also an another popular approach, which is usually assisted by layer-by-layer (LBL) deposition [21-22] Monodispersed CdS–SiO2 core-shell particles ranging from nanometers (30–100 nm) to micrometers (1.5–2_m) were prepared in situ in the nonionic reverse microemulsions [20] .After treating the core-shell particles with concentric nitric acid, the hollow silica spheres were obtained correspondingly. The study showed that the core size and shell thickness could be tuned simply by controlling the addition amount of the reactants and the addition way and that the hollow silica spheres could be potentially used as a novel class of catalyst supports.

Three microemulsions were used, and the reverse microemulsion system consisted of NP – 7, n – butanol, cyclohexane and aqueous phase. Three microemulsios system contained the composition but different aqueous phases: 0.2 mol l-1 Cd $(NO_3)_2$ solution, 0.2 mol l-1 Na_2S solution and 25 wt% NH_4OH solution, respectively. The Cd $(NO_3)_2$-, Na_2S- and NH_4OH – containing microemulsions were designed as ME – 1, ME – 2 and ME – 3, respectively. To guarantee the three systems stable, the weight ratios of aqueous phase, NP – 7, *n*-butanol and cyclohexane were kept at 11:23:12:53. In order to prepare the CdS–SiO_2 core-shell particles, ME-1 was mixed with ME-2 with equal volumes under stirring gently. After ageing for 2 h, ME-3 and TEOS were added dropwise. After ageing for 24 h, acetone was added to demulsify the system, and the particles were recovered by high-speeded centrifugation. To remove the impurity ions and surfactant molecules, the particles were washed with water and alcohol at least for five to six times in sequence, respectively, and then dried in vacuum at 60°C for 12 h. In order to obtain the larger cores, seeding growth procedure was carried out. The small CdS seeds were firstly prepared by mixing a small amount of ME-1 and ME-2. After an appropriate interval for seeds maturation, a definite amount of ME-1 and ME-2 were further added. The small CdS particles grew up into the desired size gradually. The similar procedure was used to control the thickness of SiO_2 shell. Firstly, a small amount of ME-3 and TEOS were added to form the thin shell; and then, a definite amount of ME-3 and TEOS were added.

Size of the CdS core was controlled through tuning the addition amount and the addition way of the reactants. In order to prepare small CdS cores, ME-1 was mixed directly with ME-2 with equal volumes under stirring vigorously. The Na2S- and Cd(NO3)2-containing micelles collided and associated. During the process, the matter exchanged simultaneously. The reactants reacted, nucleated and grew within the reverse micelles. Because of the protection of the interface film, the conventional agglomeration of the particles could be effectively refrained. The monodispersed particles could be obtained. The CdS cores with average 5 nm in diameter were prepared by mixing directly 5ml ME-1 and 5ml ME-2.

Seeding growth procedure was conducted to obtain the large cores. Small amount of ME-1 and ME-2 were first mixed under stirring. After the small seeds were stabilized

for a time, a definite amount of ME-1 and ME-2 were added alternately to make the small cores grow into the desired large ones. During the process, the initially formed CdS nanocrystals might act as the growth seeds, which provided with the nucleation and growth sites; the reacting species added subsequently reacted and grew on the seed surface into large crystals. Thus the core size could be controlled precisely by altering the addition amount and the addition way of the reactants.

The shell thickness of the CdS–SiO_2 composites particles could be controlled simply by altering the addition amount of TEOS. After the CdS cores formed, ME-3 was added under stirring. Then, a definite amount of TEOS was added dropwise to hydrolyze and polymerize. The TEOS reaction was much slower in microemulsion so 24 h aging was required in the process, similar to the secondary seeding growth procedure above, TEOS hydrolyzed and polymerized on the CdS core surface. The CdS cores could provide with nucleation and growth sites for the silica, and the silica shell of different thickness formed.

