Synthesis and Characterization of S@AgBr Core-Shell Nanoparticles

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Thesis submitted

by

RAJIB GHOSH CHAUDHURI (207CH102)

In partial fulfillment for the award of the Degree of Master of Technology

In

Chemical Engineering

Department of Chemical Engineering
National Institute of Technology
Rourkela-769008, Orissa, India.
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Under the guidance of
Dr. SANTANU PARIA

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CERTIFICATE

This is to certify that the thesis entitled, "**SYNTHESIS AND CHARACTERIZATION OF S@AgBr CORE-SHELL NANOPARTICLES**" submitted by Shri Rajib Ghosh Chaudhuri in partial fulfillments for the requirements for the award of Master of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) 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.

Date: 22/05/2009

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Contents

Abstract

Core–shell nanoparticles are gaining lots of importance recently due to their exciting applications in different fields like biomedical, pharmaceutical, electronics, catalysis etc. They also show new properties than the single materials when coated one material with other. In this report we studied the preparation and growth kinetics of sulfur nanoparticles as a core in aqueous surfactant medium and then the particle was coated with AgBr. The main objective of this project is to study the effects of different parameters like types of acids, surfactants, reactant concentration, temperature, and sonication on core particle size and growth rate. Finally to coat the core with AgBr in surfactant assisted medium.

The sulfur nanoparticles were preparation by well known acid catalyzed precipitation reaction from sodium thiosulphate in presence of surfactants. We used both inorganic and organic acids, the results show organic acid gives smaller size of sulfur particles. The size of the particles is also depends on the reactant concentration and acid to reactant ratio. The effect of different surfactants (TX-100, CTAB, SDBS, and SDS) on particle size was also studied and found the surfactant can significantly reduce the particle size with out changing the shape. The size reducing ability is not same for all the surfactants, depends on the types of surfactant. Anionic surfactant SDBS is more efficient for controlling the uniform size in both the acids medium. However, in CTAB solution, we got lower size particles in a certain reactant concentration range, and we got lowest 30 nm particles in this medium. Sulfur obtained by this method was orthorhombic or α-sulfur with S_8 structure

As the sulfur nanoparticles are formed by a precipitation reaction, therefore, the overall process can be subdivided in to three steps: nucleation, growth, and particle agglomeration. For this reaction nucleation is very fast so particle size is mainly controlled by particle growth and agglomeration. Actually, as reaction rate is very fast the growth rate is mainly depends on the diffusion of newborn particle from the bulk phase to surface of the nuclei. The growth and agglomeration rate are depend on some reaction parameters, like temperature, reactant concentration, presence of different surfactants, and also on surfactant concentration. Those parameters increase the diffusion rate show higher growth rate. The increase in temperature and reactant concentration increases the size of the particle. The presence of surfactants creates a charged surface layer on the hydrophobic sulfur particle after adsorption and ultimately reduces

the growth rate and agglomeration. The particle growth rate also depends on the surfactant concentration, with increase surfactant concentration growth rate decreases, and become constant near to its CMC value.

The core sulfur particles were coated with AgBr to from S@AgBr core-shell particles in aqueous medium. The core shell particles were confirmed by DLS measurement and UV spectroscopy. The core surface was modified with CTAB miceller solution to make the coating favorable. The overall size and shell thickness can be controlled by varying the reactant concentration both the core and shell material. The core-shell particle also was characterized by TGA, DLS, SEM and BET.

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Nomenclature

AFM	Atomic force microscope
CMC	Critical micelle concentration
CTAB	Cetyl trimethyl ammonium bromide
DLS	Dynamic light scattering
K_a	Ionization constant of acid
NMR	Nuclear magnetic resonance
PBO_2	Benzoyl peroxide
PMMA	Polymethylmethacrylate
PVC	Polyvinyl chloride
SDBS	Sodium dodecyl benzene sulphonate
SDS	Sodium dodecyl sulphate
TEM	Transmission electron microscope
TGA	Thermal gravimetric analysis
TX-100	Triton X-100
XRD	X-ray diffraction

Chapter 1

INTRODUCTION

1. Introduction

"Small is beautiful

Smaller are beautiful

All good things come in small packages"

1.1   History

But from the last century, it is clear that small thing not only beautiful but also powerful. Therefore, from the last decades nanotechnology has emerged as a promising vehicle for an emerging scientific and technological revolution. The idea of nanotechnology was first highlighted by Nobel laureate Richard P. Feynman, in his famous lecture at the California Institute of Technology (Caltech), 29th December, 1959. In his talk, he 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 1970's Norio Taniguchi first defined the term nanotechnology. According to him, "Nano-technology mainly consists of the processing of, separation, consolidation, and deformation of materials by one atom or by one molecule". And in1980's another technologist; K. Eric Drexler promoted technological significance in nano scale. The main important thing in nano dimension is the properties of particles are far differing than bulk scale properties.

1.2   Definition

Nano is used as a prefix for a unit of time or length, it means one billionth of that unit. The prefix "nano" originates from the Greek word "dwarf" that means something small. In conventional view, nano material means among the three dimensions at least one dimension should be less than 100 nm. But when ever all three dimensions are less than 100 nm, it is called nano particle. Nano particles are of great scientific interest as they are effectively a bridge between bulk materials and atomic and molecular structures. A bulk material should have constant physical properties regardless of its size, but where as in nano-scale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor particles,

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surface plasmon resonance in some metal particles and super para-magnetism in magnetic nanoparticle. There fore, in recent year nanoparticle synthesis is an interesting research topic.

1.3   Approaches of synthesis

For synthesis of nano material there are two approaches, "Top Down" and "Bottom Up". The "Top Down" approach often uses the traditional workshop or micro fabrication methods where externally-controlled tools are used to cut, mill and shape materials into the desired shape and order. For example like lithographic techniques (e.g., UV, electron or ion beam, scanning probe, optical near field), film deposition and growth, laser-beam processing and mechanical techniques (e.g., machining, grinding, and polishing). Where as "Bottom-up" approaches, in contrast, use the chemical properties of single molecules to cause single-molecule components to automatically arrange themselves into some useful conformation, like chemical synthesis, laser induced assembly (i.e., laser tapping), self assembly, colloidal aggregation and 2-photon confocal processing. These approaches utilize the concepts of molecular self assembly. The trick with bottom-up manufacturing is the understanding of chemical and physical properties of nanoparticle and manipulating them to self-assemble. Neither the top-down nor bottom-up approach is superior at the moment each has its advantages and disadvantages. However, the bottom-up approach has an inherent size limit much smaller than top down approach. And also bottom up approach have the potential to be more cost-effective in the future because for this approach there are absolute precision, complete control on the process and minimum energy loss compare to top down approach.

1.4   Types of nanoparticle

Now the particles in nano dimension can be categorized in different groups, like pure solid nano particle, composite or core-shell particle, and hollow particle. The solid nanoparticle is common but core-shell and hollow nanoparticles have different characteristics. The core-shell nanoparticle is the nano sized particle that has a core material with a concentric coating by different material depending on the end use of the particles. Core-shell nano particles are highly functional material with modified properties, which are quite different from the both core and shell particles. The properties of particles can be modified by changing either constituting

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materials or core to shell ratio. (Oldenberg, et al. 1998) Due to coating of shell material, the properties of the core particle can be modified, reactivity decreases, thermal stability increases, so overall particle stability and dispersibility of the core particle increases. Core-shell material having the economic interest also, as precious material is coated over inexpensive material so that consumption of precious material reduces compare to if using pure same size material. If core material can be removed by any treatment either by dissolution or calcinations, then it is converted to hollow nanoparticle and for hollow particle both the surface inner and outer are used for catalytic reaction purpose.

Different kinds of core-shell particles and hollow particles are shown in Figure 1.1. In Figure 1.1 (a) surface of core particle modified by bifunctional molecule and shell material selectively deposited on the surface of core material. In Figure 1.1 (b), shell material deposited on core surface and formed a complete layer on it. Shell material can also deposit on the core surface directly by co-precipitation method, particle shown in Figure 1.1 (c). Small sized precious valued core material [like gold (Au), platinum (Pt), Silver (Ag)] coated by low cost stable silica material shown in Figure 1.1 (d). Even multiple core particles can be coated by single cell material shown in Figure 1.1 (e). In Figure 1.1 (f), shown the hollow particle, after core-shell particle formation; core is removed by either calcinations or by dissolution of core material using suitable solvent. These kinds of hollow particle are known as quantum bubble. Concentric nano shell of alternative coating of dielectric core and metal shell material on each other is shown in Figure 1.1 (g). These types of particles are also known as nanomatryushka. (Radloff and Halas, 2004; Wang, et al. 2007). These types of particle are mainly important for plasmonic properties study.

1.5. Applications

Actually in nano dimension percentage of surface molecule compare to bulk molecule is high, that means activity of the particle in nano dimension increases. So, normal properties of the particle like heat transfer; mass transfer, catalytic activity, etc are all increases. But compare to other nano particle hollow and core-shell nanoparticle have more industrial application. In hollow particle, both the inner and outer surface area is available for the specific application. Nano and micro sized hollow particles are used for different purpose like, micro-vessel, catalytic support (Sakanishi, et al. 1996), adsorbents (Zhao, et al. 1998), light-weight structure materials

(Sugama and Lipford, 1997; Wijnhoven and Vos, 1998), and thermal and electric insulators (Ansermet and Baeriswyl, 1994). And core-shell nanoparticle have a lot of interests for effectively use in pharmaceutical, (Caruso, 2001) electronics, (Kortan, et al. 1990; Hoener, et al. 1992; Qi, et al. 1996) biological application (Sounderya and Zhang, 2008; De, et al. 2008; Salgueirino-Maceira and Correa-Duarte, 2007; Daniel and Astruc, 2004).
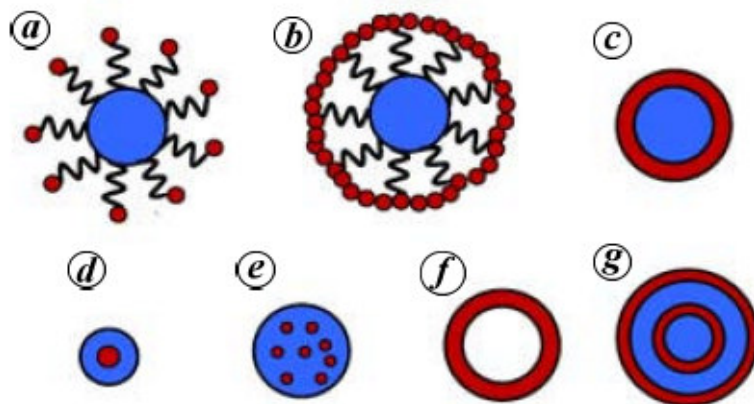
Figure 1.1. Variety of different core-shell particles. (a) surface of the core particle modified by bifunctional molecule on which shell material deposited, (b) a uniform layer of shell material on the modified core surface, (c) Smooth coating shell material on dielectric core material, (d) Encapsulation of very small precious material with dielectric material, (e) multiple small core material coated by single shell material, (f) Quantum bubble, (g) Nanomatryushka material. (Karele, et al. 2006)

Chapter 2

BACKGROUND LITERATURE

REVIEW ON TYPES, SYNTHESIS, AND APPLICATION OF CORE-SHELL NANOPARTICLES

2.1. Importance of core-shell particles

Core-shell structured nanoparticles are now attracting more and more investigation interest, since these composite nanoparticles are constructed of cores and shells of different chemical compositions. Ultimately, they show distinctive properties of varied materials together, especially, to manipulate the surface functions to meet diverse application requirements (Caruso, 2001; Daniel, 2004). The properties of the core-shell particles, in general, are different from the both pure core and shell material. The purpose of coating on the core particle was carried out for different reasons like surface modification, increase functionality, stability and dispersibility, control release of core material. The presence of shell material can alter some properties of core particle, like surface charge, functionality, reactivity. Core-shell particles are widely used in different applications like biomedical, pharmaceutical, catalysis, electronics etc.

In biomedical field these particles are mainly used for bioimaging, control drug release, targeted drug delivery, cell labeling and also for replacement and support for the tissues (Sounderya, 2008). The core-shell particles have variety of application like fluorescent diagnostics labels, catalysis, avoiding photo degradation, enhancing photoluminescence, creating photonic crystals and chemical and colloidal stability. These all applications are well reviewed by Karele, et al. 2006.

2.2. Classification of core-shell particles

The core-shell particles are diversely used for different industrial field including biological, modern electronics, coating industry, etc. So it is difficult task to classify the all core-shell material depending on their industrial application. So, here we classified the core-shell material depending on their material property. Core or shell particles are either made of inorganic or organic material. In this section, we mainly discuss about different types composite (core-shell) particles with their industrial application. According to material properties, composite material is mainly classified into four groups: (i) inorganic-inorganic, (ii) organic-organic, (iii) inorganic-organic, (iv) organic-inorganic core-shell materials.

2.2.1 Organic-Inorganic core-shell material

These types of particle core and shell are made of organic or polymer and inorganic materials respectively. The shell materials mainly studied are either metal, metal oxide, or silica. Due to coating of such inorganic material, these types of particle are having high resistance power to corrosion and abrasion. Phadtare, et al. (2003) synthesized gold coated polyurethane microsized core-shell particle for biocatalytic activity of this particle in pepsin digestion application. Polymer core with inorganic shell particle is also used for hollow particle synthesis (Yang, et al. 2008; Yang, et al. 2008; Sgraja, et al. 2006; Song, et al. 2004, Caruso, et. al. 2001; Caruso, et. al. 1998; Caruso, 2000). After formation of core-shell particle, the core polymer can be easily removed by either using suitable solvent or by calcination to make hollow particle. Inorganic coating on the organic or any polymer material increased the colloidal stability of the core material.

2.2.2. Inorganic-organic core-shell nanoparticle

These types of particles are made of metal, metal oxide or silica core with shell of polymer or any other organic material. The polymer coated inorganic material have a broad spectrum of applications, ranging from catalysis, to additives and pigments, paints, cosmetics, and inks (Hofman-Caris, 1994). Magnetic nanoparticle with polymer coating has an interest in biological field. These types of particles are used for magnetic separation of biochemical products, cells and also used for control drug releases with in the body (Dresco, et al. 1999). Different inorganic-organic composite particle have a lot of interest in biological application since their rich surface functional groups can be tailored with ease to serve as conjugates for biological application (Gittins and Caruso, 2001; Clark, et al. 2000; Watson, et al. 1999). Polymer coated nano silica particle, increases colloidal stability and broadly used as optical devices, sensors, and electrical devices. (Zhang, et al. 2007) Cellulose coating on the TiO_2 nanoparticle improve the pigment property of the particle. Polymer coated inorganic particle find the application in dentistry as a brace material and filler. (DeBruijn, et al. 1999; Olea, et al. 1996)

2.2.3 Organic-Organic core-shell nanoparticle

For these types of particles both core and shell particles are made of polymer. Polymer coating on another polymer just modified some property of the particle. Polymethylmethacrylate (PMMA) coated with antimony trioxide with polyvinyl chloride (PVC) enhances the toughness and strength of the PVC (Xie, et al. 2004). Polymer coating on another polymer with some inorganic salt increases the thermal sensitivity of the material, catalytic activity. (Lu, et al. 2006; Garito, et al. 2003)

2.2.4 Inorganic-inorganic core-shell nanoparticle

Among the all different types of core-shell nanoparticle inorganic-inorganic core-shell particles are most important. For these types of material both core and shells are made of inorganic materials. These types of particle are widely used for commercial purpose mainly for improvement in semiconductor, catalyst, quantum dots, optical bioimaging, etc. Among the different inorganic-inorganic composite particles metallic core-shell particles are having more important. For these types of particles core and shell both are made of metal, metal oxide, semiconductor, any other inorganic compound, or silica. Metal coated with silica core-shell particles have wide application in optical sensing and optical properties are changes with the silica thickness. Ung, et al. (1998) modified the coating method to control uniform silica coating on nano silver (Ag) core particle. Lu, et al. (2002) synthesized silica coated gold particle and Li, et al. (1999) synthesized the silica coated Ag particles by sol-gel method and studied the different properties of those particles. Silver/silica particles can be used in fluorescence imaging and again the region of emission is depends on the thickness of the silica. (Li, et al. 1999) Coating of Fe_2O_3 on MgO and CaO particles can enhance the capability of toxic material adsorption form the environment like SO_2 and H_2S compare to pure MgO and CaO (Decker, et al. 1996; Carnes, et al. 2002). Magnetic nanoparticle with different inorganic coating have lots of important, these types of particle used for magnetic resonance imaging (MRI) contrast agent, magnetic separation of oligonucleotides, and other biocomponents, and magnetically guided site specific drug delivery system. (Santra, et al. 2001; Wang, et al. 2005). Gold coating on any particle increases the chemical stability by protecting the core material from oxidation and corrosion and increased the biocompatibility and affinity via amine/thiol terminal groups (Wang et al, 2005).

Among the different inorganic core-shell particles, semiconductor core-shell particles are most important. The core of these types of particles is made of either semiconductor material, semiconductor alloy and shell is made of metal, metal oxide or silica and in some case both core and shell are made of semiconductor material or semiconductor alloy (Lambert, 2009; Hota, 2007; Mews, 1994). These types of particle either binary with core and shell or tertiary i.e., core with double shell coating. The most common binary structures are well known as quantum dots are mainly core and shell are made of alloy material. These types of particles are used for luminescence and fluorescent bioimaging (Schreder, et al. 2000).

