

**SYNTHESIS AND CHARACTERIZATION OF SILVER
OR SILVER SULFIDE FILLED POLY(3-HYDROXYBUTYRATE)
NANOCOMPOSITES**

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UNIVERSITI SAINS MALAYSIA

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OR SILVER SULFIDE FILLED POLY(3-HYDROXYBUTYRATE)
NANOCOMPOSITES**

by

YEO SIEW YEAN

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LIST OF ABBREVIATIONS

| | |
|--------|-----------------------------------|
| CMC | critical micelle concentration |
| CTAB | cetyl-trimethyl ammonium bromide |
| DSC | differential scanning calorimetry |
| EDS | Energy-dispersive X-ray |
| FTIR | fourier transform infrared |
| GPC | gel permeation chromatography |
| hr | hour(s) |
| NMR | nuclear magnetic resonance |
| PHB | poly(3-hydroxybutyrate) |
| POM | Polarized optical microscopy |
| PVA | poly(vinyl alcohol) |
| SEM | scanning electron microscopy |
| SPR | surface Plasmon resonance |
| TGA | thermogravimetric analysis |
| TOAB | tetraoctylammonium bromide |
| TU | thiourea |
| UV-vis | ultraviolet-visible |

LIST OF SYMBOLS

| | |
|-----------------|--|
| ΔH_m | enthalpy of melting |
| M_w | average molecular weight |
| T_c | crystallization temperature |
| T_g | glass transition temperature |
| T_m | melting temperature |
| χ_c | degree of crystallinity |
| T_{onset} | onset of the thermal degradation temperature |
| T_{max} | the maximum weight loss |
| E_d | thermal degradation activation energy |
| A | pre-exponential |
| r | correlation coefficient |
| λ_{max} | the wavelength of maximum absorbance |

SINTESIS DAN PENCIRIAN NANOKOMPOSIT POLI(3-HIDROKSIBUTIRAT) TERISI ARGENTUM ATAU ARGENTUM SULFIDA

ABSTRAK

Hidrosol Ag dan Ag₂S telah disintesis melalui tindak balas penurunan kimia dan kaedah refluks masing-masing. Teknik mudah pemindahan fasa akues ke fasa organik digunakan untuk memindahkan zarah nano Ag dan Ag₂S daripada hidrosol masing-masing ke larutan berklorofom poli(3-hidroksibutirat). Zarah nano Ag dan Ag₂S telah distabilkan oleh polimer PHB dalam organosolnya. Kehadiran logam zarah Ag atau Ag₂S dalam biokomposit nano yang baru terhasil dikenalpasti dengan teknik pembelauan sinar X-ray. Saiz zarah Ag dan Ag₂S masing-masing ialah 7-12 nm dan 14-24 nm. Pada kepekatan PHB yang rendah, zarah Ag berbentuk sfera manakala zarah Ag₂S berbentuk heksagon. Namun pada kepekatan PHB yang tinggi, kedua-dua zarah berbentuk sfera. Data penguraian terma dan bukan isoterma biokomposit nano Ag/PHB dan Ag₂S/PHB diperolehi melalui kalorimetri pengimbasan pembezaan (DSC) dan analisis termogravimetri (TGA). Kedua-dua biokomposit nano menunjukkan kecenderungan terma yang serupa seperti pengurangan suhu peleburan, peralihan kaca dan penguraian berbanding PHB tulen. Keputusan DSC dan TGA menunjukkan biokomposit nano mengalami penyusutan parameter termanya bergantung kepada kandungan Ag dan Ag₂S. Analisis kinetik penguraian bukan isoterma PHB dan biokomposit nano telah dijalankan dan parameter kinetik dikira melalui kaedah Kissinger. Nilai tenaga pengaktifan penguraian terma (E_d) untuk biokomposit nano Ag/PHB dan Ag₂S/PHB adalah lebih rendah daripada PHB tulen. Zarah nano Ag dan Ag₂S memangkinkan penguraian terma PHB dalam biokomposit nano masing-masing. Nilai E_d meningkat sedikit dengan peningkatan kandungan Ag atau Ag₂S dalam biokomposit nano yang disebabkan oleh pengagregatan dan pergumpalan zarah nano semasa proses pemanasan.

SYNTHESIS AND CHARACTERIZATION OF SILVER OR SILVER SULFIDE FILLED POLY(3-HYDROXYBUTYRATE) NANOCOMPOSITES

ABSTRACT

Ag and Ag₂S hydrosols were synthesized via chemical reduction and reflux methods respectively. A simple aqueous to organic phase transfer technique was employed to transfer the Ag and Ag₂S nanoparticles from the respective hydrosol into poly(3-hydroxybutyrate) [PHB] chloroform solution. The Ag and Ag₂S nanoparticles were stabilized by the PHB polymer in the organosols. The presence of metallic Ag or the Ag₂S particles in the newly formed nano-biocomposites were confirmed by the X-ray Diffraction (XRD) technique. The particles size of Ag and Ag₂S were within 7-12 nm and 14-24 nm respectively. At low concentration of PHB, the shape of Ag particles was sphere while for Ag₂S particles were hexagonal-like. However, at high concentration of PHB, both types of particles were sphere-like. Thermal and non-isothermal degradation data of Ag/PHB and Ag₂S/PHB nano-biocomposites were obtained via Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA) respectively. Both nano-biocomposites showed similar thermal trend where a decrement in melting, glass transition and degradation temperatures with respect to neat PHB were observed. The DSC and TGA results show the depression of thermal parameters were dependent on Ag or Ag₂S loading. Kinetic analysis of non-isothermal degradation of PHB and the nano-biocomposites were carried out and the kinetic parameters were calculated via Kissinger method. The values of thermal degradation activation energy (E_d) for Ag/PHB and Ag₂S/PHB nano-biocomposites were less than neat PHB. The Ag and Ag₂S nanoparticles likely catalyzed the thermal degradation of PHB in the nano-biocomposites. The slight increases in the E_d values with the increase in Ag or Ag₂S content in the nano-biocomposites was attributed to the aggregation and agglomeration of nanoparticles during heating process.

Chapter 1

Introduction

1.1 A Brief Overview

Microtechnology has changed our lives dramatically especially since the appearance of computer technology. Since then, current technology has developed rapidly and is now focused on the fabrication of consumer goods which incorporate technology in the nanosize range. This technology integrates material in nano range which exhibited excellent and unique properties such as optical, electrical, catalytic, biological and mechanical. Thus nanotechnology is the most promising field for generating new applications. For example, silver nanoparticles which contribute to the recent advances in antimicrobial technology are found in numerous consumer products ranging from washing machines to dishwashers. Apart from this, titanium oxide nanoparticles are used as skin-protective compounds in sunscreen. In addition, antimony-tin oxide nanoparticles are incorporated into coating to provide scratch resistance and offer transparent protection from ultra-violet radiation. All these examples point to the fact that the world is emerging into the nanotechnology era.