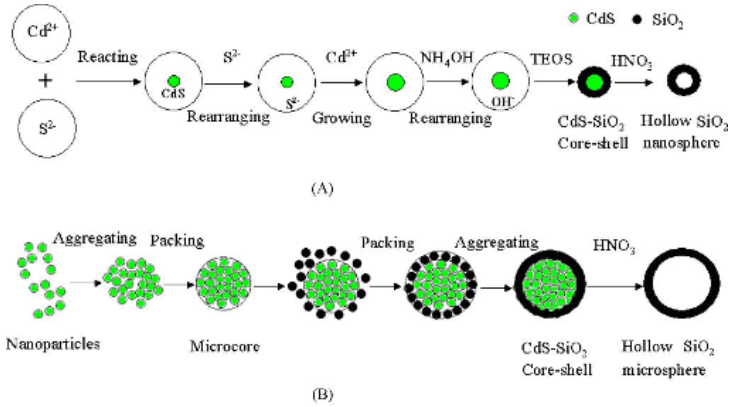


Fig 2.4.6 Schematic representation of nanoparticle formation[20]

2.5 OBJECTIVES OF THE PROJECT

The overall objective of the project is to prepare and study the formation of silica nanoparticles, by varying the governing parameters like pH, Oil medium, water to surfactant ratio (R) and others.

The specific objectives of this study are:

- To prepare microemulsions from different solutions with varying parameters such as pH, medium etc
- To prepare and study nanoparticles from metals preferably silica in the microemulsion
- To study the morphology of the nanoparticles by studying their formation and size dependency characteristics.
- If possible prepare a hollow nanoparticle from the previously prepared nanoparticles and study their characteristics.

Chapter 3

EXPERIMENTAL PROCEDURE

3.1 MATERIALS

In the experiment, all the chemicals were analytical grade and used without purification. Tetraethyl orthosilicate (TEOS, $Si(OEt)_4$) was used as a source of silica. In all the experiments performed only ultra pure water (pH=7.00 and resistivity 18.3MΩ) is used.

Non-ionic surfactant-Triton X-100 [$C_{14}H_{22}O(C_2H_4O)_{10}$] (chemical name-Glycol Tertoctylphenyl ether) of scintillation grade, *n*-butanol, cyclohexane and aqueous solution(Butyl amine or 25% ammonium hydroxide dissolved in water) were used as surfactant, cosurfactant, continuous phase and dispersed phase, respectively. Typically, a measured amount of surfactant and cosurfactant with weight ratio of 2:1 were dissolved in cyclohexane.

3.2 PROCEDURE

In this study, silica nano particles were synthesized in a water–oil (W/O) reverse emulsion system. We focused on the effects of the pH value of aqueous droplets and the R value. In particular, samples withdrawn at specific times from the nanoparticle synthesis test tube are then characterized using optical microscope and finally under scanning electron microscope (SEM). The combination of characterization techniques revealed new aspects of the process of nano particle formation and structure, which are discussed below. The experimental evidence obtained here is then discussed in the relevant context.

First of all, as mentioned in the table 3.1 different pH aqueous solution of water and ammonia or butylamine was prepared by using a digital pH meter. Table 3.1 shows different composition of different pH solution.

Then, a specified volume of aqueous solution was taken and the surfactant TX–100 was added with different R values (table 4.2). Then butanol was added to the above solution as co-surfactant (surfactant to co surfactant weight ratio 2:1). Then, cyclohexane was added as oil phase to the solution. Then, the above prepared solution was stirred continuously till the solution becomes transparent to the eye and then, the

solution was left for some time, if the solution does not separate into two liquid layer , the prepared solution is stable.

Table 3.1 pH Values

Sl no	Amount of Ammonium hydroxide (25%) (in ml)	Ultra pure water (in ml)	pH of solution
1	0.2	29.5	9
2	0.3	20	10.5
3	1.1	3	11.6

Then to that solution TEOS was added drop wise. Then, the mixture was left for 24 hr at room temperature to finish the reaction. Finally, the silica particles were precipitated by dissolving microemulsion with ethanol and then mixture was washed with ethanol for thrice.