Another important inorganic core-shell particles, the core is made of one or more lanthanide group elements where as, shell is made of silica or any other lanthanide group elements. This type of particles shows high luminescence and has a potential application in the field of electronics and bioimaging (Yi, et al. 2006).

2.3   Synthesis of core-shell particles

Considering the synthesis techniques of core-shell particles, it can be classified into two types depending on the availability of core particle. (i) The core particles can be synthesized separately incorporated to the system for coating of shell material, (ii) the core particles are synthesized in situ in the medium and followed by coating of shell material (Phadtare, et al. 2003; Wang, et al. 2009). In this case, at first core particle synthesize in the reactor by using suitable reagent then after complete core formation again reagents are added to form shell particle in situ (Wang, et al. 2005; Bao, et al. 2008), and core surface modified so that shell material selectively deposited on core surface and core-shell particle will formed.

Preparation of core-shell particle involves multistep synthesis procedure. But the most important step during synthesis is to maintain uniform coating and controls the shell thickness. There are various methods for synthesis of core-shell particles used by different research groups, those are precipitation (Imhof, 2001; Ocana, et al. 1991), polymerization (Zou, et al. 2008; Okaniwa, 1998; Dresco, et al. 1999), micro emulsion (Hota, et al. 2004, 2007; Han, et al. 1998), sol-gel condensation (Song, et al. 2008; Li, et al. 1999), layer by layer adsorption techniques (Srivastava, et al. 2008; Shenoy, et al. 2003), etc. Although several researchers are attempted to control the thickness and uniform coating of the shell using several methods but still it is difficult

to proper control. The main difficulties are: (i) agglomeration of core particles in the medium, (ii) preferable formation of separate particle of shell material rather than coating of core, (iii) incomplete coverage of core surface, (iv) it is not possible to generalize the method for a wide range of materials. So now in the recent year, to overcome these difficulties, core-shell particle synthesis with uniform coating with proper thickness is a challenging research topic. Infact, for complete uniform coating the control of reaction rate and modification of core particle surface so that the shell material can selectively deposited on the core surface are the most important parameters. Usually, for the core surface modification purpose surface active agents (Wu and Chu, 1998) and polymers (Hofman-Caris, 1994; Liz-Marzan, et al. 1996; Perro, et al. 2006) are widely used by different research groups. These surfactants or polymers can change surface charge and selectivity of core particles so that shell material selectively deposited on the core to form uniformed and completely coated core-shell particles.

2.4 Mechanism of core-shell particle formation

Different methods are widely used for core-shell particle formation. Among the all methods, mechanisms of some methods are well reviewed by different researchers (Caruso, 2001; Sounderya and Zhang, 2008; Karele, et al. 2006; Zou, et al. 2008).

2.4.1. Core synthesis

Core particle can be synthesized either in situ or separately and incorporated directly to the reaction system. When ever core particles synthesized separately, the core particle is supplied to reaction system as a template with surface modifier. So that shell material is selectively deposited on the template surface. The basic advantage of external synthesis of core particle, the cores are in pure form, less possibility of the impurities on the core surface. But where as in situ synthesis, the main problem is some impurity from the reaction medium may be entrapped between core and shell layer.

Mainly for inorganic core particle synthesis chemical precipitation reaction in microemulsion or bulk aqueous system is common technique. For metal core particle synthesis the best techniques is reduction of metal salt by suitable reducing agent. This method is used by different research group (Song, et al. 2008; Li, et al. 1999; Marinakos, et al. 1999; Salgueirino-

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Maceira and Correa-Duarte, 2006). For metal oxide core particle synthesis sol-gel method is also used by different group (Sertchook and Avnir, 2003; Ocana, et al. 1991; Pena, et al. 1997; Wang, et al. 2009; Zhou, et al. 2006). But for polymeric core particle synthesis different polymerization techniques are mainly used (Imhof, 2001; Shenoy, et al. 2003).

2.4.2. Shell Synthesis

2.4.2.1 Organic/Polymerization method

One of the most important mechanisms for polymer shell formation is the polymerization; it would be either radical polymerization or chemical oxidation polymerization. In radical polymerization, it would be either free radical or atom transfer polymerization. In case of in situ polymerization, the first step is nano scale additive are prepared with appropriate surface modifier and then the modified additives are dispersed in the monomers. And this is followed by bulk or solution polymerization. Hofman–Caris (1994) comprehensively reviewed the process used to obtained inorganic core and polymer shell particle through polymerization. Zou, et al. (2008) reviewed the different types of polymerization for silica-polymer composite particle formation. Lei, et al. (2007) discussed about surface modification of silica by bromine attachment to silica and then polymer coating of t-butyl acrylate. Dresco, et al. (1999) discussed about the different microemulsion methods for formation magnetite core (Fe_3O_4) and hydrophilic polymeric shell coating. Ballauff, et al. (2007) synthesized organic core and organic shell nanoparticle by polymerization method and characterized by cryo-TEM, DLS, NMR, AFM etc. Wang, et al. (2009) used direct method for core-shell particle formation. Those people used AAEM (Acetoacetoxyethylmethacrylate) modified ZrO_2 core as template for synthesized ZrO_2/PAAEM/PS core-shell nanoparticle though the polymerization of the emulsifier-free emulsion process. Pena, et al. (1997) was synthesized TiO_2-polymer composites material by free radical polymerization. For particle synthesized, they were using poly-(methyl metacrylate) (PMMA) in acrylic acid with 0.5% of benzoyl peroxide (PBO_2) for core surface modification.

2.4.2.2 Sol-Gel Method

The sol-gel process is a wet-chemical technique (chemical solution deposition) widely used recently in the fields of material science and ceramic engineering for mainly metal oxide particle

synthesis. The sol-gel process is a two step process; hydrolysis of metal salts followed by condensation process. This method is mainly used for the synthesis of metal or metal oxide/polymer core-shell particle. Some people used this method for core-shell semiconductor particles synthesis (Boissiere, et al. 2006; Caruso, et al. 2001).

2.4.2.3. Microemulsion Method

In microemulsion method particle size and morphology can be controlled precisely. Microemulsion is a mixture of oil and aqueous phase with suitable surfactant and cosurfactant. In the microemulsion surfactants are formed reverse micelles and cosurfactant reduce the electrostatic repulsion force between charged head group of the surfactant molecules. For particle formation by this method, reagents are added in aqueous phase. Here micelles act as a center for nucleation and epitaxial growth of nanoparticles. By changing the molar ratio of water to surfactant (R), the particle size and morphology can be controlled. By this method mainly inorganic core-shell like metal, metal oxide or semiconductor particles are synthesized. Hota, et al (2004, 2007) synthesized CdS-Ag$_2$S nanoparticles. Carpenter, et al (1999) synthesized gold coated iron core-shell nanoparticles. Lambert, (2009), Decker, et al. (1996); Carnes, et al. (2002) synthesized different core-shell nanoparticles by microemulsion method. Different research group (Viswanadh, et al. 2007; Ethayaraja, et al. 2008; Shukla, et al. 2006; Kumar, 2003; Tojo, et al. 2004) predict for particle formation in microemulsion considering the intermiceller exchange of reactants and newborn particle by both single and multiple double microemulsion system.

2.4.2.4. Mechanochemical Synthesis

This is one kind of nanoparticle synthesis techniques where both mechanical force and chemical treatment both are applied for nanoparticle synthesis. There are different types of mechanical forced used for particle synthesis but among them most common and widely two types of mechanical force are applied for particle synthesis are describe here.

2.4.2.4.1. Sonochemical synthesis

This synthesis technique involves chemical reaction for nanoparticle synthesis and with constant sonication to improve reaction rate, breakdown the agglomerates, and enhance the dispersion of

the particles in the solvent medium. Ultrasonic irradiation of the frequency range 20 kHz to 1 MHz has been used in most of the sonication methods. Ultrasonic irradiation speeds up the reaction because of the localized cavities that are formed and they last only for a short time. Thus, these cavities act as micro reactors for the reaction to occur and the mechanical effects to also take place. The mixture of reactants in suitable solution is subjected to ultrasonic waves and the temperature and pH maintained to obtain the nanoparticles dispersed in core material. The chemical reaction that occurs depends on the shell material formation as core is synthesized separately and added to the reactant mixture (Pol, et al. 2002). Composites such as iron oxide with gold shell and iron/cobalt alloy nanoparticles are ones with metallic shell (Wu, et al. 2007), Ag coated silica particle was synthesized in presence of inert argon gas (Pol, et al. 2002), and those such as Fe/Co composite is synthesized by this method (Li, et al. 2003)

2.4.2.4.2. Electrodeposition

Formation of shell over the core with charged polymers or inorganic material can be carried out by this method in presence of electrical potential. In general electric field is varied like a wave with positive and negative cycles. It is found that the metal deposits on the core surface during negative cycle but where as charged polymer deposited during the positive cycle. There fore, by controlling the cycle time span the thickness of the shell material can be controlled. The material deposition occurs on one of the electrodes. The matrix material for core-shell nanoparticles formation can be the electrode or the electrolytic medium. Banerjee, et al. (2000) studied the synthesis of iron oxide shell iron in silica nanoparticles. Chipara, et al. (2007) describes the synthesis of polypyyrole-iron nanoparticles. Both the procedures are almost similar, the only difference being that in the iron oxide shell on iron in silica nanoparticles, the electrolytic medium, and silica gel is used as the matrix for the nanocomposite. While for the PPy-Fe, it doesn't have a matrix material and belongs to the class of nano-nanoparticles. The PPy-Fe can be dispersed in the desired matrix material later (Ivan, 2004). CuI-Au and CuS-Au core-shell nanoparticles were synthesized by Gu et al (2008) using electrochemical atomic layer deposition.

2.5   Applications

Core-shell particles as a combined form have an industrial importance especially in biomedical and electronics field. But separately, core and shell have different use in presence of other. Here, in short we discuss about some industrial use of core-shell nanoparticle, and also use of core and shell in presence of other.

2.5.1   Core material property is important

For hollow particle synthesis form core-shell particle, the property of core material is an important factor. It is easy to synthesize hollow particle if the burning temperature of the core material is low or core material have high solubility in a suitable solvent and for that purpose polymeric core are most suitable (Caruso, et. al. 2001; Caruso, et. al. 1998; Caruso, 2000; Yang, et al. 2008; Sgraja, et al. 2006; Yang, et al. 2008; Sgraja, et al. 2006). Magnetic nanoparticle Iron oxide or cobalt core particles are used to enhance MRI image by improving contrast (Sounderya and Zhang, 2008).

2.5.2   Shell material property is important

Shell material coating on core surface increase the colloidal stability of core particle. Among the different inorganic material coating, silica is most common one. Silica is an inert material, so it dose not affect the redox reaction of core material, it just block the core particle so that colloidal stability of the particle increases. Another thing silica shell is optically transparent so chemical reaction of the core particle can be studied by spectroscopically. The important thing silica shells reduce the bulk conductivity of the metal particle; prevent the photo catalytic degradation of polymeric material. Silica shell also used for modulates the position and intensity of colloidal metal surface plasmon adsorption band (Ung, et al. 1998).

Polymeric shell particle core-shell and hollow particles are used for control drug delivery, cell (Crotts and Park, 1995; Pathak, et al. 1992), enzyme transplantation (Pathak, et al. 1992), contaminated waste removal, gene therapy.

2.5.3 Core-shell both material properties are important

Carbon coated TiO_2 (Zhang, et al. 2009) and carbon coated with $Li_3V_2(PO_4)_3$ core-shell particles (Ren, et al. 2008) are use to increases the efficiency of lithium ion batteries. The core-shell particles are biocompatible and used for control drug delivery purpose and encapsulated drug with out affecting the core material. Au/Ag core-shell nanocomposite particles are used for labeling cancer and tumor cells (Lee, et al. 2007).

2.6 Concluding remarks

From the above study it can be concluded that core-shell particles have lots of importance in different important areas especially biomedical, pharmaceutical, and electronics. There fore, last ten years different research groups are trying to synthesize core-shell particles by different routs. For organic shell, polymerization is one of the widely used methods for core-shell particle synthesis. But considering all different types of particles microemulsion is the best method for controlling the size and morphology of the particles. But in all methods there are some limitations either particle separation is difficult or reaction steps are complicated. But in aqueous surfactant medium it is easy to separate the particle after complete reaction and also cost effective. People are tried to synthesize particles in aqueous medium but all are mainly for single composite pure particles. Very less literatures are available on core-shell particle synthesis in aqueous surfactant miceller solution.

In this project, we are trying to synthesize core-shell particle in aqueous surfactant miceller solution. Specifically we chose sulfur particle as a core material with an intension, in future we can easily remove the core material and can produce a hollow particle of shell material. First we have studied the different parameters of growth kinetics and equilibrium particle size of sulfur nanopaticles. Then, also we have studied sulfur-AgBr core-shell nanoparticle in aqueous surfactant medium.

2.7 Motivation of the project

Among the different methods for nanoparticles synthesis, microemulsion method is widely studied method due to its advantages in controlling of particle size and morphology very nicely. In contrast, as microemulsion is a mixture of oil and aqueous phase with suitable surfactant and

co-surfactant, it is important to maintain proper composition for microemulsion formation, as well as after completion of the particle formation, particle separation and purification is a difficult task. Although, according to literature it is possible to reuse the oil and surfactant both after separation of the particles (Sarkar, et al. 2008), but in practical it is difficult. Therefore, in the microemulsion method, purification of the particles, consumption of huge amount of oil, surfactants, and co-surfactants is become an important issue. Therefore, in this project attempt has been made to synthesize sulfur core and sulfur-AgBr core - shell nanoparticles in aqueous medium. The size of the particles was controlled in presence of surfactants.

2.8   Objectives of the project

The overall objective of the project is to synthesize and characterized the S@AgBr core-shell particles in aqueous surfactant assist medium.

The specific objectives are:

(1)   To optimize the acid to thiosulphate ratio of equilibrium sized particle for a fixed sodium thiosulphate concentration in presence of both organic and inorganic acids for preparation of sulfur nanoparticles.

(2)   To know the change in particle size with the variation of sodium thiosulphate (reactant) concentration in presence of both organic and inorganic acids.

(3)   To know the effect of different surfactants on particle size in presence of both organic and inorganic acids medium.

(4)   Characterization of the core particle (sulfur) by SEM, TGA, XRD, DLS.

(5)   To know the growth kinetics of the core (sulfur) particle formation.

(6)   Uniform coating of shell material on the core surface and evaluate the overall core-shell particle size with changing the reagent concentration.

(7)   Characterization of the core-shell particle by XRD, TGA, SEM, DLS, BET.

2.9   Organization of thesis

The thesis is organized into six chapters. The Chapter-1 contains the introduction. Here, mainly definition, the history of nanotechnology, different type of nanoparticles, and the approach of synthesis of the nanoparticles etc. are discussed. In Chapter-2, related to literature review on

different types of core-shell nanoparticles with synthesis and application of those particles are discussed. Chapter-3 presents the preparation and characterization of core (sulfur) particles in aqueous surfactants medium. Chapter-4 presents detail studies on growth kinetics of sulfur nanoparticles in presence of aqueous surfactant medium. Chapter-5 is about the preparation and characterization of sulfur-AgBr core-shell nanoparticles. Finally, Chapter-6 presents the overall conclusion of the research output of this project and some suggestions for the future work.

Chapter 3

SYNTHESIS AND CHARACTERIZATION OF CORE (SULFUR) PARTICLES

3.1. Introduction

Elemental sulfur in nano, micro or bulk state is widely used for different industrial purpose like production of sulfuric acid, nitrogenous fertilizers, phosphatic fertilizers, plastics, enamels, antimicrobial agent, gun powder, petroleum refining, other petrochemical, ore leaching, pulp and paper industry, and in different other agrochemical industries.(Ober, 2002). Nanosize sulfur particles also have many important applications like pharmaceutical, synthesis nano composites for lithium batteries, (Yu, et al., 2004; Zheng, et al. 2006; Yong, et al. 2007; Kanno, et al. 2008), modification of carbon nano tubes, (Barkauskas, 2007), synthesis of sulfur nano wires with carbon to form hybrid materials with useful properties for gas sensor and catalytic applications (P. Santiago et. al., 2006) etc. In the area of agricultural field, sulfur is used as fungicide against the apple scab disease under colder conditions, (Ellis, et al. 1998), and also a major fungicide in conventional culture of grapes, strawberry, many vegetables and several other crops. Sulfur is one of the oldest pesticides used in agriculture and it has a good efficiency against a wide range of powdery mildew diseases as well as black spot.

Different methods are used for nano size particle synthesis, among them micro emulsion method is one of the very important method to control the particle size. But microemulsion itself is a very complicated system, composing of oil, surfactant, co-surfactant and aqueous phases with specific composition. The main disadvantages of microemulsion method include separation of the particles from the microemulsion is difficult, surfactant consumption is more.

In spite of many exciting applications, there are only a few very recent literatures available on synthesis of sulfur particles by different investigators (Deaspande, et al. 2008; Cheng, et al. 2005, 2006; Xie, et al. 2009) in both, aqueous and micro emulsion phase with different reagents. Deshpande et al. (2008) have prepared sulfur nanoparticles from H_2S gas using biodegradable iron chelate catalyst in reverse microemulsion system. They have prepared α-sulfur or rhombic sulfur of average particle size 10 nm with a distribution from 5 – 15 nm. They have also studied the antimicrobial activity of sulfur nanoparticles and shows it is very much effective, especially when the particle size is low. Guo et al. (2006) have prepared sulfur nanoparticles from sodium polysulfide by acid catalysis in reverse microemulsion system. They found monoclinic or β-sulfur with average particle size of around 20 nm. Xie et al. (2009) have prepared nano sized sulfur particles from sublimed sulfur itself. They added aqueous cystine

solution drop wise on a saturated alcoholic saturated sulfur solution with constant ultrasonic treatment and crystine – nano - sulfur sol was obtained.