To date, nanotechnology is still a relatively fresh and a new arena in scientific research, especially for the fabrication and characterization of nanomaterials. Related research activities and innovations are flourishing worldwide. Over the last decades, there has been increasing interest in the development of sustainable nanomaterials. This is because synthetic materials have raised a number of environmental and human health concerns. Virtually, most of the synthetic materials are non-biodegradable and are derived from non-renewable resources such as petroleum. As a result, they can lead to problems such as increasing waste and diminishing resources. In addition, the synthesis and decomposition of these

materials involves the use of toxic compounds or release of harmful and poisonous gases.

Basically sustainable nanomaterials involve biodegradable and renewable materials. Among the biodegradable materials, biopolymers such as epoxidized natural rubber¹, poly(3-hydroxybutyrate) (PHB)², chitosan³⁻⁵ and starch⁶⁻⁸ have been widely used. For instance, they have been employed in food packaging⁹ and biomedical appliances¹⁰. The undeniable advantages of these materials also have led to intensive studies on metal/polymer nanocomposites which may be utilized for a number of technological applications. Without a doubt, the studies based on the biodegradable and environmental friendly nanomaterials are one of the most active research activities for the present and even in the future, due to its environmental impact as well as from an academic perspective.

1.2 Problem Statements

The excellent and unusual properties of metal and semiconductor nanoparticles are dependent on size and shape. Therefore, controlling the size and morphology of the metal nanoparticles is very important to ensure its unique properties for potential applications. Nano-sized Ag and Ag₂S are favourable among the metallic and semiconductor nanoparticles due to their unique properties which are not exhibited in bulk. Generally, various surfactants, ligands and polymers have been employed as stabilizers in the synthesis of these nanoparticles. Nonetheless, to the best of knowledge, PHB has yet to be used as a stabilizer or matrix for the synthesis of well-dispersed and stable Ag and Ag₂S nanoparticles.

PHB is known as a hydrophobic polymer and only dissolves in certain organic solvents such as chlorinated solvents. Hence, the as-synthesized Ag or Ag₂S particles need to be transferred into a chloroform solution containing PHB to prepare PHB-stabilized Ag or Ag₂S colloidal solutions. No fundamental studies exist

on the synthesis of PHB-stabilized Ag or Ag₂S nanocomposites prepared using this technique. Therefore, it is important to study the effect of the transferring agent and PHB concentration on the particles stabilization and morphology, as well as the chemical interaction between these two nanoparticles with PHB.

The properties of the synthesized nanocomposites are very important for their potential applications. The presence of inorganic fillers within the polymer matrix can affect thermal stability¹¹, electrical conductivity^{12, 13} as well as the mechanical properties¹⁴ of the resultant composite. It is noted that thermal property of the metal/polymer nanocomposites is one of the most important criteria. Hence, understanding the thermal behavior and stability, as well as the kinetic study of thermal degradation of the Ag/PHB and Ag₂S/PHB nanocomposites is significant to provide valuable quantitative information for the manufacturing and chemical recycling processes.

1.3 Research Objectives

The objectives of this research are:

- 1.3.1 To synthesize and characterize Ag and Ag₂S nanoparticles.
- 1.3.2 To study the effect of various synthesis parameters (such as concentration of CTAB and PHB, or reaction time and temperature, etc) for Ag and Ag₂S nanoparticles respectively.
- 1.3.3 To synthesize Ag/PHB or Ag₂S/PHB nano-biocomposites via phase transfer method
- 1.3.4 To investigate the thermal behavior and kinetic study of the thermal degradation of PHB in the presence of Ag or Ag₂S nanoparticles in the respective nano-biocomposites.

1.4 Scope of Study

This study is limited to the synthesis of Ag and Ag₂S nanoparticles stabilized using a biodegradable polymer, PHB. The metal nanoparticles were synthesized via chemical reduction using sodium borohydride, NaBH₄ as the reducing agent and cetyltrimethylammonium bromide (CTAB) as stabilizer in the aqueous phase. The Ag or Ag₂S organosols are prepared via a simple phase transfer method. PHB was employed as the stabilizer in the organic layer. The prepared Ag and Ag₂S nanoparticles were characterized using UV-vis and XRD. TEM and SEM were employed to study the morphology and particle size of nanoparticles. The effect of Ag or Ag₂S nanoparticles on the thermal behaviour and degradation of PHB in the nanocomposites were studied via DSC and TGA. The kinetic of non-isothermal degradation of Ag/PHB and Ag₂S/PHB nanocomposites were studied via the Kissinger method.

1.5 Thesis Layout

This thesis consists of 8 chapters. The first chapter gives a brief overview of the intended work in this thesis. In the second chapter, literature review concerning Ag and Ag₂S nanoparticles, metal based biodegradable nanocomposites, various characterization techniques and thermal studies of nanocomposites is presented. Chapter 3 is the details of the materials and experimental procedures employed in this work. Chapter 4 and 5 are the results and discussions of the synthesis and characterization on Ag/PHB and Ag₂S/PHB nanocomposites respectively. Following this, Chapter 6 and 7 deals with the thermal behavior and kinetic studies of thermal degradation of Ag/PHB and Ag₂S/PHB nanocomposites respectively. Finally, a conclusion of this work and recommendations for future work in this field is presented in Chapter 8.

Chapter 2

Literature Review

2.1 Nanoscience and Nanotechnology

Nanoscience, is the scientific study of the chemical and physical phenomenon of a group of atoms, molecules and objects whose size is in the region of 1-100 nanometer (nm)¹⁵⁻¹⁸. On the other hand, the technology of design, fabrication, production and applications of structures and materials by controlling shape and size at nanometer scale is referred to nanotechnology^{15, 16, 19}.

Nanoscience and nanotechnology are not new concept and technique. In 1959, Nobel Prize winning physicist, Richard Feynman has described nanotechnology in an oral presentation entitled "*There's Plenty of Room at the Bottom*"²⁰. Since then, nanoscience and nanotechnology have been developed extensively and intensively. For example, the discovery of fullerenes (buckyballs)²¹ in 1985, the invention of atomic force microscope (AFM)¹⁵ in 1986, carbon nanotubes²¹ in 1991 and the DNA molecular robots²² in 2011. To date, the possibilities of nanoscience seem endless and the evolution of this emerging nanotechnology will keep refresh by the new synthesis techniques and a realization of their potential in many different areas.