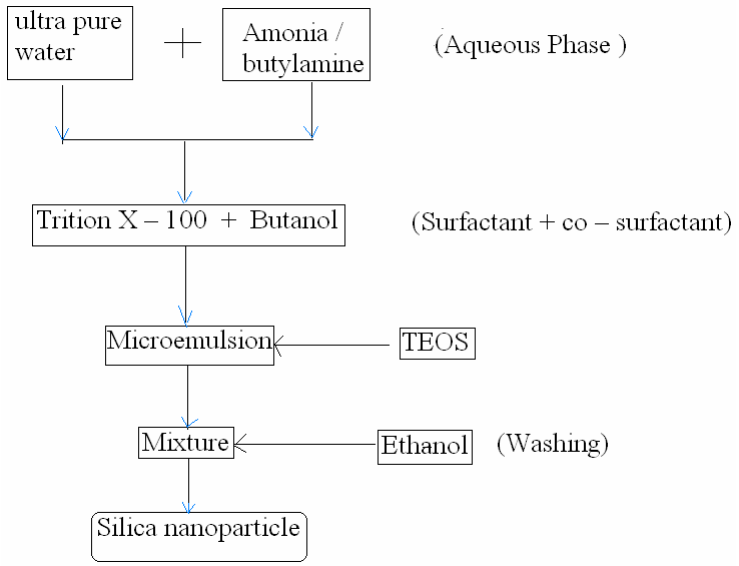


Fig 3.1 Step wise procedure for the formation of silica nano particle

3.3 CHARACTERIZATION

Hund Weltzar with JVC-TK C1351 Optical Microscope of 4000X resolution was first used to observe the formation of particles if any. Then, the nanoparticle morphology was observed with images obtained from a JEOL model JSM-6480LV scanning electron microscope (SEM), using a resolution at 5.9keV-133 eV and a drive frequency of 39Hz. The samples were deposited on a thin brass film plate or film circular in design of about 10mm diameter. The surface was smoothened using an emery paper before the solution was added dropwise. Elemental analysis was performed on a JESCO UV–vis-NIR spectrometer in a monomer-free 0.1 M $TBAPF_6$ solution via incrementally increasing applied potential between 0.4 V and 1.2 V Spectrophotometer, to study the presence of the particle formation by studying the deflection of the UV rays in the path of the particles.

Chapter 4

RESULTS AND DISCUSSION

The results and data used for the preparation of nanoparticle are tabulated as shown below. The results obtained were compared on basically two important parameters i.e. keeping the R constant and keeping the pH constant. All other parameters apart from these were considered variable at any time apart from these two singularly.

Table 4.1 Material values at a constant R = 10

Sample no	Aqueous phase pH	Surfactant/ Co-Surfactant(w/w)	Water/TEOS (molar ratio)	Water/oil (v/v)
1	9	2	10	5
2	10.5	2	10	5
3	11.6	2	10	5

Table 4.2 Material values at a constant pH = 11.6

Sample no	R value	Surfactant / Co- surfactant (w/w)	Water /TEOS (molar ratio)	Water/oil (v/v)
1	20	2	10	5
2	25	2	10	5
3	30	2	10	5

Upon addition of TEOS to the reverse micellar system, the formation of silica particles involves a series of steps which can be identified as:

(i) Association of TEOS molecules with the reverse micelles

(ii) TEOS hydrolysis and formation of monomers

(iii) Nucleation

(iv) Particle growth

(v) Nuclei dissolution

(vi) Inter-micellar exchange of monomers

(vii) Ionization of monomers and

(viii) particle surface ionization.

The association of TEOS molecules with the reverse micelles is viewed as a distribution process. The partition of TEOS(step I) between the reverse micellar pseudo phase (m) and the bulk oil phase (b) is considered to be brought about by the formation of the monomer having one silica group (i.e. $Si(OR)_3OH$), which is known to be amphiphilic from interfacial tension measurements[37]. Further hydrolysis of this species (step II) generates monomeric species with up to four silanol groups (i.e. silicic acid). All these species (i.e. $Si(OR)_3(OH)$ to $Si(OH)_4$) are designated as 'monomers', and are assumed to remain associated with the reverse micellar pseudo phase due to their enhanced polar character. These species can participate in particle nucleation and growth.