Now, realizing the importance of sulfur nanoparticles in different application we feel that development of some easy method is highly essential. In the method of Deshpande et al (2008) H_2S gas was used as a source of sulfur, as it is in gaseous state so the arrangement of the contact between solid chelate and gaseous H_2S is more complicated apart from the complicacy of microemulsion. And for the method of Wang Zi Cheng et al (2005, 2006) polysulfide used as a source of sulfur but for synthesis of polysulfide; nano sized sulfur particles are require as a raw material. In Xie et al. (2009) proposed method also have same problem, i.e., for nano sulfur particle synthesis sulfur itself used as raw material. In the present method large amount of sulfur particles are possible to prepare easily using a cheap raw material and aqueous surfactants solution for agricultural and other applications where consumption is more. Even, from the basic understanding point of view also it is very important if we apply this route in microemulsion based synthesis.

We found in this study orthorhombic or α-sulfur with S_8 structure was formed. Here, we have attempted to understand the basic mechanism of particle formation in presence of different inorganic and organic acids, reactant to acid ratio, effect of reactant concentration. Finally, we have studied the effect of micellar solution of different surfactants (TX-100, SDBS, SDS, CTAB) on size and zeta potential of sulfur particles.

3.2.   Experimental Section

3.2.1. Materials

The required all chemicals were taken from the following companies: Sodium thiosulphate ($Na_2S_2O_3$, $5H_2O$), Oxalic acid ($H_2C_2O_4$, $2H_2O$) from Rankem (India), Triton X-100 (TX-100), Sodium dodecyl sulphate (SDS), Cetyl trimethyl ammonium bromide (CTAB) from Loba Chemie Pvt. Ltd. (India), Sodium dodecyl benzene sulphonate from Sigma Aldrich (Germany), and Hydrochloric acid (HCl), Sulfuric acid (H_2SO_4), Nitric acid (HNO_3) Merck (India). All chemicals were used as it is received without any further purification. Ultra pure water of 18.2 MΩ.cm resistivity and pH 6.4 – 6.5 (Sartorius, Germany) was double distilled again and used for all the experiments.

3.2.2. Particle Synthesis

Stock sodium thiosulphate was prepared dissolving solid thiosulphate, in double distilled water and different acid solution also prepared from the pure stock. Both reagents were filtered with 0.2 μ nylon 6, 6 membrane filter paper from Pall Life science, USA. In presence of acid (say HCl) sodium thiosulphate is disproportionate to sulfur and sulfonic acid according to the following reaction.

$$Na_2S_2O_3 + 2HCl \rightarrow 2\ NaCl + SO_2 + S\downarrow + H_2O \hspace{3cm} (3.1)$$

$$SO_2 + H_2O \rightarrow H_2SO_3 \hspace{5cm} (3.2)$$
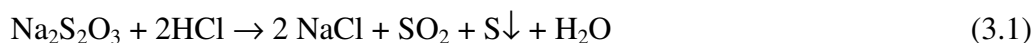
After mixing the reactants, 30 and 40 minutes equilibrium time was given for the completion of reaction and particle growth for inorganic and organic acids respectively. After equilibration, the sample was sonicated in a bath and particle size was measured immediately after sonication. In presence of three times CMC of individual respective surfactants, the reactants are mixed and same procedure was followed throughout the experiments to see the effect of surfactants.

3.2.3. Particle Characterization

The structure of sulfur particles was characterized by X-ray diffraction (XRD) using Philips PW 1830 HT X-ray diffractometer with scanning rate of 0.01º/sec in the 2θ range from 20º to 40º. Particle size measurement was carried out by dynamic light scattering (DLS) using Malvern Zeta Size analyzer, U.K. (Nano ZS). The size and shape of particles were observed under a scanning electron microscope (JEOL JSM-6480LV). Particles were characterized by DT-TGA using Shimadzu.

3.3. Results and Discussion

3.3.1. Effect of stoicheometry ratio of acids on particle size

According to the stoicheometry of the reaction one mole of thiosulphate reacts with two mole of monobasic acid to precipitate one mole sulfur. So at first, we have studied the effect of stoicheometry ratio on particle size for a particular reactant concentration (5 mM) and later we used same ratio for that particular acid. Figure 3.1 shows that with increasing acid (H^+) to

thiosulphate molar ratio the particle size increases, but the size is almost constant above the ratio 2:1 for inorganic monobasic acid, 4:1 for inorganic dibasic acid and 6:1 for organic dibasic acid. So, all the experiments with inorganic monobasic (HCl, HNO_3) and dibasic (H_2SO_4) acids were carried out with the acid (H^+) to thiosulphate ratio of 2:1 and 4:1 respectively. However, in case of organic dibasic acid (oxalic acid) we used that ratio of 6:1 for the all experiments. As a general rule, larger the ionization constant values (K_a) stronger the acid, to get an idea about the ionization constants of different acids we have presented the values in Table 3.1. The acid requirement of H_2SO_4 is about twice than HCl is probably due to first ionization constant value of H_2SO_4 is high and second is low and that of oxalic acid is more due to low values of both the ionization constants.
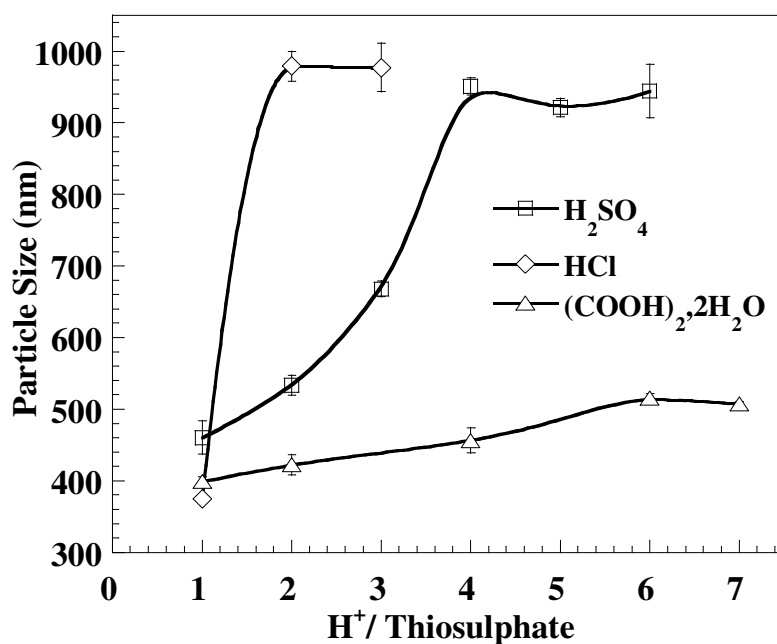
Figure 3.1. The effect of acid to thiosulphate ratio on the size of sulfur particles. Thiosulphate concentration 5 mM.

Table-3.1. Ionization constants of different acids

Acid		Ionization constant (K_a)
HCl (Marsh,1985)		1.74×10^6
HNO$_3$(Nelson,5th edition)		40
H$_2$SO$_4$	(H$_2$SO$_4$) K$_1$	2.4×10^6
	(HSO$_4^{-1}$)K$_2$	1.02×10^{-2}
	(Feng,1995)	
H$_2$C$_2$O$_4$(Qin,2001)	(H$_2$C$_2$O$_4$)K$_1$	5.6×10^{-2}
	(HC$_2$O$_4^{-1}$)K$_2$	5.1×10^{-5}

3.3.2. Effect of types of acids and reactant concentration on particle size

Figure 3.2 shows the effects of both types of acids and thiosulphate concentration on particle size. Let us first consider the effect of reactant concentration on particle size for a particular acid; it is very clear from the Figure that the particle size increases when concentration of thiosulphate increases. The size of the particles are influenced by simultaneous two factors (i) nucleation and followed by (ii) particle growth. Nucleation is instant as soon as reactant is mixed with acids, nucleation process is started. After that when there is a sufficient density of nucleate molecule then growth process is predominated over the nucleation process. But, with increasing reactant concentration the rate of reaction is increases. According to LaMer (1948) rate of the reaction depend on both the concentration of thiosulphate and acid. According to him, rate of reaction = k [T] $^{1.5}$ [A] $^{0.5}$. Where, k is reaction rate constant, [T] and [A] are the thiosulphate and acid concentration respectively. That means with increasing reactant concentration the density of nucleate particles also increase, therefore, after growth process the ultimate particle size and density also increases for a particular acid. Finally, there is more collision between those particles and due to coarsening those smaller particles lead to larger sized particles are stable by minimizing the overall energy of the system (Hu, et al.2005).

Similarly, comparing the results in presence of different acids it is very clear that the particle sizes are also dependent on types of acids. There is a distinct size difference between the organic and inorganic acids at higher reactant concentration; the organic acid shows smaller size particles. At lower reactant concentration HCl shows lowest particle size among all the acids but

the difference is less. Among the inorganic acids size in H_2SO_4 is always higher than HNO_3 but HCl is showing a different behavior. When the reactant concentration is high HCl is showing highest particle size and at low reactant concentration lowest size. In further, we can clearly see from the Figure 3.2 that at higher reactant concentration (10 mM) the increasing order of particle size in presence of different acids are: $C_2H_2O_4 < HNO_3 < H_2SO_4 < HCl$ which exactly same order of acid ionization constants, although the difference between the inorganic acids are very small. As all the inorganic acids are strong and ionization is very fast, the reaction rate is also expected to be fast in compare to organic acid. In presence of inorganic acids as the reaction is very fast, formation of nucleate particles also will be very fast with more particle density, which leads to higher equilibrium particle size. Since all the inorganic acids are strong, ionization is very fast and the differences in ionization constant are also very less. Whereas, for oxalic acid catalyzed reaction rate of nucleation may be slow and the particle density also may be low in compare to inorganic acids, which may lead to formation of smaller particle size. In case of oxalic acid, another reason of lower particle size is probably due to the adsorption of oxalate ion $(C_2O_4^{2-})$ on particle surface, which is clear from zeta potential value. Zeta potential of the particles in presence of oxalic acid is more negative (-8.05 mV) than in hydrochloric acid (-4.17 mV) at a same pH 2.8. The zeta potentials in presence of all other inorganic acids are very close. Higher zeta potential in presence of oxalic acid may reduce the agglomeration tendency of the particles and finally the size become small and particle size distribution is also sharp. The values of zeta potentials in presence of different acids are given in Table 3.2. From the Table 3.2, it is clear that as zeta potential values are low for inorganic acids, so agglomeration tendency also high. Apart from the average particle size, the size distribution is also very important parameter in particle formation. Figure 3.3 shows the particle size distribution among four acids used in our study. Sulfuric and nitric acids have similar size distribution, hydrochloric acid is having little sharp distribution than other two acids but the change is not very significant. The difference was found for the oxalic acid where the distribution is narrow.
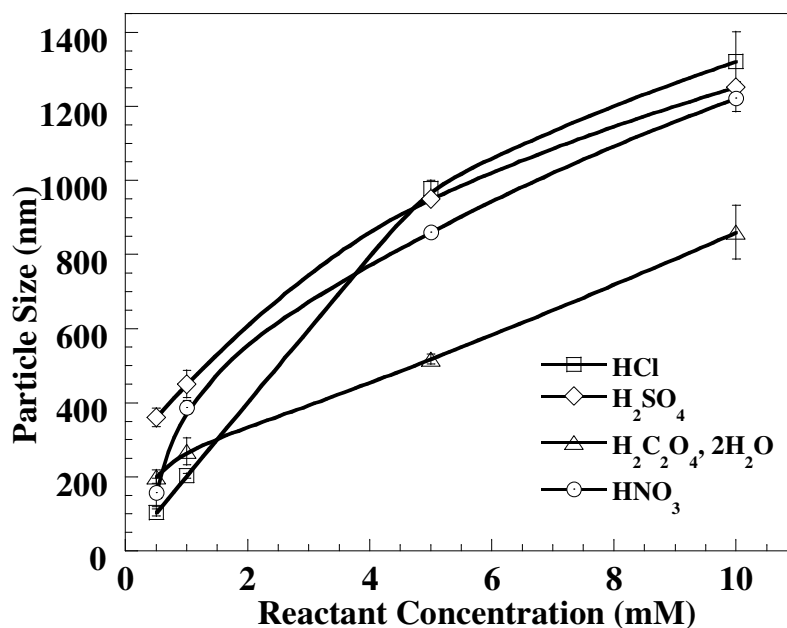
Figure 3.2. The effect of reactant concentration on the particle size in different aqueous acidic medium.
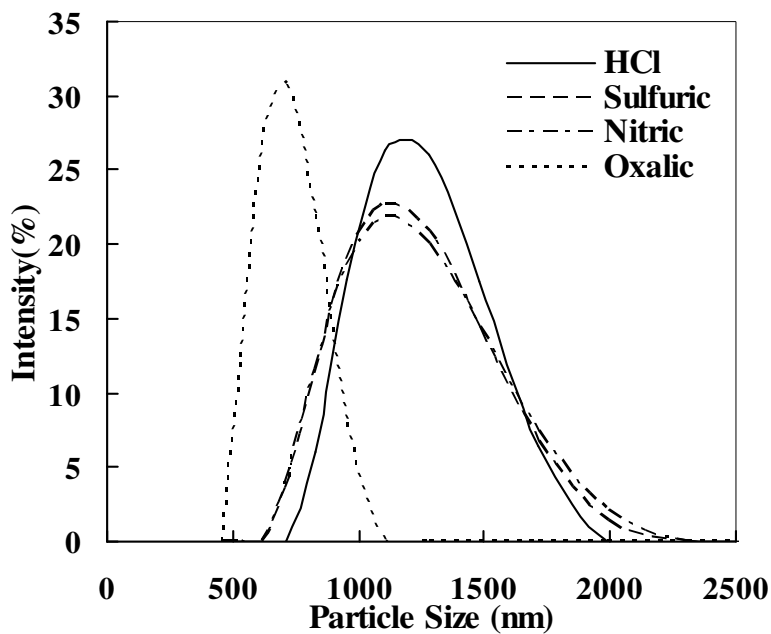
Figure 3.3. Particle size distribution in different acid medium of 10 mM thiosulphate concentrated solution

Table-3.2 Zeta potential of sulfur particles in different medium, Thiosulphate concentration 5 mM.

Medium	Acid	Zeta Potential (mV)
Water	HCl	-2.99
Water	H_2SO_4	-1.85
Water	HNO_3	-2.17
Water	$(COOH)_2$	-8.05
TX-100	HCl	-0.557
SDS	HCl	-76.3
SDBS	HCl	-85.0
CTAB	HCl	23.8

3.3.3. Particle size in presence of surfactant solution

The effect of surfactants on sulfur particle size was tested in presence of HCl and oxalic acid catalyzed reactions with different reactant concentration. The surfactant concentration was kept three fold CMC of respective surfactants. Figure 3.4 shows the effect of surfactants on particle size for HCl catalyzed reaction. In aqueous solution the particle size was continuously increased with the reactant concentration, and after 10 mM reactant concentration the size was so large that the particles were settled down from the liquid phase. But from the Figure 3.4 it is clear that in presence of surfactants there is a significant change in particle size than that in absence of surfactant at 10 mM thiosulphate concentration. Also it is worthy to note that the effect is not same for all the surfactants. At very low thiosulphate concentration (0.5 mM) where the particle size is small in aqueous medium, the effect of surfactant not very significant. At that concentration SDBS is showing almost no change in particle size but other surfactants are showing little higher particle size. It is observed from the figure that the plot of particle size vs. reactant concentration in presence of anionic and nonionic surfactants pass through a maximum. The maximum particle size was observed at same reactant concentration (5 mM) in presence of both anionic surfactants and slight higher (10 mM) in presence of nonionic surfactant (TX-100). Comparisons of maximum particle size in presence of surfactants show in the following order: SDBS < TX-100 < SDS. However, the behavior in presence of CTAB is bit uncommon and interesting. We found that at 5 mM reactant concentration there is a sharp decrease in particle size (~ 55 nm) then again particle size increases up to 10 mM after that trend is as usual to that of

other surfactants. Due to this sudden change between 5 mM to 10 mM reactant concentration we have repeated the experiments several times and got repeatable results. We are still unable to explain this behavior and needs further investigation. Inset of Figure 3.4 clearly shows the size distribution in 5 mM reactant concentration is very narrow whereas at 4 mM it is very wide with large particle size. We believe that type of surfactant plays an important role for this type of behavior. For 5 mM thiosulphate concentration; we also studied the effect of surfactant concentration on particle size. It shows with increasing surfactant concentration particle size decreases and shows minimum 30 nm size particle at 1 mM (close to CMC) surfactant concentration but after that again size of the particle increases and becomes constant to 50-60 nm size (Plot shown in Figure 3.8). Figure 3.5 shows the particle size distribution at 10 mM thiosulphate solution in different surfactant medium. We can clearly see the particle size distribution in presence of SDBS is sharp than other surfactant medium at constant reactant concentration (10 mM). In addition to narrow size distribution at constant reactant concentration, for the total range of reactant concentration studied here the change in size with thiosulphate concentration is less as the height of maxima is less in presence of SDBS. So, SDBS can be use as better size controlling agent.