2.2 Nanomaterials

The most common definition for nanomaterials is the materials with at least one of the three dimensions is less than 100 nm¹⁵. In nanoscale, a particle has different properties from their macroscopic (bulk) or atomic and molecular system^{15, 19}. Interestingly, the unique properties of nanomaterials such as mechanical, optical, chemical, magnetic and electronic are size dependent as well as morphology and

spatial organization dependent^{16, 19, 23}. For example, the gold nanoparticles with particle size less than 100 nm exhibit intense red colour as compared to the golden lustre in the bulk form. Figure 2.1 illustrate the comparison of nanoscale relative to the bulk and atomic levels.

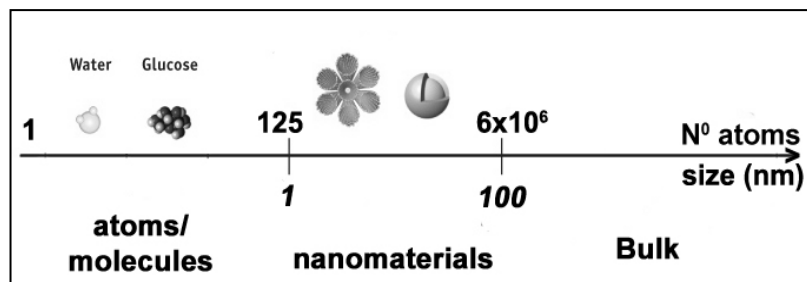


Figure 2.1: The comparison of nanoscale with the bulk and atomic levels¹⁷.

Nanomaterials range from inorganic or organic, crystalline or amorphous particles, and even can be found as single particles, aggregates, powders, dispersed in a matrix, as colloids, suspensions and emulsions, nanolayers and films, and supramolecules like dendrimers, micelles or liposomes^{19, 24}. In all, there are numerous types of nanomaterial. Therefore, categorization is needed for the proper understanding on nanomaterials. Based on the literatures, the approaches for a classification of nanomaterials are either in term of the dimension, manufacturing process or phase composition. Among all, identifying nanomaterials according to their dimension is the most typical way of categorizing them. The Figure 2.2 show the classification of nanomaterials based on the dimensions²⁴ as (i) zero-dimensional (0-D), (ii) one-dimensional (1-D), (iii) two-dimensional (2-D) and (iv) three-dimensional (3-D) systems. For example²⁴, spherical nanoparticles such as silica nanoparticles are nano-sized in all three dimensions. Nanotubes, nanorod, or nano-needles have two nanometer dimensions. Nanosheets such as layered silicates have only one dimension in the nanoscale.

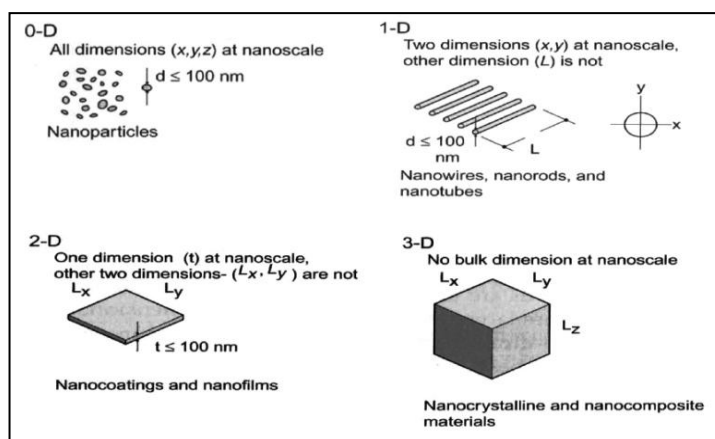


Figure 2.2: Classification of nanomaterials according to dimensions, i.e 0-D, 1-D, 2-D, and 3-D²⁴.

2.2.1 Nanoparticles²⁴

Typically, nanoparticle is defined as cluster of atoms or molecules (several ten or hundred unit) with size in range of 1-100 nm. The nanoparticles can either be in form of amorphous or crystalline, single or polycrystalline, composed of single or multi element, exhibit various shapes and forms, exist individually or incorporated in a matrix and also can be metallic, ceramic or polymeric.

Almost every element in the Periodic Table can form nanoparticles especially metals and transition metals, together with their combination to form various alloys and compounds. Among these nanoparticles, the syntheses of noble metal nanoparticles have been extensively studied due to their promising unique properties, well-defined or well-dispersed morphology¹⁵. In fact, metal nanoparticles have a long history since the Chinese used gold (Au) nanoparticles as an inorganic dye more than a thousand years ago while Michael Faraday has prepared red-deep solution of Au colloid in 1857¹⁹. In modern age, metal nanoparticles like silver (Ag), palladium (Pd), platinum (Pt), and copper (Cu) have also gained much interest of researchers besides Au^{16, 19, 25}. Moreover, bimetallic nanoparticles²⁶ and nano-sized metal oxide also have been studied^{27, 28}. A recent development on the synthesis or

preparation of nanoparticles has also been extended to metal chalcogenides, for example CdS, HgTe, Ag₂S and CuS^{16, 19}. Recently, biodegradable polymeric nanoparticles coated with poly(ethylene glycol)²⁹ or poly (D,L-lactide-co-glycolide)³⁰ used in drug delivery devices have also been reported

2.2.2 Nanocomposites

In the current area of nanotechnology, nanocomposites can be defined as the materials that incorporate nanosized particles into a matrix of standard material in order to improve or modify the performance properties of the material³¹. According to the type of matrix, nanocomposites can be classified into ceramic matrix nanocomposites, metal matrix nanocomposites and polymer matrix nanocomposites^{18, 24}.

Among the above mentioned nanocomposites, polymer-based / matrix nanocomposites have become a prominent area of current research. As the name suggests, it is at least one-dimension of the dispersed particles is in the nanometer range^{31, 32}. The earliest dispersed material used in polymer matrix nanocomposites is nanoclay³³. The studies with carbon nanotubes, carbon nanofibers, graphite, nanocrystalline metals and a host of additional nanoscale inorganic filler-based polymer nanocomposites have also been reported³³. Basically, the extensive studies of polymer/clay nanocomposites are attributed to the physical properties and mechanical performance which have been improved by nanoclay^{31, 33}. The thermal stability of the nanocomposites combining montmorillonite (MMT) and polymer matrix have been reviewed³⁴.