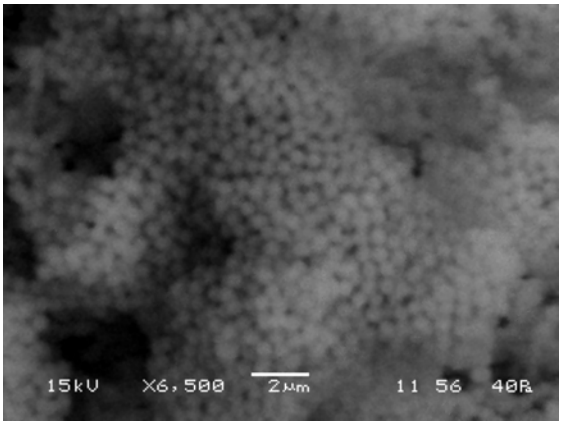


Fig 4.1 SEM images of a highly concentrated bunch of Si nanoparticles

The assumption that the monomers are confined to the reverse micellar pseudo phase i.e. in a two-phase cyclohexane, water system, partially hydrolyzed TEOS species partition preferentially into the aqueous phase. Nucleation involves the condensation of monomers, and it can be an intra-micellar oriented-micellar event (step III). Particle growth(step IV) may occur by addition of monomers to nuclei (an intra- or inter-micellar process), or by aggregation of nuclei. Other possible events are nuclei dissolution with generation of monomers (step V), monomer exchange by inter-micellar collisions (step VI), monomer (silicic acid) ionization to produce anionic species (step VII), and surface ionization to give charged silica particles (step VIII).

(I) TEOS partition

$$Si(OR)_4\,(b) \xrightleftharpoons{OH^-} Si(OR)_4(m)$$

$$Si(OR)_4(m)+H_2O(m) \xrightleftharpoons{OH^-} Si\,(OR)_3(OH)(m) + ROH(m)$$

(II) Hydrolysis

$$Si\,(OR)_4\,(b) + xH_2O\,(m) \xrightarrow{OH-} Si\,(OR)_3\text{-}x(OH)x(m)+ xROH(m)$$

$$Si\,(OR)_3\text{-}x(OH)_x+1(m) = \text{“monomer”}(m)$$

$$X= 1,2,3$$

(III) Nucleation

$$n.\ momoner(m) \xrightarrow{OH-} nucleus\ (m)$$

$$Monomer(m) + monomer(m`) \leftrightarrow nucleus(m \text{ or } m`)$$

(IV) Particle Growth

$$monomer(m) + nucleus(m`) \leftrightarrow growth\ (momoner\ addition)$$

$$monomer(m) + nucleus(m) \leftrightarrow growth\ (momoner\ addition)$$

$$nucleus(m`) + nucleus(m) \leftrightarrow growth(nucleus\ aggregration)$$

(V) Nuclei Dissolution

$$nucleus\ (m) \xrightleftharpoons{OH^-} n.momoner(m)$$

(VI) Monomer Exchange

$$monomer(m) \leftrightarrow monomer(m`)$$

(VII) Monomer Ionization

$$Si(OH)_4(m) + y\ OH^- \leftrightarrow SiO_y\,(OH)_4\text{-}y^{y-}(m) + yH_2O(m) \qquad y= 1,2$$

(VIII) Surface Ionization

$$Si(OH)(s) \xrightarrow{OH-} SiO(s)$$

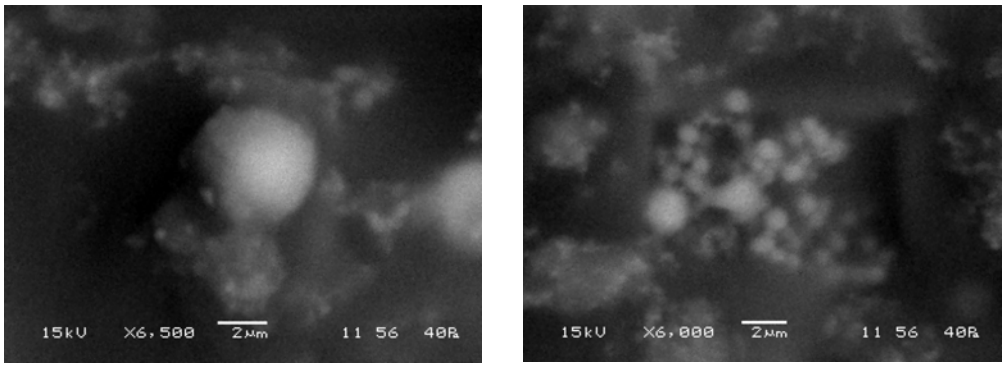


Fig 4.2 shows the SEM characterized nanoparticles synthesized at a pH value controlled around 11