Figure 3.6 shows the particle size change for oxalic acid catalyzed reaction in presence of different surfactants. The main difference found in presence of organic acid is the absence of maximum in particle size with the thiosulphate concentration in SDBS solution. Furthermore, the change in particle size with the increase in reactant concentration is also very less for SDBS. TX-100 shows higher particle size than other two ionic surfactants similar to that in presence of HCl. The changes in particle size with reactant concentration also very less in presence of TX-100 in contrast to that for HCl. By comparing the results in presence of SDBS and TX-100 we can conclude the change in particle size with the increase in reactant concentration is less, as well as overall lower particle size obtained in oxalic acid catalyzed reaction than HCl. In presence of CTAB similar to HCl catalyzed reaction minimum in particle size was found in 4 mM to 6 mM thiosulphate concentration range. Minimum particle size obtained is ~ 35 nm at 4 mM thiosulphate concentration.

The particle size distribution at 10 mM thiosulphate concentration (See Figure 3.7) also shows the distribution is narrow for oxalic acid and SDBS combination. Unlike the aqueous medium in presence of surfactants, the particle size is not continuously increased with the reactant concentration. As sulfur is a non polar element, so the surface charge is almost near to

zero. In presence of higher surfactant concentration (thrice of CMC), the monomer surfactant molecules adsorbed on the sulfur particle surface through the tailgroup. As a result, after adsorption of the ionic surfactant molecules higher charge is developed on the particle surface. Therefore, even at high reactant concentration agglomeration tendency of particles are reduced due electrostatic repulsion between the particles adsorbed by ionic surfactants. For TX-100 solution, due to hydration of the headgroups there is also minimum tendency towards agglomeration. This explanation can be supported by zeta potential value of sulfur molecules in aqueous and different surfactant solutions.

Zeta potentials values of sulfur particles in different medium are given in Table 3.2. From the Table, it is clear that sulfur is having very low negative potential at aqueous medium and closed to zero in presence of TX-100. Among the ionic surfactants, anionic surfactants show higher zeta potential value than cationic, even, between two anionic surfactants (SDS and SDBS) SDBS shows more negative potential. So, lower particle size and sharp particle size distribution in presence of SDBS can be explained in terms higher negative zeta potential due to adsorption of surfactant, that prevent growth as well as the agglomeration of particles. Even, we have observed that the dispersing ability of the particles in presence of both the anionic surfactants was more than TX-100 or CTAB, when the concentration of thiosulphate was more than 50 mM particles were separate very fast from the aqueous medium except anionic surfactants.
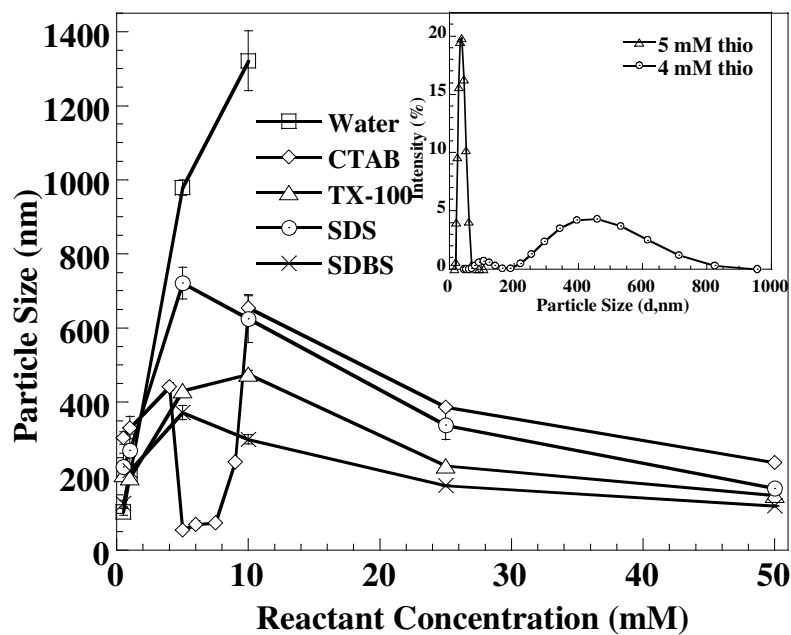
Figure 3.4. Plot of different size of sulfur particle with different sodium thiosulphate concentration in aqueous medium with out any surfactant and in presence of different surfactant for hydrochloric acid (HCl).
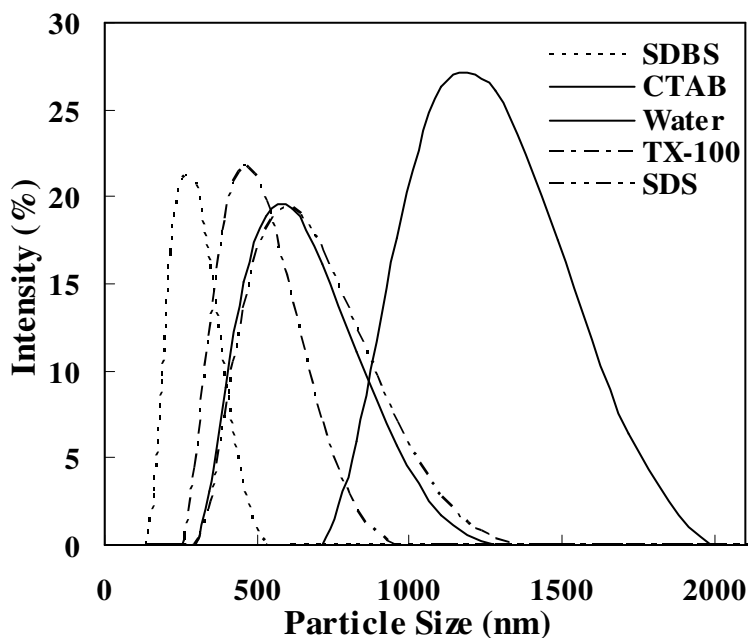
Figure 3.5. Plot of particle size distribution in different medium for 10 mM concentrated sodium thiosulphate solution and HCl.
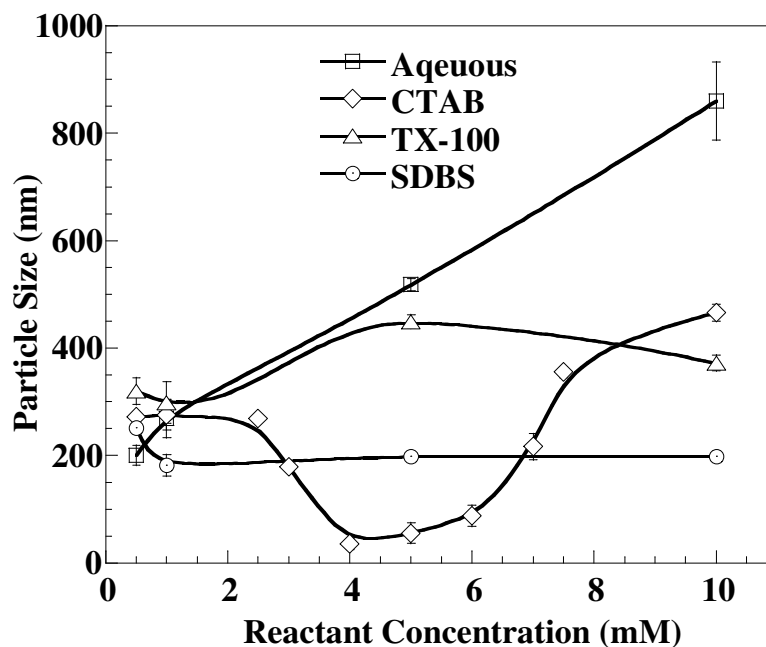
Figure 3.6. Plot of different size of sulfur particle with different sodium thiosulphate concentration in aqueous medium with out any surfactant and in presence of different surfactant for oxalic acid ($H_2C_2O_4, 2H_2O$).
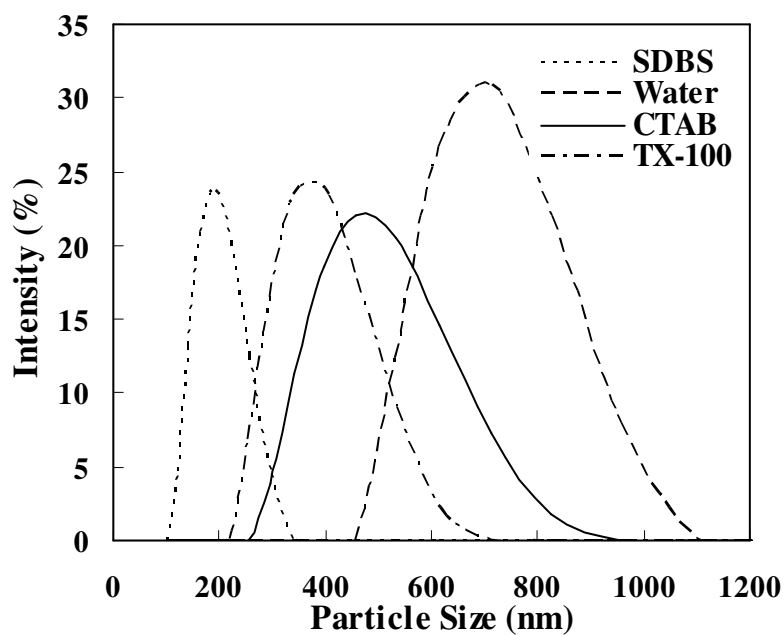
Figure 3.7. Plot of particle size distribution in different medium for 10 mM concentrated sodium thiosulphate solution and oxalic acid

3.3.4. Effect of surfactant concentration on particle size

From the previous discussion it is clear that using different surfactant we can control the size of sulfur particles. In the above study we have used the concentration of surfactants thrice of their respective CMC. Here, we have studied the effect of surfactant concentration (CTAB) on particle size for a fixed reactant concentration (10 mM) and the results are plotted in Figure 3.8. Figure 3.8 shows there is a sharp decrease in particle size till little below the CMC, above CMC the size becomes almost constant.

Zeta potentials were also measured for different CTAB concentration for the same reactant concentration. The Figure clearly indicates that the zeta potential values are increasing with the increase in surfactant concentration and ultimately become constant close to the CMC of the surfactant where particle size was also become constant. The increase in zeta potential is due to the adsorption of surfactant molecules on sulfur surface by tailgroup and forming a complete saturated monolayer near to CMC, also zeta potential values indirectly proofs there is no bi-layer formation in adsorption. The particle size in presence of surfactant is minimum when surface charge is maximum and surface is saturated by the adsorbed monomer surfactant molecules.
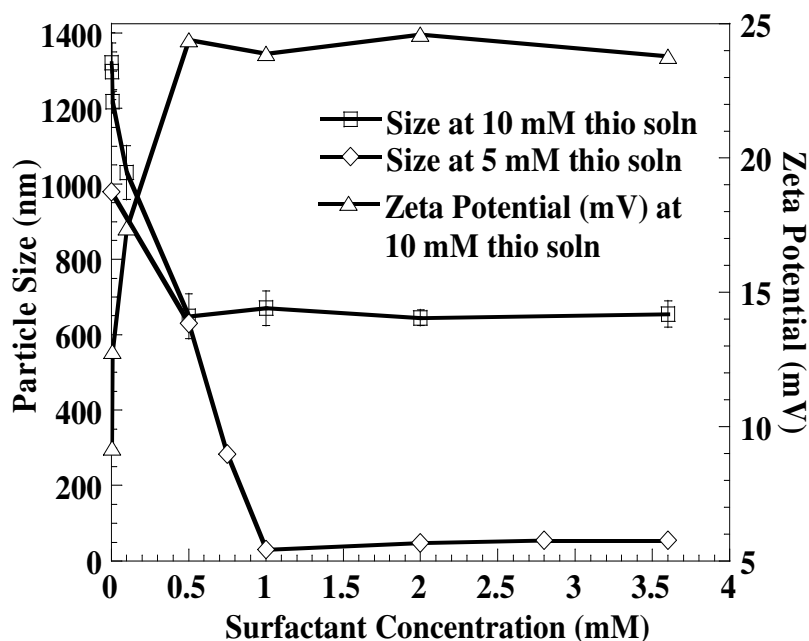
Figure 3.8. Particle size and zeta potential with different CTAB concentration solution for 10 mM reactant concentration and Particle size for 5 mM reactant concentration (HCl).

3.3.5. Analysis of X-ray diffraction (XRD)

Figures 3.9 (a) and (b) show the XRD pattern of sulfur particles in different acids and in presence of surfactants with HCl respectively. The positions and intensities of the diffraction peaks are in good agreement with the literature values for rhombic or α-phase sulfur with S_8 structure (85-0799). The phase obtained is also independent of acid medium. Figure 3.9 (b) also shows the similar structure is formed, with the difference of sharp peak indicates highly crystalline nature in presence of surfactant system than aqueous medium.

3.3.6. Analysis of particle by TGA

The decomposition path of sulfur particle was studied by TGA analysis. Figure 3.10 shows the weight loss for the particle during heat treatment under constant air flow, 40 ml/min. A very sharp weight change was observed at 320^OC due to burning of sulfur to sulfur dioxide. The sample for TGA analysis was prepared by successive washing of the sulfur particle by water. So sample is surfactant free. Therefore, weight loss occurred in one step and as there is no other impurity the total sulfur burned to sulfur oxides, the weight % is change to zero. From the DTA values negative peak is obtained that means the conversion is endothermic in nature.

3.3.7. Analysis of particle by Scanning Electron Microscope (SEM)

Figure 3.11 shows the SEM image of sulfur particle synthesize in HCl and oxalic acid medium without any surfactant and also particle in HCl acid medium in presence of CTAB and SDBS surfactants for thiosulphate concentration of 5 mM. From the Figure it is clear that the sulfur particles are almost spherical shape and uniform size Figure 3.12, shows the EDX of SEM. From the figure it is clear that the particle on the plate is mainly sulfur. Cu and Zn peaks are due to cupper plate only. Figure 3.13 shows the comparison of sulfur particle size in HCl medium in presence of CTAB surfactant for 4, 5, 9 mM thiosulphate concentration solution. The SEM images also support the results obtained from the DSL measurements, in case of 5 mM thiosulphate concentration the particle size is lower but above (9 mM) and below (4 mM) of this concentration the particle size are larger compare to 5 mM thiosulphate solution. But form the figure we can say sulfur has a tendency towards agglomeration, so we are not getting separate discrete sulfur particle image.