The metallic nanoparticles/polymer (metal/polymer) nanocomposites has emerged due to the ability of particle stabilization exerted by polymers^{19, 23, 35}. The metal nanoparticles in polymer matrices have drawn special attention due to the imparted unique physical and chemical properties onto the composite, enhanced

thermal and mechanical stability³⁶⁻³⁹ and film forming ability of polymers⁴⁰. Some of the fundamental studies on the preparation and nature of metal-polymer nanocomposites have been described by Nicolais and Carotenuto²³ while Bordes and Averous⁴¹ have reviewed the nano-biocomposites system. The trends and future perspectives of nanoscale particles for polymer degradation and stabilization have also been well reviewed by Kumar et al.³¹.

2.3 Properties of Nano-scaled Materials

2.3.1 Surface Energy^{15, 16, 19, 23}

As particle size become smaller, materials possess a huge fraction of surface atoms per unit volume. The ratio of surface atoms to the interior atoms increases noticeably for a nano-sized particle as compared to bulk. The total surface energy increased with the overall surface area. Owing to the vast surface area, all nano-scaled materials possess a large surface energy and become thermodynamically unstable or metastable. These changes lead to the change in the physical and chemical properties, which is unique to the nanomaterials.

As reported by Cao¹⁹, the reduction for overall surface energy can be achieved via the following processes: (i) surface restructuring, (ii) formation of faceted crystal, (iii) combining individual nanostructures into large structures through sintering or Ostwald ripening and (iv) agglomeration of individual nanostructures.

2.3.2 Optical Properties

Physical properties such as optical, of nano-scaled materials can be significantly different from bulk materials^{16, 19, 23}. For example, solutions of colloidal gold and silver particles have a very distinctive red and yellow colour respectively, which arises from their tiny dimensions⁴². The colour of metallic nanoparticles may

change with size due to the surface plasmon resonance (SPR)⁴³. In fact, SPR is the collective oscillation of electrons within a metal nanoparticle, activated by an incident electromagnetic field^{19, 44, 45}. SPR is generated when the size of metal nanocrystal is smaller than the wavelength of incident radiation¹⁹. The schematic of the excitation of the dipole SPR is shown in Figure 2.3. Here, an incident field polarizes the nanoparticles, thus shifting the electrons collectively to one side of the system. This is only possible in metal nanoparticles with high electron mobility in the lattice due to the conduction and valence bands lie very close to each other. After their initial perturbation, the electrons will oscillate and confined by the surface of the nanocrystal. The frequency of this oscillation corresponds to the energy at which photons will be most strongly absorbed. Because of this, the SPR absorption is strongly dependent on the nature of the nanostructured materials and its structure including size and shape, and interparticle interactions⁴⁶.

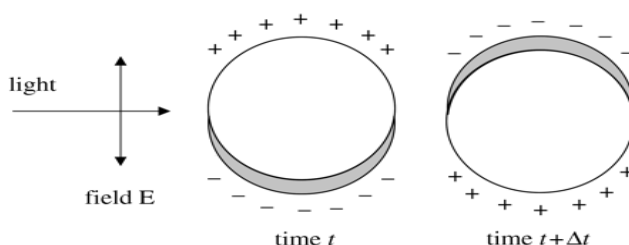


Figure 2.3: A schematic of the excitation of the dipole surface plasmon oscillation¹⁹.

2.4 Stabilization of Colloid Nanoparticles

2.4.1 Stabilization Mechanisms

There are two stabilization mechanisms to prevent particles combination or agglomeration in the synthesis of nanoparticles^{16, 19, 47}. There are (i) electrostatic stabilization, which induce kinetic stability and (ii) steric stabilization, which induce thermodynamic stability to the particles⁴⁷.

2.4.1.1 Electrostatic Stabilization^{16, 19}

The stability of colloidal particles is achieved with an electrical double layer on the surface of particles. In liquid, ionic groups can adsorb on the surface of a colloidal particle to form a charged layer. To maintain electro-neutrality, an equal number of counterions with the opposite charge will surround the colloidal particles and give rise to overall charge-neutral double layers. For examples, in the preparation of gold nanoparticles by the reduction of aqueous $[\text{AuCl}_4]^-$, the colloidal gold particles are surrounded by an electrical double layer formed by adsorbed chloride ions.

2.4.1.2 Steric Stabilization^{16, 19}

Steric stabilization, of colloid particles is achieved by attaching or adsorption of stabilizing agents such as polymers, surfactants, ligands or dendrimers onto the surface of the particles as shown in Figure 2.4. In general, polymers are widely used to exert steric stabilization of colloidal particles.

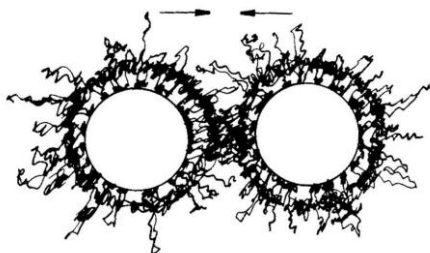


Figure 2.4: Steric stabilization scheme¹⁹.

2.4.2 Stabilizing Agents

To sterically stabilize the high surface energy nanoparticles, there is a wide selection of stabilizing agents or stabilizers available. Generally, the stabilizers are

employed to overcome the Van der Waals interaction between nanoclusters which otherwise leads to agglomeration, as well as to control the growth and shape of particles^{16, 19}. Figure 2.5 illustrates the surfactants and polymers stabilization on nanoparticles in a typical wet chemical synthesis method.

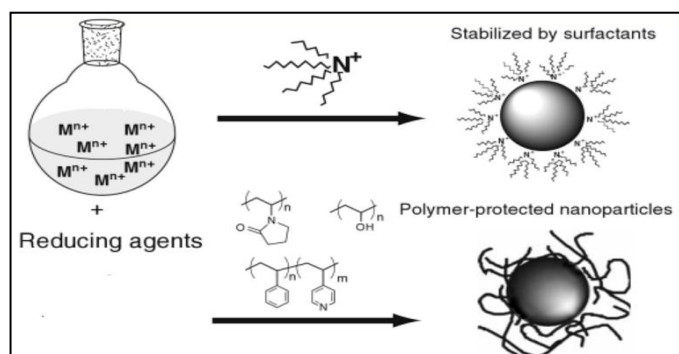


Figure 2.5: A typical scheme for preparation of surfactant-stabilized and polymer-protected nanoparticles via chemical reduction^{16, 19}.

2.4.2.1 Surfactants

Large numbers of anionic, cationic and non-ionic surfactants have been used as stabilizer in the preparation of nanoparticles. It is worth noting that the ability of surfactants in the particles stabilization is influenced by the concentration and solubility of the surfactants⁴⁸. Table 2.1 lists of some examples of surfactant used in the particles stabilization.