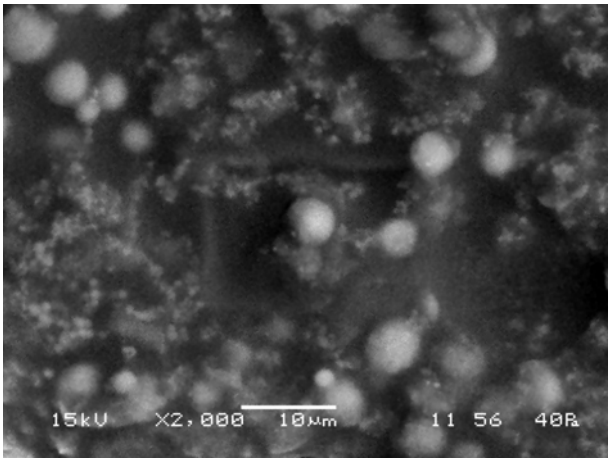


Fig 4.3 SEM images at pH value 11.3

From previous literature it could be concluded that the hydrocarbon tail length of the amine catalyst will affect the shell thickness of the prepared hollow spheres. The longer the hydrocarbon tail length of the amine catalyst, the thicker the shell of the prepared hollow spheres. The diameter of the silica hollow particles varied from several hundred nanometers to about 10 nm.

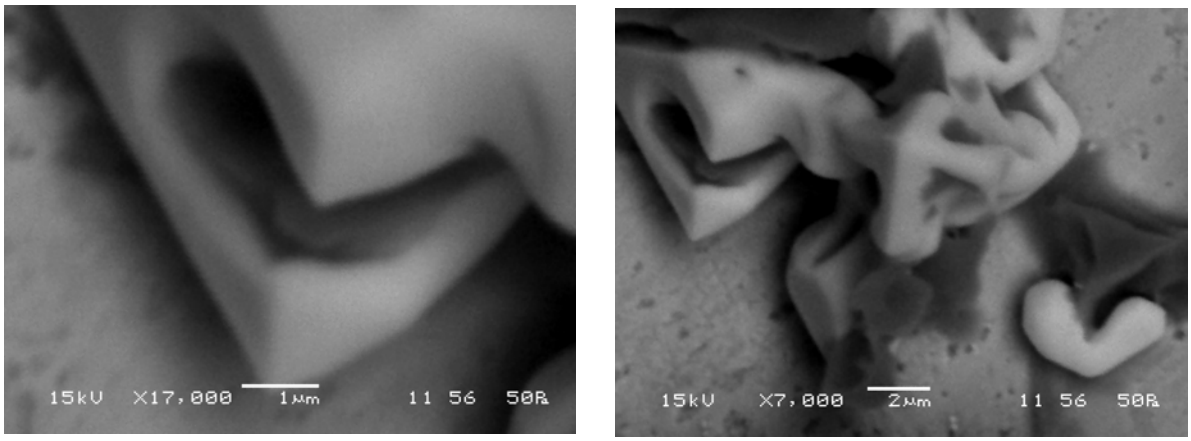


Fig 4.4 The SEM images of the hollow silica particles characterized at pH 10 and R = 8-9

4.1. The effect of the pH value of aqueous phase

During the preparation of the silica hollow particles in W/O reverse emulsion system, there are three main steps in this sol–gel process (Fig. 4.1.1)

1. The association of TEOS with the W/O emulsion
2. TEOS hydrolysis and formation of monomers at the W/O interface
3. Condensation of monomers and silica nucleation in suit.