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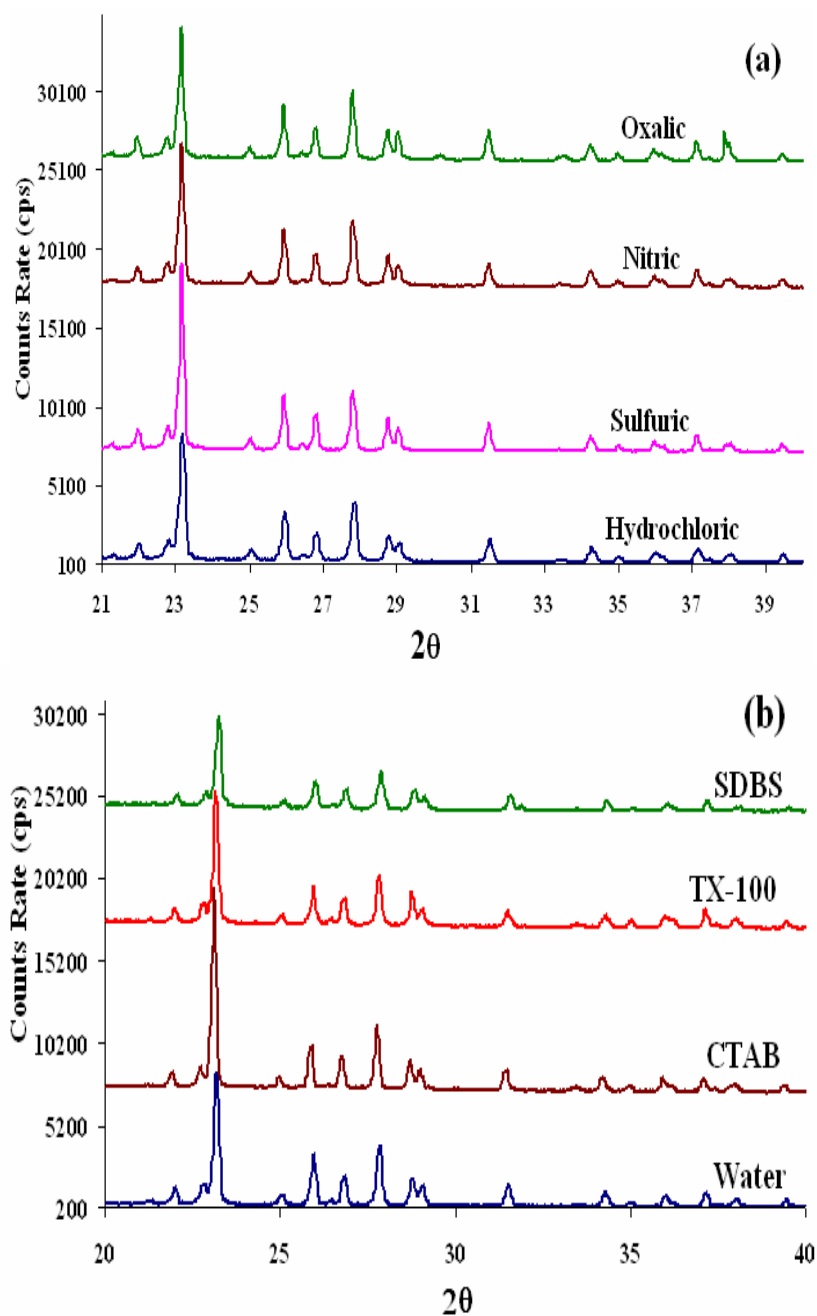
Figure 3.9. XRD diagram of sulfur particle in different acid medium (a).and aqueous medium with out any surfactant and in presence of different surfactant for hydrochloric acid (b) [HCl].
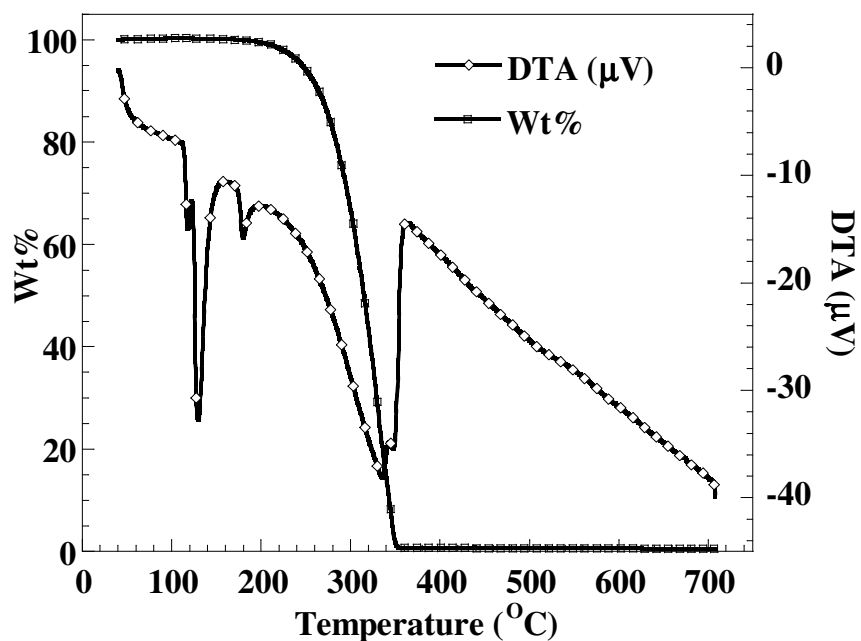
Figure 3.10. TGA/DTA curve of the core (sulfur) particle during heat treatment under air flow.
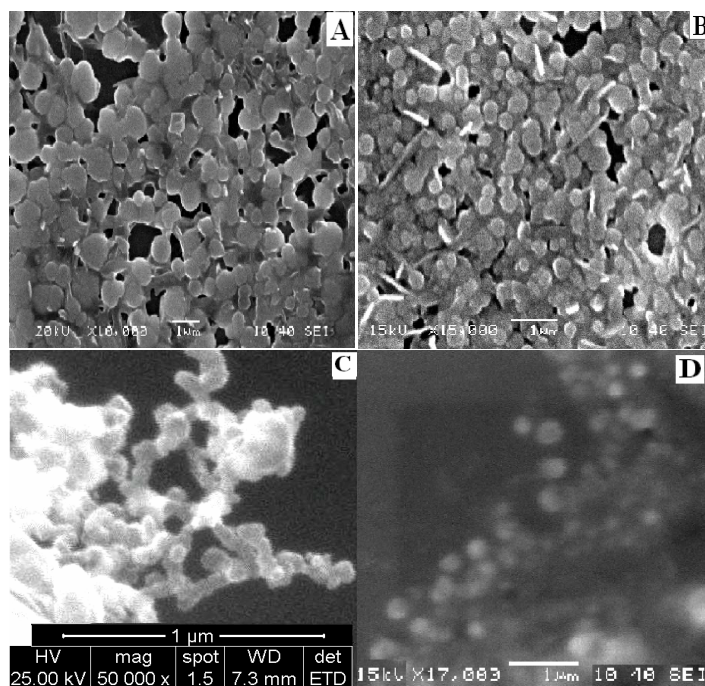
Figure 3.11. SEM image of sulfur particle for 5 mM thiosulphate concentration in (A) HCl and
(B) oxalic acid medium without any surfactant and in HCl medium in presence of (C) CTAB and
(D) SDBS surfactants.
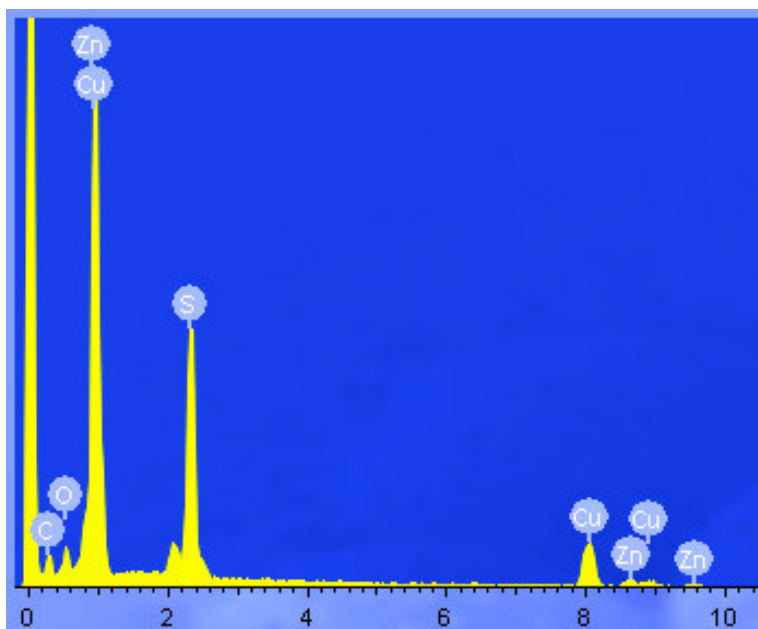
Figure 3.12. EDAX analysis of core particle by scanning electron microscope (SEM)
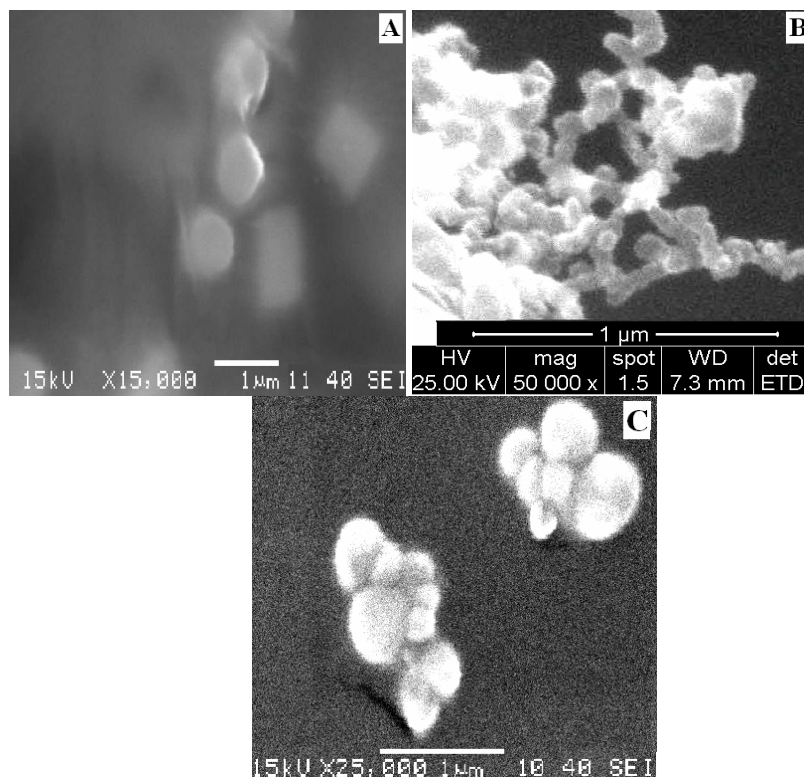
Figure 3.13. SEM image of sulfur particle synthesis in HCl acid medium in presence of CTAB surfactant for (A) 4 mM, (B) 5 mM, (C) 9 mM thiosulphate concentration respectively.

3.4. Conclusion:

Mostly spherical shape orthorhombic or α-sulfur with S_8 structure was formed acid catalyze thiosulphate reaction. Sulfur particle size is depends on the ionization constant value of the acids and acid (H^+) to thiosulphate ratio also. Inorganic acids give larger size particles than organic acid. The particle size distribution also more uniform in organic acid catalyzed reaction as zeta potential of the particle high in organic acid medium so agglomeration tendency less. All the surfactants anionic, cationic and nonionic surfactants play a major role in reducing the particle size. Compare to nonionic and cationic surfactants, in anionic surfactant medium the particle size is low and even in our working concentration range the change in particle size also less, and among two anionic surfactants studied here SDBS is more effective for controlling the size of the particles. Surfactant concentration of the medium also one important factor for the particle size and it seems that above CMC concentration is required. In presence of CTAB with in a certain reactant concentration range very low particle sizes are obtained in contrast to the other surfactants if all other conditions remain same. We have obtained minimum 30 nm sulfur particles in aqueous medium in presence of CTAB.

Chapter 4

GROWTH KINETICS OF SULFUR NANOPARTICLES
FORMATION IN AQUEOUS MEDIUM

4.1. Introduction

The fundamental study on kinetics of precipitation reaction is important to improve the industrial precipitation process (Schuth, 2001a, b). The precipitation reaction is a combination of two stage process, nucleation and growth. Nucleation plays an important role to controlling many properties of the final product, like particle size, particle size distribution, and nature of the phase. Precipitation reaction nothing but a phase transformation from liquid to solid with chemical reaction, so it is also known as reactive crystallization. According to classical nucleation theory (Gibbs 1961), the nucleation is a minimization process in term of energy of the overall system. When ever particles are generated from the homogeneous liquid mixture, a new solid-liquid interfacial area is generated with a specific surface energy proportional to square of its radius. Where as, considering the bulk energy, due to formation of solid the energy gained is proportional to the cube of the particle radius. These two energy terms are opposite in nature. The change in total energy is mainly the contribution of these two energies but, some other factor like, motion of the particles in the medium, defect energies, electrostatic contribution and so on (Tiller, 1991) are also little bit contributed the overall total energy. In case of precipitation reaction, initially, surface energy dominates the total energy and the precipitation process become unfavorable. But after certain radius volume contribution term favor the overall process reducing total energy. So the overall precipitation reaction isn't favorable up to certain radius after that, it is favorable. This radius is known as critical radius. Nucleation and growth for sulfur sols formation is extensively studied by V. K. LaMer and coworkers (LaMer, 1947, 1950, 1952) and developed the mechanism for the formation of nano crystals or colloids from a homogeneous super saturated aqueous medium. According to them, in short time period nucleation process is completed, and then those particles having the size higher than critical radius are started to grow. The growth process is controlled by either one or both the resistance; diffusion and surface reaction depending on there relative rate and rate expression are also different in each case (Rao, 2007).

With high computational power, lots of theoretical model (Noguera, et al. 2006; Clouet, et al. 2006; Talapin, et al. 2001; Sugimoto, 2007; Tojo, et al. 1997) already develop considering both nucleation and growth rate. Actually, for precipitation reaction main complication is that it is a combination of nucleation and growth process like normal crystallization. The nucleation is very fast but the growth rate is mainly depending on diffusion rate or reaction rate which one

slower. But rather than these two factor growth rate is also depend on other different parameter like temperature, super-saturation, hydrodynamic condition in the crystallizer, reactant concentration, presence of different impurities, crystal size, etc. According to LaMer, (1950) in case of sulfur sols formation from thiosulphate and acids solution, the nucleation rate is very fast and diffusion rate is mainly controlled the growth. So the overall size of sulfur in sols depends on the growth process and finally on agglomeration and ripening factor.

In our previous section, we show the main importance of nano to micro size sulfur particle and also synthesis sulfur particle from thiosulphate with different acid combination in presence and absence of different surfactants. Now, in this chapter we are presenting the effect of different parameter on the growth process of the sulfur nanoparticle in acid catalyzed precipitation reaction of sodium thiosulphate. Here, we attempted to understand the effect of different parameters like, effect of sonication, temperature, different acid, thiosulphate concentration, presence of different concentration surfactants solution on the growth process of sulfur particle in aqueous phase.

4.2. Experimental Section

4.2.1. Materials

The required all chemicals were taken from the following companies: Sodium thiosulphate ($Na_2S_2O_3$, $5H_2O$), Oxalic acid ($H_2C_2O_4$, $2H_2O$) from Rankem (India), Triton X-100 (TX-100), Cetyl trimethyl ammonium bromide (CTAB) from Loba Chemie Pvt. Ltd. (India), Sodium dodecyl benzene sulphonate from Sigma Aldrich (Germany), and Hydrochloric acid (HCl), Sulfuric acid (H_2SO_4) Merck (India). All chemicals were used as it is received without any further purification. Ultra pure water of 18.2 MΩ.cm resistivity and pH 6.4 – 6.5 (Sartorius, Germany) was double distilled again and used for all the experiments.

4.2.2. Method

Stock sodium thiosulphate was prepared dissolving solid thiosulphate, in double distilled water and different acid solution also prepared from the pure stock. Both reagents were filtered with 0.2 μ nylon 6, 6 membrane filter paper from Pall Life science, USA. In presence of any acid, sodium thiosulphate is disproportionate to sulfur and sulfonic acid according to reaction mentioned before (3.1 and 3.2). After mixing the reactants, the temperature was controlled inside

a jacketed bath using a temperature controlled water circulator and successively particle size was measured by dynamic light scattering (DLS) using Malvern Zeta Size analyzer (Nano ZS). The growth kinetics of the core particle was also studied by UV-Visible Spectroscopy at 280 nm wave length (UV-3600, Shimadzu).

4.3. Results and Discussion

4.3.1. Effect of sonication

From the basic concept of precipitation reaction, we know that whenever there is sufficient number of nucleate particle, after that growth process predominant over nucleation and particle size continuously increased. According to thermodynamics, every process tries to minimize the total energy so that it gains maximum stability. So in precipitation reaction, during growth process there are other factors like Oswald ripening, coalescence (Tiemann, et al. 2008) so that small size particle converted to large size particle with releasing energy. So by this ripening factor, overall energy of the system is decreases. In our study, we first study the effect of sonication on the particle size during the growth process. Here we carried out our experiment (i.e., particle size measurement with time for 5 mM thiosulphate concentration) by three different manner, (i) taking freshly separate individual sample, (ii) stepwise sonication, i.e., taking one sample and sonicated just before size measurement, and (iii) continuous sonication, i.e., the sample continuously sonicated with in the reaction period. Figure 4.1 shows the change in particle size with increasing time for 5 mM thiosulphate concentration for all three cases. In our previous study, we show to attain the equilibrium size of sulfur particle minimum 30 minutes require for any inorganic acids. Figure 4.1 show for separate solution 30 minutes require to get equilibrium size but for other two cases we need more time. Because, during precipitation undisturebed particles have an inherent tendency towards agglomeration by loosing energy. In the first case as we used separate solution that means every time we use fresh solution for size measurement and before measurement just sonicated it once. Therefore, particle attained equilibrium size with in 30 minutes and growth rate i.e., the change in particle size with time is maximum. But in other two cases we supplied energy in the form of sonication, so more time was required to attending the equilibrium size. For stepwise sonicated sample, we measured size of sulfur particle with increasing time using same solution and each time before measurement that solution sonicated for 2 minutes only other remaining time it was remain stationary. But for

continuous sonicated sample, after the mixing of reactants the sample was continuously sonicated. So for continuous sonicated sample more energy is supplied through sonication. There fore, for continuous sonicated sample more time, 190 minutes was required to attain the equilibrium size than stepwise sonicated sample, 150 minutes.
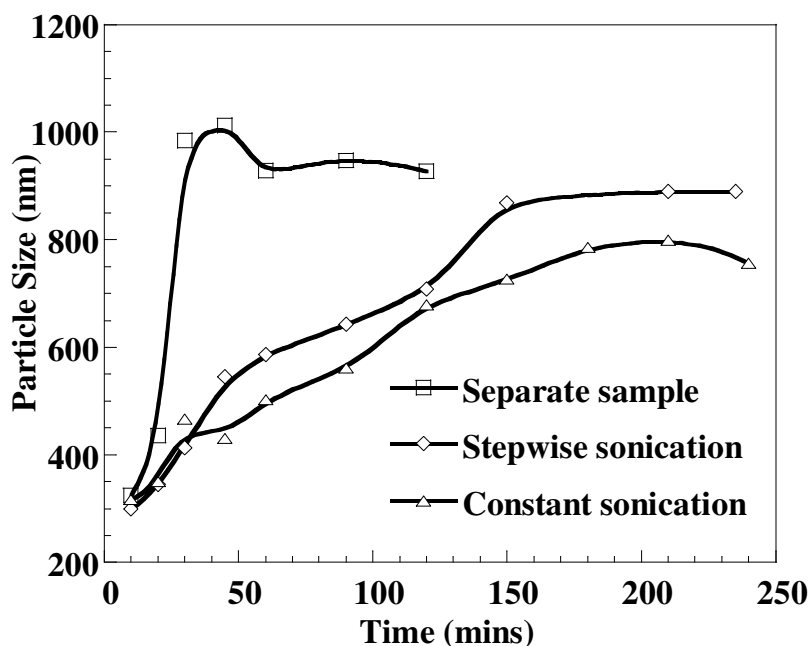
Figure 4.1. Growth kinetics of sulfur nanoparticles for 5 mM thiosulphate solution with HCl under different sonication condition.

4.3.2. Effect of temperature on the growth process

Figure 4.2 shows the sulfur particle size increases with increasing time at different temperature for 5 mM thiosulphate reactant concentration in HCl acid solution. The particle growth rate at separate temperature can be say as the slope of the individual curve. From the Figure 4.2, it is clear with increasing temperature the growth rate also increases.