Table 2.1: Types of surfactant used in the nanoparticle stabilization.

| Type of surfactant | Surfactant |
|--------------------|---|
| Anionic | Aerosol OT (sodium bis-2-ethylhexyl-sulfosuccinate), AOT ⁴⁹ , sodium dodecyl bromide, SDS ⁴⁹⁻⁵¹ |
| Cationic | CTAB ^{48, 52-59} , TOAB ⁶⁰ , CTAC ⁶¹ |
| Non-ionic | Triton-X 100 ⁵⁰ |
| Gemini surfactant | 2-hydroxy-1,3-bis(octadecyldimethylammonium) propane dibromide ⁶² |

Among the surfactants, cationic surfactants have shown good ability in term of particle stabilization and controlling particle morphology of noble nanoparticles. In essence, the quaternary ammonium surfactants such as TOAB and CTAB stabilized the metal clusters via surface ion-pair electrostatic interactions^{51, 63, 64}. Furthermore, the surfactant formed monolayer⁶⁴⁻⁶⁶ or bilayer^{48, 59, 67-70} structures surrounding the surface of nanoparticles. Figure 2.6 (a) shows the model for a single CTAB-stabilized Ag nanoparticles via electrostatic ion-pair interaction⁷¹ while Figure 2.6 (b) is the possible bilayer structure of CTAB capped nickel (Ni) nanoparticles⁷².

It is also noted that surfactants have played an indispensable role in the morphology facilitation or shape-controlling in the synthesis of metal or metal chalcogenide nanoparticles, besides of the role as stabilizer^{54, 73}. For example, CTAB and/or SDS have been shown to participate in the shape-controlled synthesis of PbS nanostars⁷⁴, as well as faceted and cubic Ag₂S nanocrystals⁷⁵. CTAB has been widely used in the synthesis of hollow nanoparticles such as Cu₂O⁷⁶ and Ag₂S⁷⁷. The mechanism of formation of hollow Cu₂O nanoparticles involving CTAB is displayed in Figure 2.7⁷⁶.

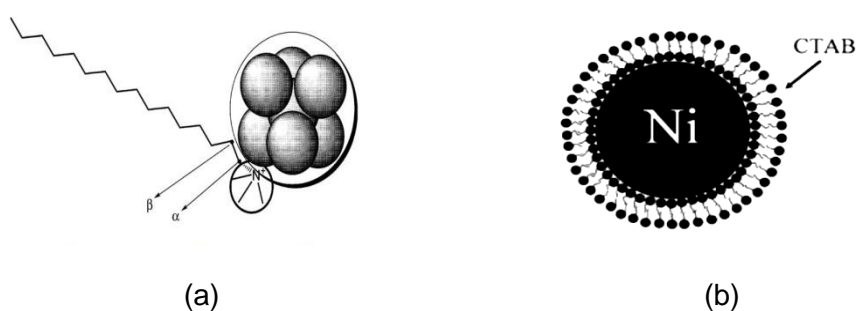


Figure 2.6: (a) single CTAB layer on Ag nanoparticles⁷¹ and (b) double CTAB layers on Ni nanoparticles⁷².

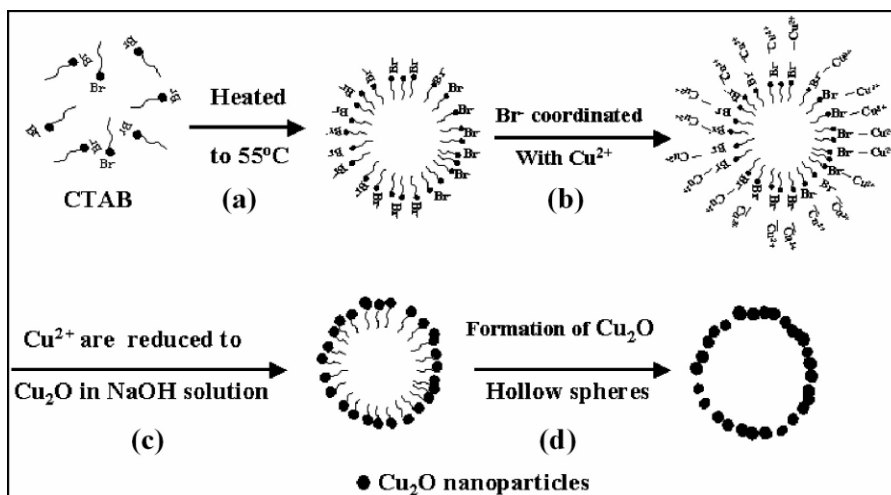


Figure 2.7: A mechanism of formation of hollow nanoparticles involving CTAB⁷⁶.

2.4.2.2 Polymers

Polymer is a macromolecule made up of repeating units (monomers). The utilization of polymer(s) in the synthesis of metal or semiconductor nanoparticles, the polymer(s) selected may fulfill the following functions⁷⁸⁻⁸⁰:

- (i) the stabilization for the colloidal dispersion and the prevention of agglomeration,
- (ii) the protection from deactivation (e.g. from water vapor or air),
- (iii) the influence on the nanoparticles feature during the preparation by the interaction with the metal precursor or the zerovalent metal colloids, and control of the nanoparticle growth,
- (iv) the technological processability of the materials (such as film-forming property),
- (v) the additional tuning of the composite materials and their properties.

In the stabilization of metal or semiconductor colloids, polymer acts as a protective layer by adsorption on the surface of nanoparticles^{15, 16, 19, 23}. A strong adsorption by polymer protects the growth sites and thus reduces the growth rate of nanoparticles. A full coverage of polymer stabilizer would also hinder the diffusion of growth species from the surrounding solution to the surface of growing particles.

Meanwhile, polymer stabilizer can be a soluble linear or branched or functionalized macromolecules or micellar aggregates which “wrap” the particles in solution⁴⁷. Thus, the particles are prevented from sintering and precipitation.

Commercially available polymers such as poly(vinyl alcohol) (PVA)⁸¹, poly(vinylpyrrolidone) (PVP)⁸² and poly(methylmethacrylate) (PMMA)³⁷ have been used in the synthesis of noble metal nanoparticles because of their excellent surface capping ability. Natural polymers or biopolymers like starch, cellulose, chitosan, and natural rubber also have been used as stabilizers or matrices on stabilization of nanoparticles^{3, 83-85}. The choice of polymer is determined by consideration of the solubility of the metal colloid precursor, solvent and temperature.

2.4.2.3 Ligands

The use of ligands as stabilizers in metal nanoparticles synthesis is becoming more extensive. The main advantage of using these stabilizers is the possibility to tune the surface state of the particles via chemical interactions between the particles and the ligands. Some examples of ligand are thiols⁸⁶, amines⁸⁷⁻⁸⁹, citrate⁹⁰, carboxylic acid and phosphines.