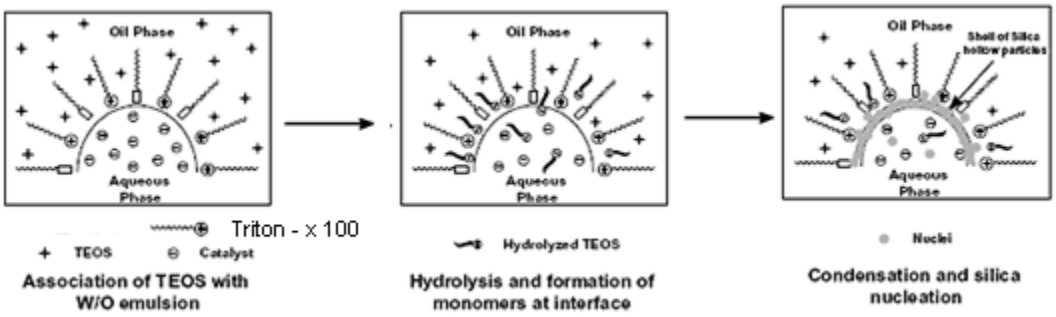
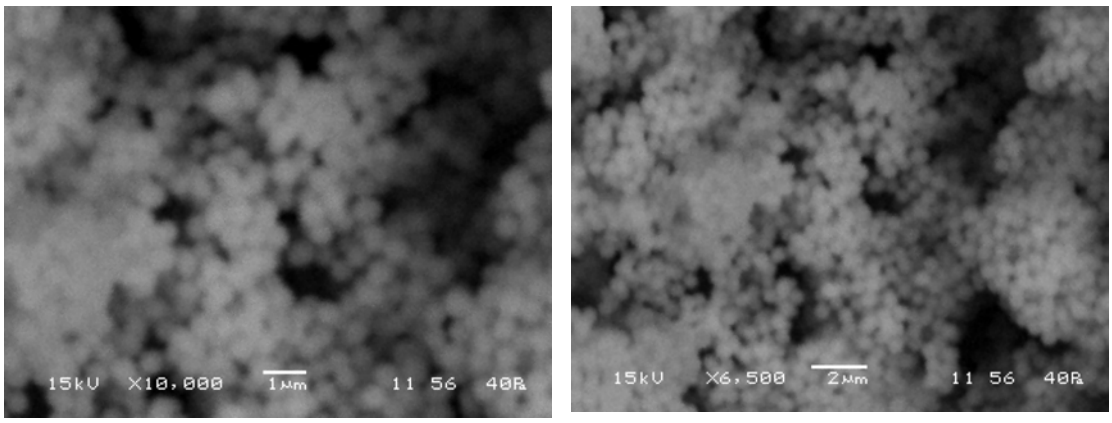


Fig. 4.1.1 Schematic illustration of silica hollow particles formation in W/O emulsion[21].

It is well known that the pH value of aqueous phase affects the hydrolysis and condensation reaction rates and colloid stability in the process of particle formation. In general, ammonia or NaOH is used as a basic catalyst to increase pH for the hydrolysis of TEOS in water–alcohol solution. Here ammonia was used as the basic catalyst. It exists in the aqueous cores of reverse micelles in the W/O emulsion system since it is water-soluble. When the TEOS molecules diffuse from the oil phase to the W/O interface, three main reactions would take place. First, the TEOS molecules contact with the basic catalyst in the aqueous phase, the hydrolysis of TEOS occurs.

Then the hydrolyzed TEOS molecules will condensate at the interface. At the same time, the polycondensate silica will depolymerize under the existing of base catalyst. Finally, the resultant negatively charged silicates and the ammonium cation of TX-100 steadily self-assemble at the interface to form a silica shell. It is well-known that the hydrolysis rate of TEOS will increase with the pH value of the aqueous phase when the base is used as the catalyst. While the rate of condensation will reach a peak at neutral environment then decrease with the continually increase of the pH value. At the same time, the rate of depolymerization almost keeps constant when the pH is over 7 [35].



(a) (b)

Fig 4.1.2 Effect of pH on particle size (a) pH=9-10 (b) pH>11

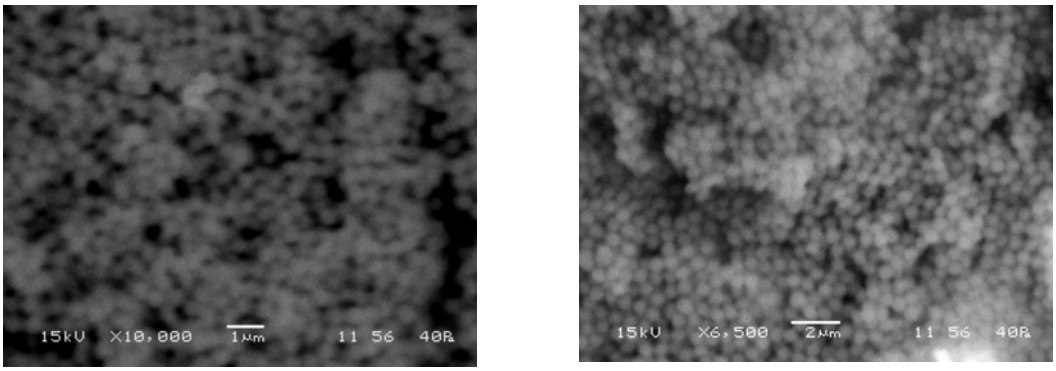
The competition of hydrolysis, condensation and depolymerization will determine the nucleation and the growth position of silica nuclei in the reverse emulsion system. When the pH is over 10, the rate of condensation will be slower than that of hydrolysis and depolymerization[36]. So the nuclei mainly occurred at aqueous droplets and nanoparticles were obtained finally as shown in Fig. 4.1. Whereas, when the pH was controlled near the neutral, the condensation reaction will be quicker than the hydrolysis, the hydrolyzed TEOS molecules will condensate at the interface rapidly and in the end, silica particles were prepared as shown in Fig. 4.1.2.