The comparisons of slope of the curve follow the following order: 42 °C > 28 °C > 15 °C. At 15 °C temperature the particle size increases from 205 nm at 10 minutes to 505 nm at 90 minutes. But in other cases, particle changes from 426 nm at 10 minutes to 1075 nm at 150 minutes and 300 nm to 870 nm at 150 minutes respectively for 42 °C and 28 °C. Thiosulphate disproportionate to sulfur and sulfonic acid reaction is an endothermic reaction, so with increasing temperature the rate of the reaction increases. And another factor, at higher temperature the kinetic energy of new born sulfur particle is also high. So there is more collision

between those particles and due to coarsening of those smaller particle are combined to larger sized particle (Hu, et al. 2005). There fore, the rate of change of sulfur particle sized is increases continuously with increases temperature.
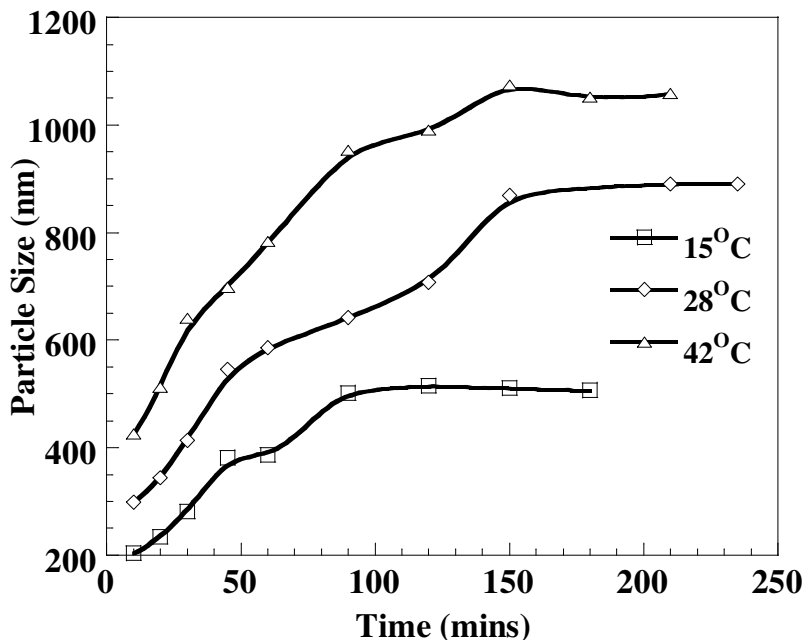
Figure 4.2. Growth kinetics for 5 mM thiosulphate solution with HCl at different temperatures.

4.3.3. Effect of different acids on growth process

Depending on the ionization constant of the acids, the rate of the reaction also changes. With high ionization constant i.e., with strong acid the rate of the reaction rate is fast compare to weak acid. In the previous section, we got low sized sulfur particle in organic acid solution than any other inorganic acid. Here, in case growth study also we got slow growth rate in case of weak organic acid than other inorganic acids. Figure 4.3 shows the change in particle size with time for 5 mM thiosulphate concentration in different acid solution. The Figure 4.3 shows in organic acid the initial growth rate is same as in hydrochloric acid but with increasing time the growth become slow and attending the equilibrium size, 525 nm at 60 minutes. But in case of both inorganic acids the time required to attend the equilibrium size are high. In sulfuric acid and hydrochloric acid solution the equilibrium sizes are 950 nm and 875 nm attending at time 120 and 150 minutes respectively.

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To further support, the growth kinetics was also studied by measuring the absorbance in UV region using the spectrophotometer. Various ions in the reaction medium absorb light below the 300 nm but sulfur particle have prominent absorbance in 300 nm to 245 nm wave length range. At 280 nm the absorbance of sulfur is much higher compare to all other ions presents in the system. Therefore, all growth kinetics measured at constant 280 nm wave length where sulfur has high absorbance rather than absorbance of other ions like thiosulphate. For the measurement, reference state was taken as same sodium thiosulphate concentrated solution. Figure 4.4 shows absorbance of newborn sulfur particle in different acid medium. From the figure it is clear that the absorbance in organic acid medium is higher than other inorganic acid medium. From the previous section, we know that in organic acid medium particle size is much smaller compare to other acids, so for a fixed reactant concentration the particle density is much higher compare to larger size particle system.
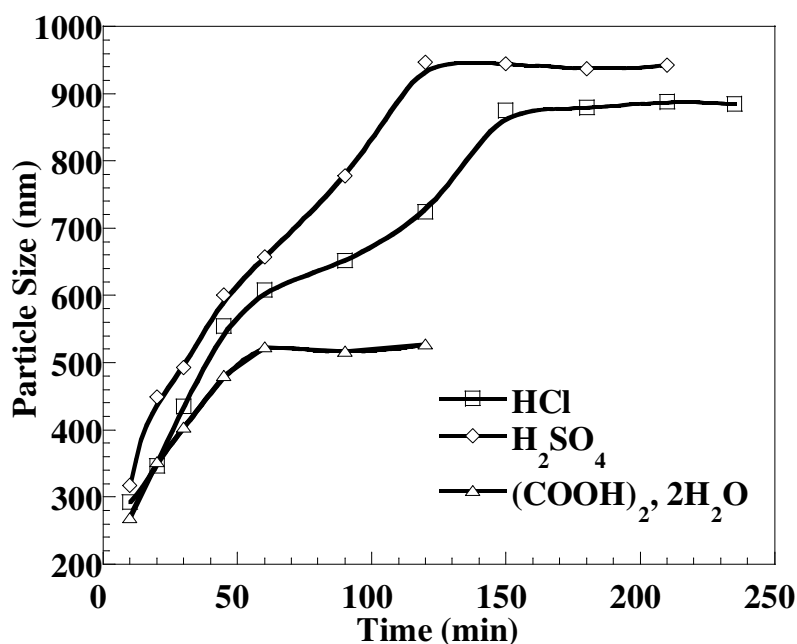
Figure 4.3. Growth kinetics for 5 mM thiosulphate solution with different acid at 28 °C.
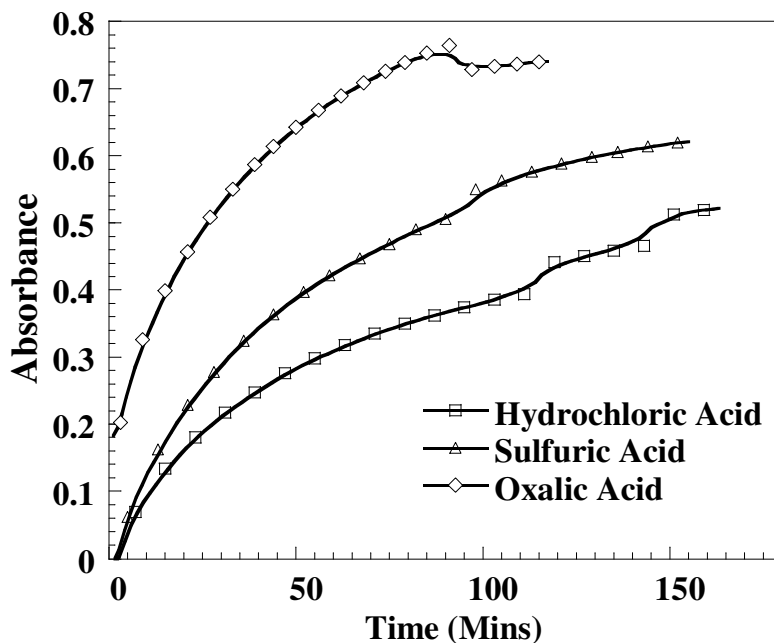
Figure 4.4. Growth kinetics of sulfur nanoparticle for 5 mM thiosulphate concentration in different acid medium.

Therefore, when the particle density is more in the medium absorbance is also high. For growth study by UV-Vis Spectroscopy, a constant 5 mM sodium thiosulphate solution is used. For 5 mM thiosulphate solution, particle size in HCl acidic medium is smaller than H_2SO_4 acidic medium. So in H_2SO_4 sulfur particles having high absorbance. From the absorbance Figure 4.4, constant absorbance obtained at 90 minutes almost in each case but from the particle size analyzer data except organic acid. In case of other two inorganic acids the particle size is vary up to 130 or 150 minutes. This is due to only agglomeration of particle; particle size continuously increases but absorbance become constant.

4.3.4. Effect of reactant concentration on the growth process

In this section we studied the effect of reactant concentration on the growth process shown in Figure 4.5. We change the thiosulphate concentration from 1mM to 10mM, and with changing time measuring size of the sulfur particle. From the Figure 4.5, it is clear that with increasing reactant concentration the slope of the curve that means growth process increases. With minimum concentration, 1 mM thiosulphate concentration the growth rate is minimum but very

fast with in 30 minutes, it reaches the equilibrium size 206 nm. But in case of higher concentration 5 or 10 mM concentrated solution the growth rate increases. For 5 mM solution 150 minutes required to achieve the equilibrium size 870 nm. In case of 10 mM thiosulphate concentration, although the growth rate is maximum but it needs more time 180 minutes to achieve the equilibrium size 1250 nm. According to V. K. LaMer (1948) (LaMer, 1948) rate of the reaction depend on both concentration of thiosulphate and acid. According to him, rate of reaction = k $[T]^{1.5}$ $[A]^{0.5}$. Where, k is reaction rate constant, [T] and [A] are the thiosulphate and acid concentration respectively. So with increasing reactant concentration, rate of the reaction increases so the particle growth rate also high. But, for low concentrated reactant concentration, the particle density is low so there are less collision between particles so less coalescence. Therefore, we get lower size in low reactant concentration. But in case of high reactant concentration, the initial reaction rate as well as the particle density both is increasing with reactant concentration. So with increasing reactant concentration there are more ripening so particle size also increases and more time require to attend the equilibrium size. Figure 4.6 shows the absorbance data for different sodium thiosulphate concentrated solution. From the figure, we also got same thing, for equilibrium size long time required by zeta size analyzer where as for UV-V spectroscopy absorbance becomes constant short time as sulfur concentration becomes constant. So the comparing the both figures, we can say, after complete reaction due to agglomeration the particle size continuously increases.
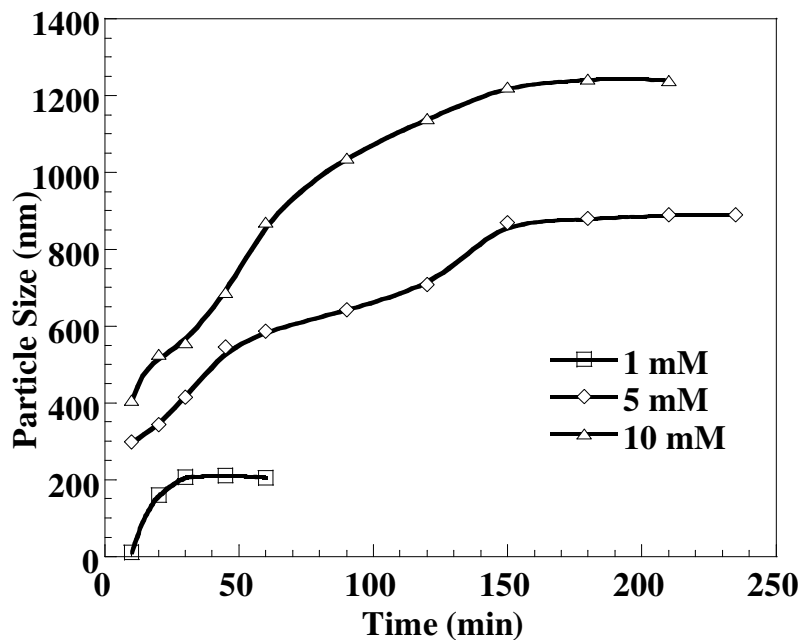
Figure 4.5. Growth kinetics of sulfur nanoparticle for different thiosulphate concentration in HCl solution at 28 °C.
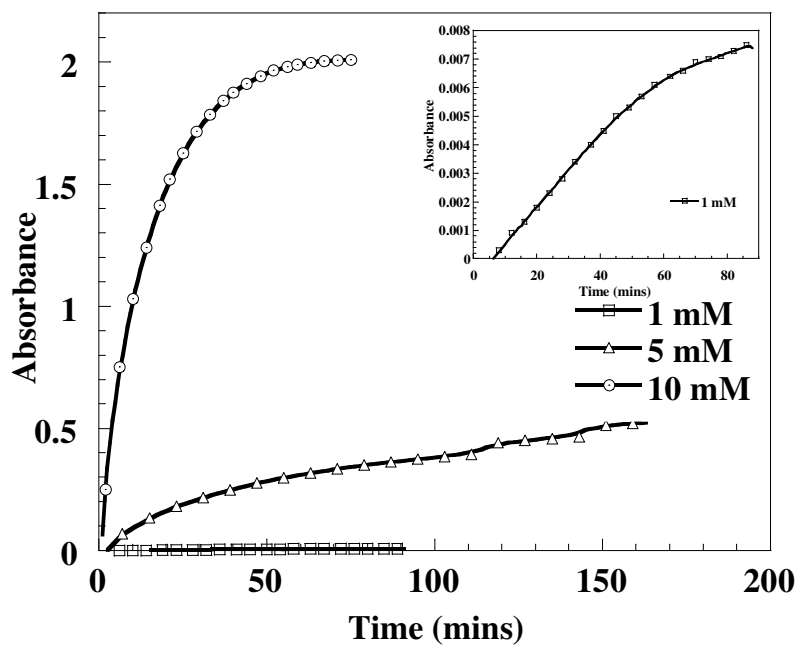

Figure 4.6. Growth kinetics for different concentrated sodium thiosulphate solution in HCl medium.

4.3.5. Effect of different surfactant on the growth process

In this section, we studied the growth kinetics of sulfur particle formation in absence and presence of three types (cationic, anionic, and nonionic) of surfactants. Like in the previous section, here we also got the similar results. In presence of any surfactant we got lower sized particle than without any surfactant medium. Figure 4.7 shows the difference in sulfur particle size for 5 mM thiosulphate concentration in HCl acid solution for different surfactant medium. In presence of surfactant, same reaction is takes place but only difference is as sulfur is a neutral element, surfactant molecules are adsorbed through their hydrophobic tailgroup on the particle surface. Ultimately, a net charge is developed on the particle surface. Therefore, the collision tendency between the particles reduces. So there are fewer tendencies towards the agglomeration. In our previous study we find out the zeta potential of sulfur particle in different surfactant medium. The zeta potential of sulfur particle in with out surfactant and presence of nonionic surfactant are low but in presence of any ionic surfactant zeta potential increases. So in presence of any ionic surfactant, there is much lower tendency towards agglomeration by collision between smaller size particles. From the figure 4.7, without surfactant the growth rate and equilibrium size are maximum. There is not much difference in growth rate between with out surfactant and non ionic surfactant. But in ionic surfactant solution the growth rate become very slow and it is minimum in cationic surfactant (CTAB) solution. Also from the literature (Paul, 1997) it is shows that in nonionic surfactant solution the growth rate is not change so much but in ionic surfactant solution growth rate become slow that also supported our results. For the growth kinetics study by UV-Vis spectroscopy we are using same combination as particle size measurement. Here we got maximum absorbance in CTAB surfactant solution, as for 5 mM sodium thiosulphate solution in CTAB solution have the minimum sized 55 nm particle. Therefore, the particle density is much higher compare to other medium. So, absorbance values in CTAB medium are far higher compare to other medium. Figure 4.8 shows the absorbance value of sulfur in different surfactant medium. As in TX-100 and SDBS surfactant medium the particles size not differ in large extent so absorbance value almost same in both cases. But in case of without surfactant system the absorbance value is low because size is maximum compare to other systems. In case of without surfactant system absorbance value changes for long time as there are high agglomeration tendency, as surface charge is low compare to other surfactant system. But comparing the both Figure 4.7 and 4.8, from UV data absorbance almost become constant near to 60 minutes for with out surfactant, SDBS, and TX-100 surfactants but from the

particle size data size is still increasing up to minimum 150 minutes. That means 60 minutes required completing the reaction and due to growth particle size continuously increases up to 150 minutes, as sulfur concentration becomes constant, therefore absorbance reached a constant value. But after that size is still continuously increases measured by Malvern Zeta size analyzer is only due to agglomeration.
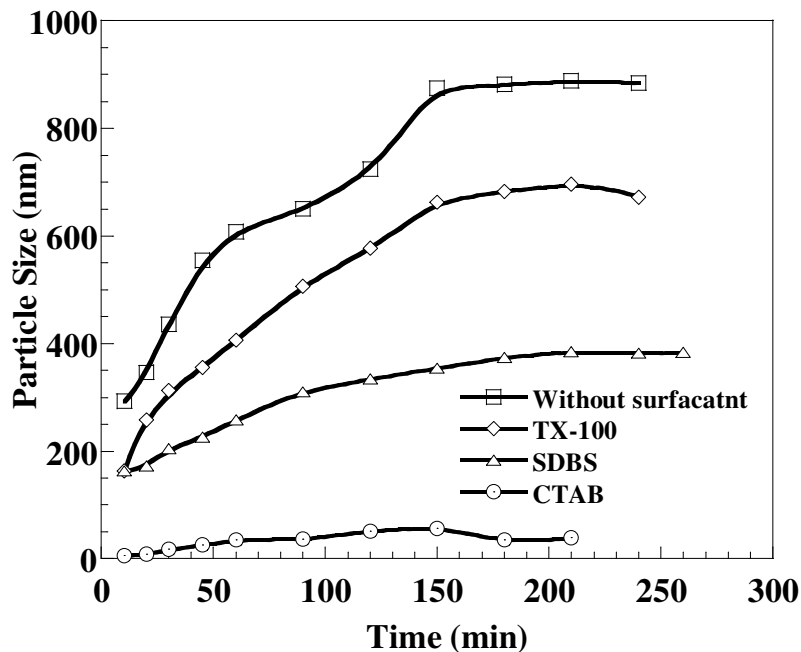
Figure 4.7. Growth kinetics of sulfur nanoparticles for 5 mM thiosulphate concentration in presence of HCl and different surfactants medium at 28 °C.
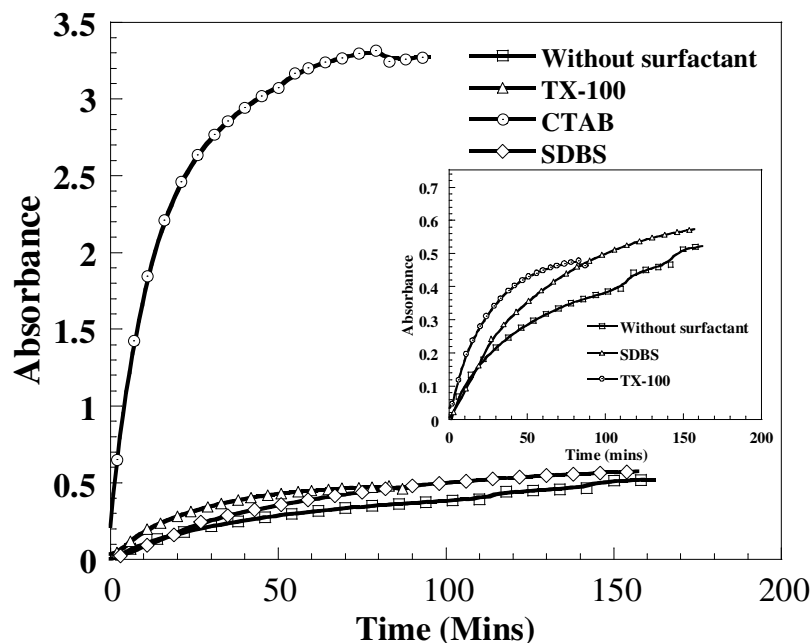
Figure 4.8. Growth kinetics for 5 mM thiosulphate concentration in HCl medium in presence of different surfactants (TX-100, CTAB, SDBS) medium and without surfactant medium.