2.4.2.4 Dendrimers

Dendrimers are highly branched, well-defined, synthetic macromolecules available in nanometer dimensions. It is well known that both the interior and exterior functional groups of dendrimers can complex metal ions through various interactions, including covalent bonds, electrostatic interactions and complexation reactions⁹¹. One of the unique properties of dendrimers is the presence of cavities inside the molecules. Dendrimers are able to stabilize the nanoparticles either by encapsulating the particles within the dendrimer, or by having several dendrimers

stabilize the particles cluster. A major advantage of using dendrimer is that the produced particles have narrow size distribution and thus have significant applications in chemical sensing, catalysis and so on. The most commonly used dendrimers as stabilizer is the poly(amidoamine)^{92, 93}.

2.5 Preparative Routes to Inorganic Nanoparticles

The success of the synthetic strategies for nanomaterials is dependent on a variety of key issues. These are,

- (a) particle size distribution (uniformity: monodispersity of nanoparticle),
- (b) particle size control,
- (c) shape control: high yield with the desired shape,
- (d) scale-up: optimization of the synthetic at large scale, and
- (e) compatibility: ease of the synthesis for the realistic application.

The nanoparticles can be synthesized either via top-down or bottom-up approach^{16, 19, 94}. The top-down approach is where the nanomaterials are constructed from larger entities without atomic-level control using machining and etching techniques. The typical techniques of top-down approach are: photolithography, electron-beam lithography and mechanical grinding. However, this approach has disadvantages in that (i) large amount of material is needed, (ii) not suitable for preparation of uniformly shaped particles, and (iii) very small-size particles are difficult to realize. On the contrary, the bottom-up approach concerns materials built from molecular components and assemble themselves chemically. It is noted that this later approach is particularly attractive synthetic route for nanoparticles because it is simple and fast. Some techniques of bottom-up approach are chemical precipitation, reduction, colloids and so on. However, the bottom-up approach is plagued by the problem of poor monodispersity.

2.5.1 Synthesis of Metal Nanoparticles

Among the bottom up approaches, the reduction of metal precursors in solution is the common method employed in the synthesis of metal nanoparticles^{19, 95}. Thus, synthesis can be carried out either in aqueous or non-aqueous solution⁶⁶. The reduction of metal ions in aqueous is preferable than in organic solvent because most metal precursors are water-soluble. The preparation of metal colloid in non-aqueous solvent, however, has the advantage over the aqueous solvent preparations due to better control on the particle shape and size, as well as maintaining particles reactivity. Summary of the several routes to the synthesis of metal nanoparticles are given below:

2.5.1.1 Chemical Reduction⁹⁶

All wet chemical-based synthetic routes to nanosized metal particles start with the reduction of positively charged metal atoms. The resultant metal colloids are subsequently isolated as powder. Generally, there are two main types of reducing agents, which are (i) strong and (ii) weak agents. In the more recent years, the “green” reducing agent has been widely used, which are natural and environmental friendly materials. Table 2.2 gives a list of various kinds of reducing agents commonly used together with the appropriate conditions.

Table 2.2: The types of reducing agent used in the synthesis of metal nanoparticles via chemical reduction method.

| Reducing agent | Example | Properties | Ref. |
|------------------------|--|--|--------------------------|
| Strong | NaBH ₄ KBH ₄ | -promotes a rapid reaction rate -favors the formation of smaller and fairly monodisperse nanoparticles - difficult to control to generate larger particles | 37, 62, 83, 87, 96-105, |
| Weak | sodium citrate, hydrazine, alcohol, tannic acid | -induce slow reaction rate -favors relatively larger particles | 50, 81, 88, 100, 106-109 |
| Environmentally benign | glucose, ascorbic acid sago-starch, orange peel | -Produce larger particle sizes -heat or irradiation is needed | 35, 100, 103, 110-115 |

2.5.1.2 Irradiation Method

Noble metal nanoparticles can be successfully synthesized by using irradiation methods such as microwave heating, ultrasonic radiation, UV radiation or laser ablation, as tabulated in Table 2.3. In general, no reducing agent is required in this method.

Table 2.3: Typical irradiation methods used in the preparation of metal nanoparticles.

| Method | Properties | Advantages | Ref. |
|------------------------|---|---|------------------|
| Microwaves | - electromagnetic waves - heating is created by the interaction of the permanent dipole moment of the molecule with high frequency (2.45 GHz) electromagnetic radiation. | - heating is uniform and quick -shorten reaction time by a factor approximately 20 | 82, 112, 116-118 |
| ultrasonic irradiation | - ultrasonic waves is more than 20 000 KHz. - the solution was ultrasonic irradiated at room temperature for certain reaction time. | -control the size distribution of metal nanoparticles in narrower range -penetration property through solution resulting in a uniform activation energy for the reaction solution. | 119-121 |
| UV radiation | - a wavelength of 250 nm with an intensity of 300 W was used | -provide a relatively easy, controlled reduction of metal salts. | 78, 94 |

2.5.1.3 Thermal Decomposition

The syntheses of metal nanoparticles through thermal decomposition have been done by heating the sample at high temperature¹²²⁻¹²⁴. For instance, Ag nanoparticles have been prepared by thermal decomposition at 300°C for 2 hr¹²⁵. The advantage of thermal decomposition method is that it only involves the chemical precursor with no additional chemicals needed.

2.5.2 Synthesis of Metal Sulfide Nanoparticles

In general, the transition metal sulfide nanoparticles are synthesized in two conditions (i) template-free or template-assisted and (ii) at room temperature or under heating. It is interesting to note that the obtained metal sulfide nanoparticles are in various shapes such as hollow, hexagonal, cube or faceted structures. The tunable shapes are dependent on the ratio of reagents, concentration of surfactants, ligands or polymers and reaction time. These can be varied to achieve better control over the particle size and morphology. The summary of several methods available for the preparation of metal sulfide nanoparticles is as tabulated in Table 2.4.