4.2. The role of butylamine/ammonia as base catalyst

As discussed above, the pH value of the aqueous phase will affect the morphology of silica particles. To control the pH value of an emulsion system, amine is a good choice. Compared with ammonia or NaOH, the types of amine are very ample and they are commercial available widely. The relative strength of amine base is usually expressed as either pKb or pKa of the conjugate acid [37]. The strong base has a low pKb value. In our experiments, ammonia (pKb = 4.75), butylamine (pKb = 3.39) were used to catalyze the hydrolysis and the condensation of TEOS in W/O emulsion. The key factor was the pH of aqueous droplets otherwise the relative strength of base. This phenomenon is also believed to relate with the competition among the three reactions of the sol–gel process. It is obvious that the increase of OH^- ions causes an increase in the rate of hydrolysis of TEOS molecules, hence a large number of monomers are produced. Micelle and intramicellar nucleation will occur when the number of monomers inside the aqueous core exceeds a critical value. And the ethanol as a hydrolysis byproduct also enhances the nuclei formation by increasing the fluidity of the interface and the intermicellar exchange rate.

4.3 Effect of R value

In general particle sizes depend on water-to-surfactant ratio assuming constant aggregation number **[38, 39]**. However, the dynamics model of microemulsion system allow water droplets to continuously collide and coalesce in a diffusion process that promotes increase in droplet sizes and it drives the reactants through the interface due to the local ionic strength. Water-to-surfactant ratio (R) and ionic strength affect the rigidity of the interface and the reaction kinetics **[40, 41]** providing large particle formation. Sizes of particles do not increase as R increases from 8 to 10. Nevertheless at R=10 there are larger particles and a distribution in sizes. Silica particles from TEOS hydrolysis in Triton X-100-cyclohexane-ammonium hydroxide microemulsions of 50±70 nm range were observed. Particle size increases as R increases. Upon increasing the surfactant concentration there is an increase in the population of the host reverse micelles in the organic phase. Higher nanoparticle uptake increased the rate of collisions and the probability of aggregation between nanoparticle-populated reverse micelles, which led to the formation of larger particles.



(a) (b)

Fig 4.3.1 Effect of R on particle size (a) R=10 (b) R=20

The increase in the nanoparticle uptake as the water content increases can be explained as follows. At low values of R most of the water contributed to the bound water As R increased the size of reverse micelle increased and more free-water was available in the water pools to dissolve higher amounts of TEOS. Increasing R reduces the interaction between the surfactant head groups and the stabilized nanoparticles. Moreover, higher water content reduces rigidity of the surfactant protective layer and promotes particle aggregation upon collision and the formation of larger particles, which precipitate under gravity effect. This with increase in R value, the size of the nano particle increases accordingly.

Chapter 5

CONCLUSION

There have been many methods employed to synthesize silica nanoparticles. Using different methods, the obtained nanoparticles show significant difference in both particle diameter and morphology. Thus, the choice of synthetic methods in the synthetic process depends on the materials applications requirement. For example, small particles are desirable in catalysis where the main emphasis is on surface-to-volume ratio, whereas larger particles are often necessary for optical applications. Silica nanoparticles with size below 10 nm have been prepared by traditional chemical methods, however the tiny particles tend to grow and aggregate into large particles. The major problems for non-traditional physical methods are its high cost; the obtained nanoparticles also have a wide particle size distribution. In microemulsion, the nucleation and growth of particles are restricted within the water core of inverse micelles. Thus, microemulsion method is often used to synthesize nanoparticles with specific size and morphology. The advantage of the method is the ability to control the particle size and morphology easily by adjusting the concerned parameters, e.g., the concentration and type of surfactant, the type of continuous phase, the concentration of precursors and molar ratio of water to surfactant.