4.3.6. Effect of surfactant concentration on the growth process

Here we study the effect of surfactant concentration on the growth process. For this study we use 5 mM thiosulphate in HCl acid solution in different concentrated SDBS solution. We know the SDBS have critical micellar concentration (CMC) 1.2 mM (Segota, et al. 2006)**.** In the previous chapter, we find that for a fixed reactant concentration particle size decreases with increasing surfactant concentration and become constant just near to CMC. Here we also got similar type of result. When surfactant concentration is low growth rate is faster and high equilibrium size.

The Figure 4.9 shows that in dilute surfactant concentrated (0.1 mM) solution the growth rate is faster than high surfactant concentrated medium but much slower than in without any surfactant medium. But with increasing surfactant concentration the growth rate decreases and almost become constant at below the CMC. Actually, monomer surfactant molecules are mainly responsible for lower equilibrium sized particle and slower growth rate. As sulfur is a neutral element so surface charge is almost zero there fore, monomer surfactant molecules adsorbed through its hydrophobic tail group and generated charge on the surface. Due to these charge repulsion there is less tendency towards the agglomeration so that the growth rate as well as the

ultimate equilibrium size are low. And even at very high surfactant concentration (thrice of CMC) the growth rate is same as in 0.5 mM surfactant concentration.
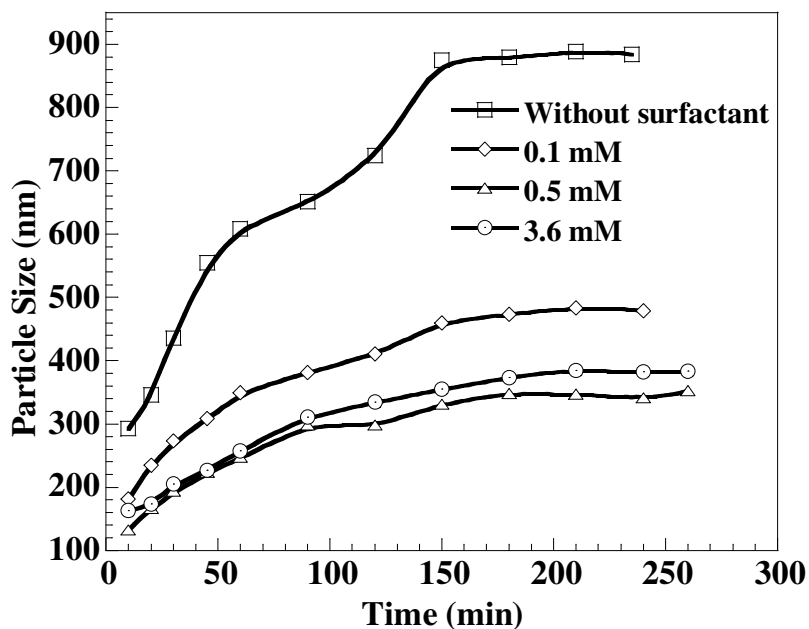
Figure 4.9. Growth kinetics for 5 mM thiosulphate concentration in HCl solution at 28 °C with different SDBS concentration using DLS.

4.4. Conclusion

Kinetics of sulfur nanoparticle formation is totally depends on the growth process. As initial nucleation process is fast, after mixing the reactant with in 2-3 minutes nucleation process completed. And growth process is mainly controlled by the diffusion. That means new particle formed in the bulk phase at faster rate and slowly diffused towards nuclei and deposited on it. So the all factors which can affect the diffusion rate are also responsible for the kinetics of the particle formation. From the above study, it is clear that the particle size depends on the parameters like temperature, sonication of the reaction system, sodium thiosulphate concentration, types of the acids, presence of different surfactants, and also surfactant concentration. With increasing temperature the rate of diffusion of newborn particle towards nuclei surfaces increases therefore, ultimate size of the particle also increases. With sonication of reacting system the total energy increases, so there are less tendencies towards the agglomeration, so the particle size also low in continuous sonication system compare to other

system. With increasing sodium thiosulphate concentration and strong acids the rate of reaction is increases; therefore the particle densities in the bulk phase high. So there is a concentration variation between the nuclei surface and bulk, so the diffusion rate increases and finally growth rate also increases. Finally depending on the different dispersion medium the growth rate also changes. According our study, in presence of cationic (CTAB) surfactant the growth rate is minimum and even in presence of other dispersion medium like nonionic and anionic surfactants growth rate is low is low compare to without surfactant medium. Same as in the previous chapter, the particle growth rate also depends on the concentration of dispersing medium. From the overall results it can be say that up to CMC concentration the growth rate is changing but after that it almost constant.

Chapter 5

SYNTHESIS AND CHARACTERIZATION OF SHELL AND
CORE-SHELL PARTICLES

5.1. Introduction

The nanosized material has a great interest due to its potential application in the field of science and technology. The synthesis of nanoscale metal in simple solution under mild reaction conditions and with control over particles size, shape and crystallinity remains a major task for researcher. Among these metals silver halide has an importance considering the industrial application. Silver bromide (AgBr) is a soft, pale-yellow, insoluble salt well known (along with other silver halides) for its unusual sensitivity to light. This property has allowed silver halides to become the basis of modern photographic materials. AgBr is widely used in black-and-white photography film and due to these photosensitive properties silver bromide is considered also an ionic semiconductor. Overall AgBr have a promising application in the field of semiconductor (Zhiyun et al. 2005), antibacterial material (Sambhy, et al. 2006, Elahifard, et al. 2007), photographic materials (Sturmer, et al 1989, Jeunieau, et al. 2000) and for adsorption study of dyes (Jeunieau, et al. 2000, Pal, et al. 2007) has been studied that bactericidal properties of the silver nanoparticles depends on its shapes.

5.2. Experimental Section

5.2.1. Materials

The required all chemicals were taken from the following companies: Sodium thiosulphate ($Na_2S_2O_3$, $5H_2O$) from Rankem (India), Cetyl trimethyl ammonium bromide (CTAB) from Loba Chemie Pvt. Ltd. (India), Sulfuric acid (H_2SO_4) Merck (India), $AgNO_3$ from Ranbaxy (India). All chemicals were used as it is received without any further purification. Ultra pure water of 18.2 MΩ.cm resistivity and pH 6.4 – 6.5 (Sartorius, Germany) was double distilled again and used for all the experiments.

5.2.2. Core-Shell Particle Synthesis

First the core (sulfur) particle was prepared in presence of H_2SO_4 and CTAB according to the method mentioned in Chapter 3. After the formation of core particle, the $AgNO_3$ solution was added into the reaction mixture. $AgNO_3$ reacts with counter ion (Br^-) of surfactant to form a uniform coating of AgBr on core sulfur particle.

$$AgNO_3 + CTA^+Br^- \longrightarrow AgBr \downarrow$$

Again 30 minutes equilibrium time was given for complete reaction. Then, S@AgBr sample was sonicated in a bath and particle size was measured immediately after sonication.

5.2.3. Particle Characterization

Particle size measurement was carried out by dynamic light scattering (DLS) using Malvern Zeta Size analyzer, U.K. (Nano ZS). The size and shape of particles were observed under a scanning electron microscope (JEOL JSM-6480LV). Core-Shell particle are also characterized by UV-Visible NIR Spectroscopy (Shimadzu-3600), TGA (Shimadzu) and surface area was also measured By BET (Quantachrome, USA).

5.3. Results and Discussion

Sulfur is a neutral elements, it surface charge almost near to zero. So in CTAB surfactant solution, CTAB surfactant molecules were adsorbed on the sulfur particle surface through its tail group. So a uniformed positive charge was developed on the core surface. Zeta potential of sulfur particle in CTAB surfactant medium was + 23.8 mV. Now in aqueous medium AgBr particles show negative charge. So in the reaction medium, when AgBr was formed, it selectively deposited on the surface sulfur particle so that core-shell particle will formed. For core-shell particle formation, three times of critical micelle concentration (CMC) of CTAB surfactant solution was used as dispersion medium.

5.3.1. Effect of core size on shell thickness

The shell thickness of core-shell particles is dependent on both core size, i.e., on thiosulphate concentration and $AgNO_3$ concentration. In this section, we studied the effect of core size on shell thickness. For this purpose, we synthesized core sulfur particle in different thiosulphate concentration in H_2SO_4 medium and got same trend as in HCl solution in CTAB surfactant medium. i.e., with increasing thiosulphate concentration particle size increases but in 5-10 mM concentration range got low sized particle. After formation of core particle, $AgNO_3$ solution was added to maintain Ag^+ ions concentration 0.2 mM in each solution. Therefore, in each system the

amount of total AgBr is same. So depending on number density and size of the core particles, the overall size of core-shell particles is different. The shell thickness of the particle was calculated by measuring the size of the core and core-shell particle separately. Shell Thickness = [(Core-Shell Particle Size – Core Particle Size) ÷ 2]. Figure 5.1 represent the shell thickness with increasing thiosulphate concentration. As for 5 mM sodium thiosulphate solution, the core particle size was small, so, number of core particle in the system high. As similar observation we found during the growth kinetics study of core particle, for 5 mM sodium thiosulphate system we got highest absorbance compare to other system. So during coating of AgBr on sulfur, as number of sulfur particle is high in the system, therefore, the deposition of shell material (AgBr) on the individual core particles were less. So we got minimum thickness for 5 mM sodium thiosulphate solution.
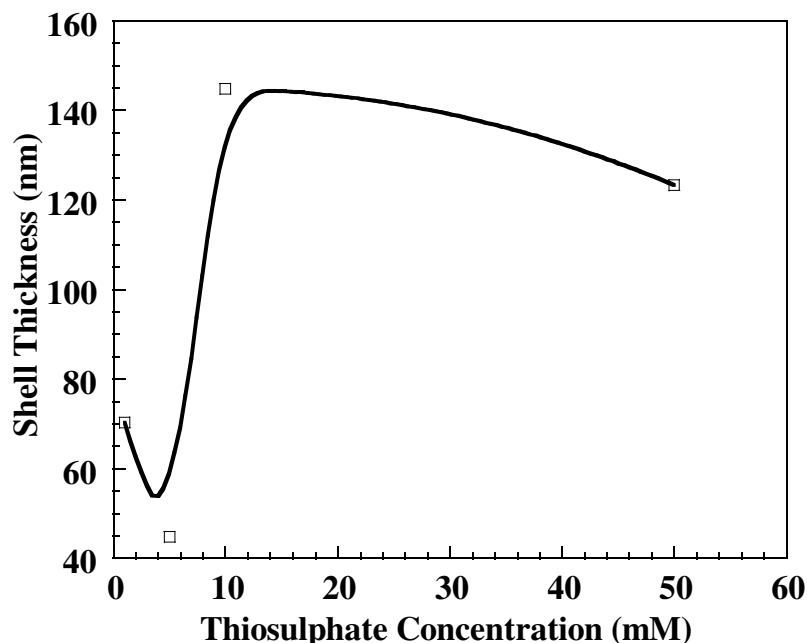
Figure 5.1. Plot of shell (AgBr) thickness with increasing sodium thiosulphate concentration in aqueous medium with constant 0.2 mM silver nitrate solution.

5.3.2. Effect of AgNO$_3$ concentration on shell thickness for fixed size core particle

In this section we have studied the effect of AgNO$_3$ concentration on the shell thickness for a fixed size core particle. In each case for core particle formation a constant 10 mM sodium thiosulphate concentration maintain in CTAB surfactant solution. After equilibrium time the size

of the core particle was 375 nm and surfactant molecule adsorbed on core surface so that a uniform positive charge developed on the surface. Then $AgNO_3$ added to form AgBr on the core surface. The Figure 5.2 shows that with increasing $AgNO_3$ concentration the thickness of the shell material continuously increases, because with increasing Ag^+ ions concentration the total amount of AgBr also increases in the system but the number density and size of the core particle were same in all cases. So the amount of shell material deposited on individual core surface also increases with Ag^+ ion concentration. After 0.5 mM $AgNO_3$ concentration, the AgBr coated particle separated from the system so size can't be measured by the particle size analyzer.
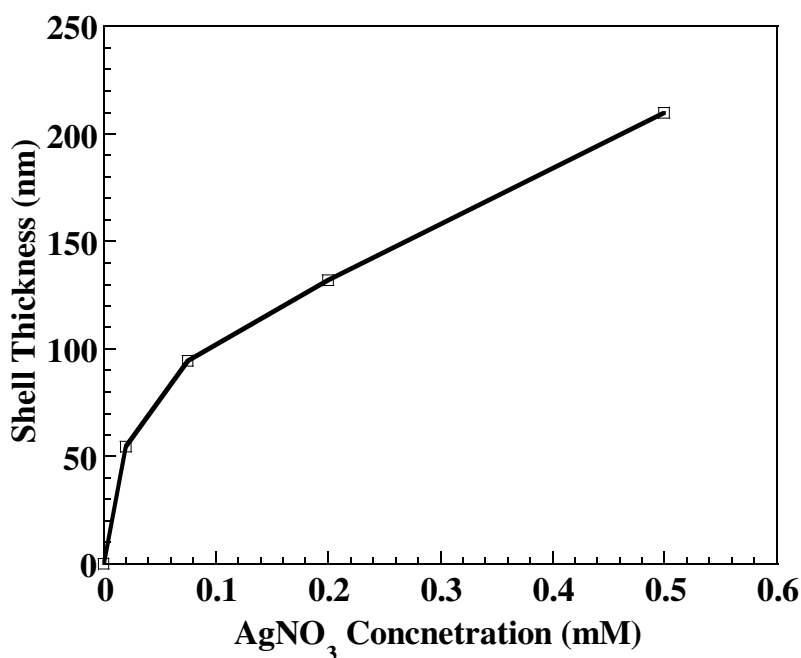
Figure 5.2. Plot of shell (AgBr) thickness with increasing $AgNO_3$ concentration for a fixed 10mM sodium thiosulphate concentration.