Table 2.4: Methods used in the preparation of metal sulfide nanoparticles.

| Method | Typical route | Advantage | Ref. |
|---|---|---|-------------------|
| Hydrothermal (solvothermal) | <p>-Teflon-lined stainless steel autoclave is used.</p> <p>-Typically, the reactant solutions such as metal salt, sulfur precursor and template (such as surfactant or polymer) were placed into the autoclave and heated in oven.</p> <p>-the temperature range has been set for the synthetic route is commonly of 60-180°C</p> <p>-the final products are precipitated or cast on PET plate.</p> | <p>-the reaction is carried out under moderate condition,</p> <p>-nano-sized powders with different morphologies (uniform, monodispersed and/or tunable shape) can be obtained,</p> <p>-the as-prepared powders might have different properties than those produced through other approaches.</p> | 126-132 |
| Reflux / Low temperature solution phase approach | <p>-under nitrogen condition to prevent oxidation.</p> <p>-the final products could be in surfactant-assisted colloid form, or precipitated/embedded in polymer matrix.</p> <p>-heating is needed for thermal decomposition of sulfur source.</p> <p>-reflux system undergoes at relatively low temperature (40-120°C).</p> | <p>-an environmentally benign and user-friendly approach.</p> | 74, 133-135 |
| Microemulsion | <p>-They are categorized as :</p> <p>(i) water-in-oil (W/O) microemulsions (reverse micelle solutions),</p> <p>(ii) oil-in-water (O/W) microemulsions where oil is dispersed in water.</p> <p>-In microemulsions, the aqueous or oil phase is dispersed as microdroplets (micelle) surrounded by a monolayer of surfactant or copolymer molecules.</p> | <p>-thermodynamically stable dispersion of immiscible liquid in the presence of emulsifier or surfactant</p> | 15, 94 136-139 |

2.5.3 Biphasic Transfer Technique

Phase transfer technique is a method of transferring the metal salt or formed nanoparticles in aqueous solution into an organic solvent or *vice versa*^{66, 140}. The transfer of the already formed nanoparticles from aqueous into organic solvent is common as compared to those of organic to aqueous phase. The main reasons to employ phase transfer technique in the synthesis of nanoparticles are most probably due to the solubility of metal precursor and stabilizer in the respective phase,

particle dispersion, shape control, separation of residues of reductants and final product, and/or itself is needed for certain application.

Numerous phase transfer agents are used to transfer the nanoparticles, such as alkanethiol, oleic acid¹⁴¹, fatty amine^{37, 88, 99, 142}, cyclodextrin^{86, 143, 144}, ionic liquid^{145, 146}, multi-dentate amphiphilic¹⁴⁷, CTAB¹⁰² and TOAB^{60, 64, 148}. The phase transfer of nanoparticles occurs either via cation-anion electrostatic interactions, covalent interaction or host-guest inclusion. For example, TOAB^{64, 140} or CTAB¹⁴⁹ electrostatically adsorbed onto the negatively charged surface of the nanoparticles that induce the phase transfer process⁶⁶. On the other hand, the surfactant hexadecylamine (HDA) phase transfer the citrate-stabilized Au nanoparticles via covalent interaction⁸⁷ while Shameli et al.¹⁵⁰ reported that the Ag nanoparticles are transferred into the organic phase due to the presence of Van der Waals interactions between the hydroxyl group of the PLA and partially charged Ag nanoparticle. Schematic representation of phase transfer of Au particles is shown in Figure 2.8⁸⁷.

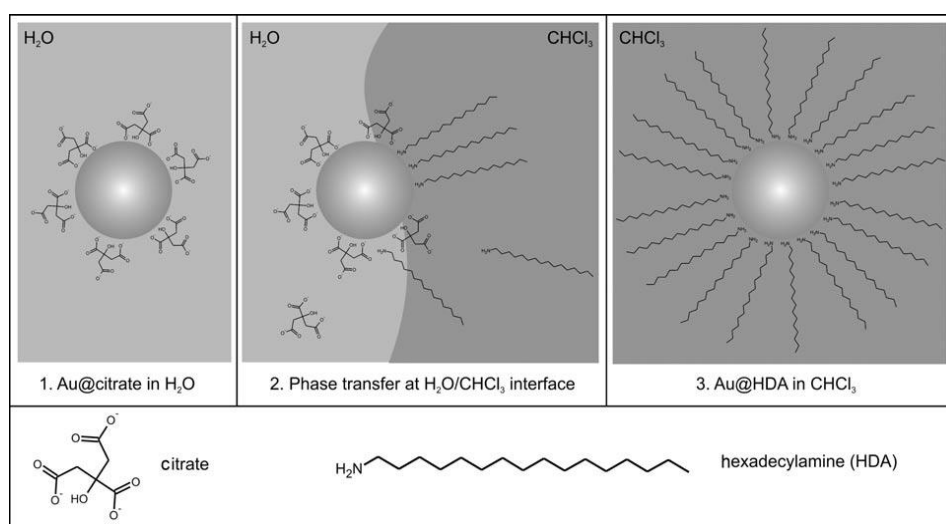


Figure 2.8: Schematic representative of phase transfer of Au nanoparticles from water into chloroform⁸⁷.

2.6 Silver Nanoparticles

Silver (Ag) compounds and ions are well known catalysts for the oxidation of methanol and ethylene, as well as extensively used for both hygienic and healing purposes. Nano-sized Ag particles exhibit remarkably unique physiochemical and biological properties or activities as compared to their bulk parent materials. For example, the bulk Ag is chemically inert but the Ag nanoparticles have shown high chemical reactivity toward hydrochloric acid¹⁵¹.

Numerous works have been done to synthesize and manipulate Ag nanoparticles with desired shapes and sizes that aimed for certain potential application. Chemical reduction is the most frequently used method as compared to microwave heating, solvothermal, reverse micelle, and others^{95, 152, 153}. According to the report of Tolaymat et al.⁹⁵, NaBH₄ and citrate are the most common reducing agents used in the synthesis of Ag nanoparticles, whereas citrate, PVP and CTAB are the common stabilizing agents/template. Recently, polymer has become significant as stabilizing agents in the synthesis of Ag nanoparticles. The polymers not only able to stabilize the Ag nanoparticles from growth and agglomeration, but it also can easily produce an Ag/polymer nanocomposite upon drying. Recently, Sharma et al.¹⁵³ reported on the polymer-silver nanoparticles based on the environmental perspective and green synthesis of Ag nanoparticles.

2.6.1 Applications of Ag Nanoparticles

Ag nanoparticles have found applications in catalysis, optics, electronics and other areas due to their unique size-dependent optical, electrical and magnetic properties. Currently most of the applications of Ag nanoparticles are in antibacterial agents in biotechnology and bioengineering, textile engineering, water treatment, and Ag-based consumer products. The summary of applications of Ag nanoparticles as tabulated in Table 2.5.