Silica nanoparticles were successfully prepared in a W/O reverse emulsion through control of the sol–gel process reaction environment. The following conclusions can be drawn from this work

- when the pH value of aqueous phase exceeded 10, the rate of hydrolysis and polymerization was quicker than that of condensation, granular or irregular shape particles formed
- when the pH was controlled around 8–9, silica nanoparticles were prepared
- Water-soluble amines were effective catalysts to fabricate a silica hollow structure. The longer the hydrocarbon tail, the thicker the shell of the hollow particles
- R ratio is found to be directly influencing the size of the nanoparticles.

In summary, the proper pH value of water phase, viscosity of outer oil phase, water to surfactant ratio were the crucial factors to the formation of the hollow structure.

Although significant advances have been made in preparation of silica nanoparticles, we are also faced some problems. One challenge is to prepare colloidal nanoparticles with high stability and good exchangeability of solvents. It is an important process to transfer silica nanoparticles to different chemico-physical environments in practical applications. Another one is to fabricate size-controlled or shape-controlled and chemically clean silica nanoparticles with narrow size distribution, which are easily incorporated into a variety of substances to form nanocomposites or assembled into higher-order nanostructures. In addition, it is an important goal for advanced projects to prepare three-dimensional nanomaterials with controlled geometry and structure. Besides theoretical and experimental studies on the novel synthetic technologies and the important influence factors, the combination of traditional and non-traditional methods needs much further attention.

REFERNCES

1. Nanostructure and nanomaterials , synthesis, properties and application by Guozhong Cao, University of Wasington, USA.
2. A practical method to production of hollow carbon onion particle, C. He et al. , journal of alloy compounds 425(2006) 329 – 333.
3. Recent advances in nanoparticle synthesis with reversed micelles, J Eastoe et al., Advances n Colloidal and Interface Science 128 – 130 (2006) 5 – 15.
4. Bommarius AS, Holzawarth Jf, Wang DIC, Hatton TA, Physical Chemistry, 34(1990),1232.
5. Rojas S, Garcia Garcia FJ, Applied catalysis A generation (2005)285;24.
6. National nanotechnology initiative 2000 leading to the next industrial revolution, A report by interagency working group in nanoscience, engineering and technology http://www.nano.gov.
7. New reactor for production of tungsten disulfide hollow onion – like nanoparticle Y. Feldman et al. , solid satate science 2 (2000)663 – 672..
8. The fabrication of hollow spherical copper sulfide nanoparticle assemblies with 2 – hydroxyprpeyl – β – cyclodextrine as a templet under sonication J – Z Xu et al. , Ultrasonics Sonochemistry 13 (2006)451 – 454.
9. Nanosized aluminum nitride hollow spheres formed through a self timplating solid – gas interface reaction , J. Zheng et al. , journal of solid state chemistry 180 (2007)276 – 283.
10. A facile colloidal templating method to monodispersed hollow Ag and Ag/Au subnicrometer spheres J. Zhang et al., Material letters 60 (2006)280 – 283.
11. Flower like bundles of ZnO nanosheeets as an intermediate between hollow nanoshpere and nanoparticles, A Eftekhari et al. material science and engineering A 437 (2006) 446 – 450.
12. A simple approach to synthesize $KNiF_3$ hollow spheres by solvothermal method M. Zhang et al., material chemistry and physics 89 (2005)373 – 378.

13. A comparative study of the microemulsion and interfacial polymerization for polyindole S. A et al, material letters 88(2007)340-345.

14. Direct preparation of hollow silica spheres in a water in oil emulsion system L. Song et al. journal of non-crystalline solids 352 (2006) 2230 - 2235.

15. Gold nanoparticle encapsulating horseradish peroxide R. kumar et al. 26(2006) 6743 – 6753.

16. Silica – PMMA core – shell and hollow nanosperes, K. Zhang et al., colloidal and surface A: phyicochem. Engineering aspects 277 (2006)145 – 150.

17. An emulsion preparation for novel micro-porous polymeric hemi-shells, K.Naidoo et al., Materials letters 289 (2004) 160-164.

18. Development of an immobilization method by encapsulating inorganic salt forming hollow microspheres, H. B Ji et al , catalysis today 105 (2005)605 – 611.

19. Facile and novel route for preparation of silica/silver heterogeneous composite particles with hollow structure, J. M Lee et al., colloids and surface A: phyicochem. Engineering Aspects 301(2007)48 – 54.

20. Preparation of CdS – SiO_2 core – shell particles and hollow SiO_2 spheres ranging from nano meters to microns the noninonic reverse microemulsion, F Teng et al., catalysis today 93 – 95 (2004) 651 – 657.