5.3.3. Characterization of core-shell particle by UV Spectroscopy

To support the formation core-shell particles in the system we did the UV spectroscopy of single particles (S and AgBr), coated particles (S@AgBr), and mixture of single particles (S + AgBr). The sulfur particle was prepared using 5 mM thiosulphate concentration in presence of CTAB and for shell and pure AgBr particles prepared using 0.1 mM $AgNO_3$ solution. The total volume of all samples was adjusted to maintained similar particle density. UV spectrum of single particles clearly shows in Figure 5.3 that both the particles are having peak 271 nm wavelength

with unequal absorbance values (S = 0.935, AgBr = 0.358). The absorbance values generally depend on both the material property and the size of the particles. The size of the single and coated particles determined by DLS was 50 nm, 90 nm, and 85 nm for S, AgBr, S@AgBr respectively. Now, from the Figure 5.3 the absorbance values of the materials can be summarized as follows: S > S@AgBr > (S + AgBr) > AgBr. To confirm whether the AgBr is really coat on the S particle surface or not we compared two samples one prepared separate S and AgBr particles under similar condition and just mixed before analysis (S + AgBr) and in another first core was prepared then $AgNO_3$ was added to coat with AgBr. We found the mixture of two particles shows absorbance (0.66) very close to that of average of two single particles absorbance (0.6465). However, the core-shell particle shows higher absorbance (0.817) than the mixture indicates separate particles are not present there. The colors of the samples in Figure 5.4 also show there a distinct difference in physical appearance.
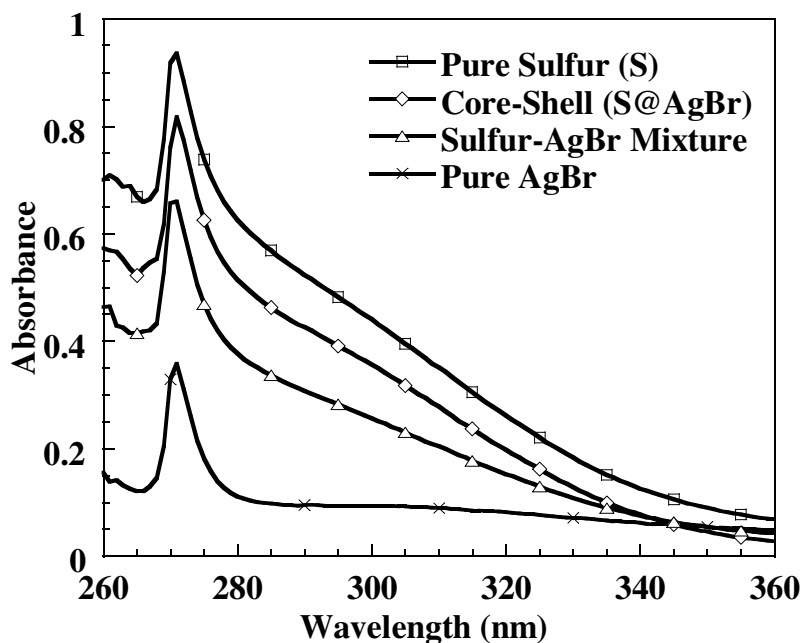
Figure 5.3. Plot of Absorbance value of pure core (sulfur), core-shell (S@AgBr), mixture of pure sulfur and AgBr and pure AgBr particle for 5mM thiosulphate and 0.1 mM $AgNO_3$ concentrated solution.

Figure 5.4. Color of the samples [A-pure core (sulfur), B-core-shell (S@AgBr), C-mixture of pure sulfur and AgBr and D-pure AgBr particle] for 5 mM thiosulphate and 0.1 mM $AgNO_3$ concentrated solution.

5.3.4. Analysis of core-shell particle by SEM

Figure 5.3 shows the SEM image of AgBr coated sulfur core-shell particle synthesize in H_2SO_4 medium in presence of CTAB surfactant for thiosulphate concentration of 50 mM and 0.2 mM $AgNO_3$ concentration. From the Figure it is clear that the AgBr coated sulfur core-shell particles are almost spherical shape and uniform size but particles have agglomeration tendency so that we got in agglomerated form. Figure 5.4, shows the EDAX of SEM image. From the figure it is clear that the particle on the plate is mainly sulfur-AgBr composite particle. The figure contain peak for sulfur, silver and bromine. The sample was coated with Pt before measurement, so Pt peak came into figure. The all AgBr particles are not in core-shell form some without coating particles also there. SEM image also shows some 100 nm sized only AgBr particles are also there. In CTAB surfactant solution separate AgBr particles was formed and the size obtained by DLS close to 100 nm. That may support some uncoated particles are also there.

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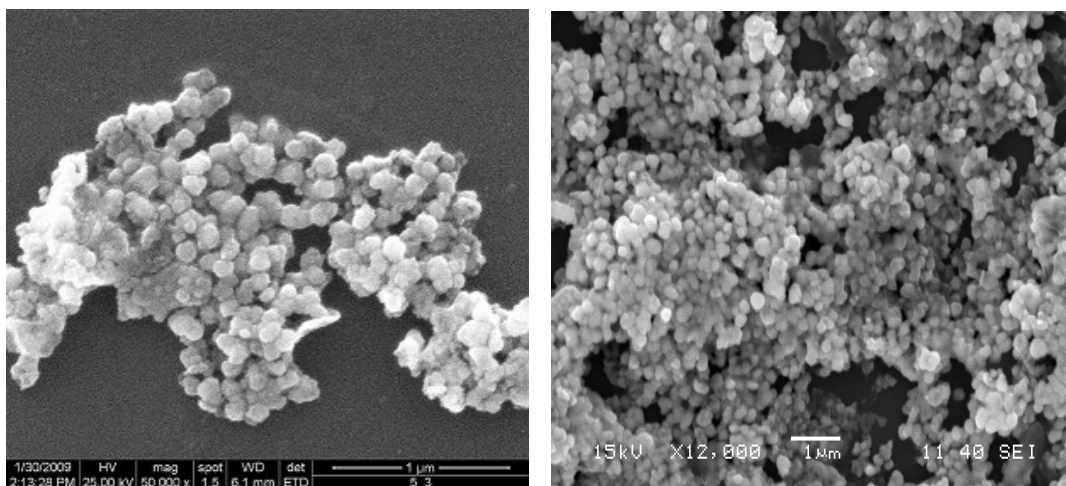
Figure 5.5. SEM image of core-shell (S@AgBr) particles for 50 mM sodium thiosulphate concentration and 0.2 mM $AgNO_3$ in CTAB surfactant solution.
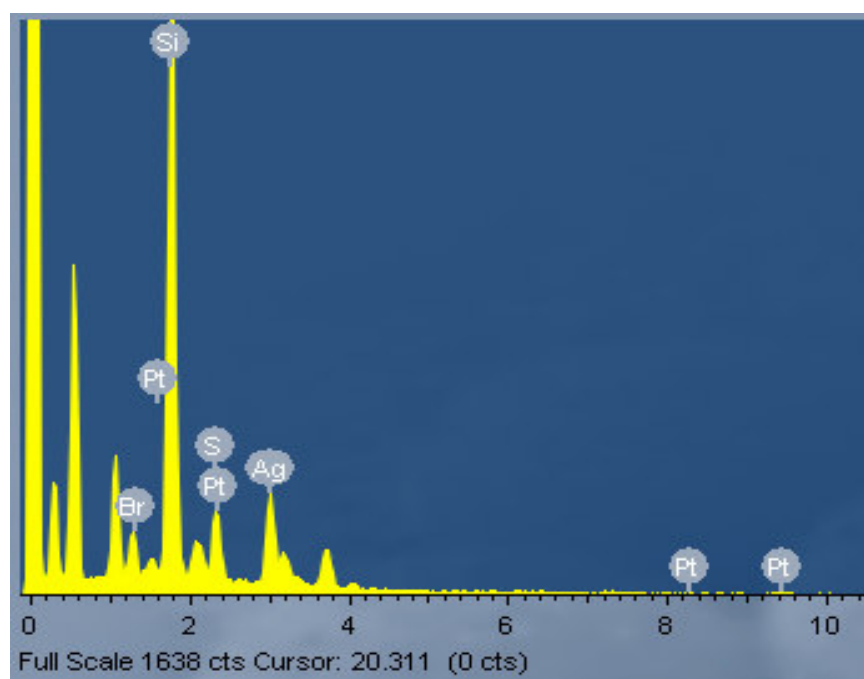
Figure 5.6. EDAX analysis of core-shell particle by scanning electron microscope (SEM)

5.3.5. Analysis of core-shell particle by TGA

The decomposition path of core-shell (sulfur-AgBr) particle was studied by TGA analysis. Figure 5.5 shows the weight loss for the particle during heat treatment under constant air flow, 40 ml/min. A very sharp weight change was observed at 300 °C due to burning of sulfur and AgBr to there respective oxides. The sample for TGA analysis was prepared by successive washing of the particle by water. So sample is surfactant free. Therefore, weight loss occurred in one step mainly. But after complete burning as AgBr is converted to Ag_2O and still with in the crucible so weight% is not become exactly zero like simple core particle. From the DTA values negative peak is obtained that means the conversion is endothermic in nature. Comparing the Figure 3.10 and 5.5, the weight loss started almost in same temperature but for core-shell particle weight loss occurred more sharply i.e. with in less temperature range. But from the DTA data, the peak value of core conversion is more negative compare to core-shell conversion. That means, core conversion is more endothermic in nature compare to core-shell particle.
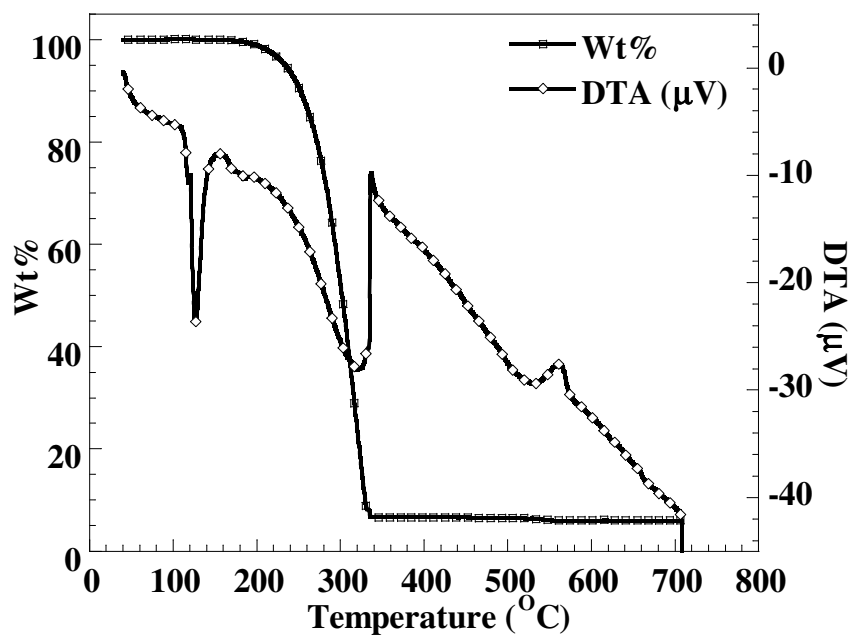
Figure 5.7. TGA/DTA curve of the core-shell (sulfur-AgBr) particle during heat treatment under constant air flow.

5.3.6. Analysis of core-shell particle by BET:

The specific surface area of the core-shell particle was measured by BET apparatus at liquid nitrogen temperature (-195.8 ^{0}C) using autosorbs-1 (Quantachrome, USA). Before adsorption and desorption study, the sample was degasified at constant 80^{0}C temperature.

The Figure 5.6 shows the adsorption and desorption of N_2 gas by the solid sample. The low adsorption at relative pressure values < 0.5 shows the absence of micro porosity. And it is also confined by the low value of BET surface area 5.08 m^2/gm. The isotherm presents a hysteresis loop that is associated with the presence of mesoporosity. Further more the adsorption limit is not well defined at the relative pressure close to one. The isotherm is rise rapidly near to relative pressure equal to one. The surface area obtained by this study is very low due to may be agglomeration of the particles so that particle size increases and gives micro sized particles.
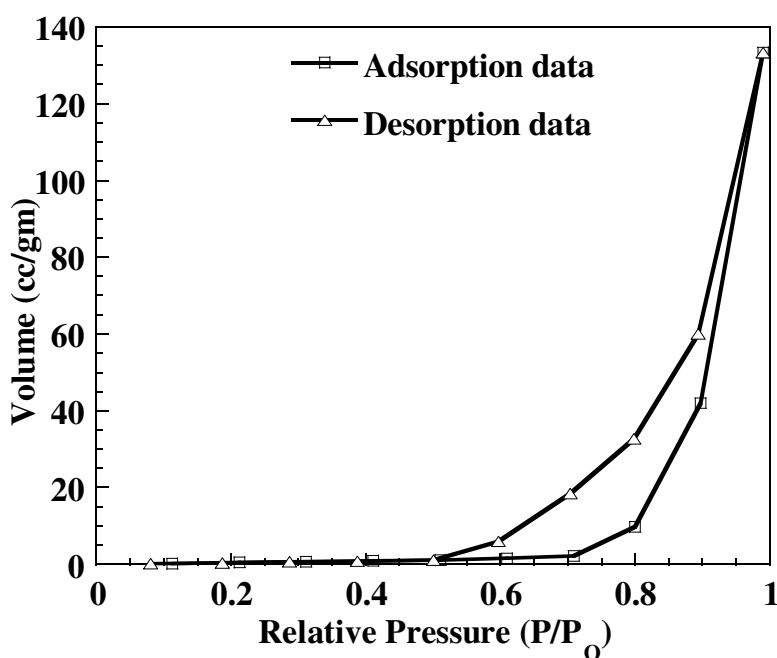
Figure 5.8. Plot of adsorption and desorption data of core-shell particle at a constant temperature -195.8 °C by BET apparatus.

5.4.   Conclusion:

By this method, we got core-shell particles with free solid AgBr particle. The overall size of the particles and shell thickness can be controlled by appropriate controlling the both sodium thiosulphate and silver nitrate concentration. The core-shell particles obtained by this route are more or less uniform spherical in size. And TGA analysis confirms the AgBr formation as after treatment there are a residue still remains due to formation of Ag_2O. But the surface area obtained by BET is very low, may be due to agglomeration of particle to large size.

Chapter 6

CONCLUSION AND SUGGESTION FOR FUTURE WORK

6.1 Conclusion

The results presented in Chapters 3, 4, and 5 on the preparation of core sulfur nanoparticles, growth kinetics of sulfur nanoparticles, and finally the sulfur-AgBr core-shell nanoparticle can be summarized as follows.

In presence of acid sodium thiosulphate is disproportionate to sulfur, but the particle size depends on the acid to thiosulphate ratio and also strength of the acid. In organic acid medium particle size much lower compare to any inorganic acids for a fixed thiosulphate concentration. As sulfur is a neutral charged element, it has an agglomeration tendency, so in aqueous solution particle size is higher. But to control the size surfactant can be use as a dispersing agent. In presence of any surfactant particle size is much lower compare to without surfactant system. But to control the size and morphology of the particle anionic surfactant SDBS is the best. Because in SDBS solution particle size is low and also the particle size distribution is narrow for a wide range of thiosulphate concentration. But in cationic surfactant like CTAB solution, we got minimum particle size 30 nm and 55 nm in organic (oxalic) and inorganic (HCl) acids medium respectively for a particular thiosulphate concentration. The particle size also depends on the surfactant concentration, with increasing surfactant concentration particle size decreases and almost become constant near to CMC. The obtained particles are orthorhombic or α-sulfur with S_8 structure with spherical shape for all the cases.

For sulfur particle formation nucleation is very fast, but the particle size is mainly controlled by growth and agglomeration. The UV-absorbance of the reaction medium during sulfur particle formation becomes constant for almost in all cases studied here in 45-60 minutes but DLS study shows the particle size changes for a long time close to 160-200 minutes. That means, the time of period the reaction was completed so that sulfur concentration become constant, but the change in particle sizes beyond that due to agglomeration. Particle growth is mainly control by diffusion of newborn particles from the bulk to core surface. Therefore, those physical parameter, are responsible for changing the diffusion rate are also responsible for different growth rate. The sonication increases the total energy of the system, so in presence of sonication the particle growth rate also high. At high temperature and high thiosulphate concentrated solution the particle growth rate is also high due to increase in diffusion rate. In presence of surfactant, due to formation of a uniform charge layer on the surface the agglomeration tendency is low and particle growth rate also slow.

For uniform coating on the core surface, core surface modification is most important. For AgBr coating in aqueous medium, the sulfur surface should be modified to positive charge so that negatively charge particle selectively deposited on the core surface and formed core-shell particle. The overall size and shell thickness can be controlled by changing the thiosulphate and AgNO$_3$ concentration. The particles obtained by this method are almost uniformed size and spherical shape.

The main limitation of this method is size of the particle can not be reduced as desire. For a particular surfactant and a reactant concentration we can prepare the particle up to a certain size.

6.2   Suggestion for Future work

The work can be continued in further in different direction. In future the following work can be done,

(1)   As in organic acid medium, we got minimum sized core particle. So other organic acids can be used for sulfur synthesis from thiosulphate solution.

(2)   Other shell materials can be used to coat the sulfur particle in presence of suitable surfactant miceller solution.

(3)   Hollow particle can be prepared by selectively dissolving core sulfur particle by suitable solvent.

(4)   The same study can be carried in microemulsion system using same surfactants to get better particle size control.

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Research Publications

1. Thesis

Communicated

- Rajib Ghosh Chaudhuri and Santanu Paria. **"Synthesis and characterization of sulfur nanoparticles in aqueous solution of surfactants".**

To be communicated

- Rajib Ghosh Chaudhuri and Santanu Paria. **"Growth kinetics of sulfur nanoparticles in aqueous medium in presence of surfactants".**

- Rajib Ghosh Chaudhuri and Santanu Paria. **"A review on synthesis and application of core-shell nanoparticles".**

- Rajib Ghosh Chaudhuri and Santanu Paria. **"Preparation of S@AgBr core-shell nanoparticles in presence of aqueous CTAB solution."**

Conference

- Rajib Ghosh Chaudhuri and Santanu Paria. **"Synthesis and characterization of nano to micro size sulfur particle in presence of surfactants"** *International conference on Environmental Research* (ICER-2008), BITS – Goa. Dec. 18-20, 2008.

2. Summer Project:

Rajib Ghosh Chaudhuri Santanu Paria. **"Dynamic contact angles on PTFE surface by aqueous surfactants solution in absence and presence of electrolytes".** Accepted in *J. Colloid and Interface Science.* DOI: 10.1016/j.jcis.2009.05.033.