Table 2.5: The applications of Ag nanoparticles.

| Application | | Ref. |
|--|---|----------------------|
| Chemical Reactivity | Ag nanoparticles have been found with high chemical reactivity in the reaction with HCl. $2\text{Ag (nanoparticles)} + 2\text{HCl} \rightarrow 2\text{AgCl} + \text{H}_2$ | 151 |
| Catalysis | -Ag/SiO ₂ core/shell nanoparticles show high photocatalytic degradation on methyl orange through the reduction of electron-hole recombination. -starch-stabilized Ag nanoparticles exhibit a catalytic activity for the reduction of hydrogen peroxide (H ₂ O ₂). | 154,155 |
| Sensor | -starch-stabilized Ag nanoparticles and PVA-capped Ag nanoparticles are used as localized surface plasmon resonance (LSPR)-based biosensor for hydrogen peroxide (H ₂ O ₂). -Ag nanoparticles/Nafion film composite material modified glassy carbon electrode was used as a kind of superior electrochemical sensor for chromium (VI) -Ag nanoparticles electrodeposited on the surface of poly(3-(3-pyridyl)acrylic acid)/carbon nanotubes film for use as a DNA biosensor. | 6, 154, 156, 157 |
| Electronic device | -the electrical conductivity of the polyaniline-Ag nanocomposites is increased by the presence of Ag nanoparticles. -hybrid poly(ethylene terephthalate) films containing Ag nanoparticles act as Ohmic conductor by showing a linear relationship established between current and voltage in the high-conductivity direction at low amplitudes. -epoxy composites showed the conductive networks formed or exhibit the excellent electrical and flexural properties by adding Ag nanoparticles | 120, 158, 159 |
| Antimicrobial agent | -The Ag nanoparticles or Ag containing polymer nanocomposites act as inhibitor to the growth of bacteria. -Ag nanocomposites are used as antimicrobial film for food packaging and are employed in washing machine Samsung, wall paint and textiles manufacturing as antimicrobial agent. | 9, 37, 153, 160, 161 |
| Surface-enhanced Raman Scattering (SERS) substrate | -protein-A modified Ag nanoparticles binding by <i>E. coli</i> produced superior molecular selectivity SERS spectra of bacterial. | 162 |
| Waste water treatment | -Ag nanoparticles were performed as an adsorbent with high removal ability of mercury ion (Hg ²⁺) in contaminated water at room temperature. -Ag nanoparticles embedded in poly(ethylene glycol methacrylate phosphate) was successfully applied for the selective preconcentration of uranium from the uranium extraction process waste stream | 101, 163, 164 |

2.7 Silver Sulfide Nanoparticles

Ag₂S is a direct, narrow band-gap semiconductor with good chemical stability and excellent optical limiting properties. The optical limiting response of Ag₂S toward nanosecond laser pulse at 532 nm are much stronger than that of

fullerene^{75, 165}. Until now, several methods have been suggested to synthesize nano-sized silver sulfide in different matrix, surfactant or template and even without any support. The study on the synthesis and characterization of Ag₂S nanoparticles is not as intense as Ag nanoparticles, but it is gaining the attention of researchers in recent years. This is most probably due to the availability of the various shape- and size-controlled syntheses of Ag₂S nanoparticles¹⁶⁶. Ag₂S nanoparticles could be produced as nanorods^{167, 168}, nanowires¹⁶⁹, nanocubes^{170, 171}, and even in faceted⁷⁵ structure. Recently, the hollow nanostructured materials including Ag₂S nanoparticles are an interesting field of nanomaterials^{77, 170, 172}. In fact, the hollow nanostructured metal sulfide nanoparticles including Ag₂S, are expected to have superior properties because of their anisotropic behavior, large surface area and low material density^{133, 173}.

A 3 nm sized Ag₂S nanocrystals with nonlinear refraction properties have been reported to act as a low power optical limiter¹⁷⁴. Shukla and co-worker¹⁷⁵ have reported the deposited Ag₂S nanoparticles on a graphite rod caused the high response function of the ion-selective electrode to detect Ag⁺ ions in solution. Wang and Qi¹⁰³ reported an electronic device built with Ag₂S and Ag nanofiber bundles. The observed switching behavior resulting from Ag⁺/Ag redox and Ag⁺ ion diffusion revealed the potential application of the synthesized Ag₂S nanofiber bundles in the memory device¹⁰³.

2.7.1 Synthesis and Characterization of Silver Sulfide Nanoparticles

In general, the synthesis of Ag₂S nanoparticles is the reaction between Ag⁺ and S²⁻ ions. A simple AgNO₃ salt is used as silver precursor and various inorganic sulfides are used as sulfur source such as thiourea (TU), thioacetamide (TAA), ammonium sulfide, hydrogen sulfide and carbon disulfide. Typically, the synthesis is carried out in aqueous solution of alkaline or acid condition. The preparation method,

experimental condition and morphology of some synthesized Ag₂S nanoparticles are tabulated in Table 2.6.

Table 2.6: Summary of preparation methods of Ag₂S nanoparticles.

| Method | Reactants | Stabilizing agent | Temperature (°C) | Morphology | Ref. |
|------------------------|---|-------------------------------|------------------|--|----------|
| Reverse micelle (W/O) | Ag(AOT), Na ₂ S, | 1-dodecanethiol | Room Temperature | Self organized particle in 2D and 3D superlattices | 176, 177 |
| Simple Precipitation | AgNO ₃ , (NH ₄) ₂ S | Surfactants (Triton-X 100) | Room Temperature | Ellipsoidal and spherical | 178 |
| | AgNO ₃ , sulfur powder | PVP | Room Temperature | Hexagonal in shape | 79 |
| | AgNO ₃ , NH ₃ .H ₂ O | TAA, Surfactant (SUDEI) | Room Temperature | Well-dispersed polycrystal | 179 |
| Solution-growth | AgNO ₃ , NaOH, TU, | - | Room Temperature | Nanorod array | 167 |
| Disproportion reaction | AgNO ₃ , CS ₂ , | PVP | Room Temperature | Flake or star- shape | 180 |
| microwave | AgNO ₃ , thioglycolic acid | - | - | nanowire | 181 |
| Reflux | AgNO ₃ , TAA | Carboxymethyl Cellulose | 80 | Hollow and concave nanocubes | 170 |
| Hydrothermal | AgNO ₃ , thiocyanate | Potassium oleate | 180 | Nanorod and nanotube | 168 |
| | AgNO ₃ , TU | CTAB | 160 | Faceted, cubic, sphere-like | 75 |
| | (NH ₂) ₂ CS, | Sodium oleate, hexadecylamine | 180 | Well-dispersed, sphere-like | 182 |
| Heating | AgNO ₃ , Na ₂ SO ₃ | CTAB | 45 | Rhombic hollow | 77 |
| | Ag(SCOPh) | - | 80, 100, 120 | Cube, faceted, network-like | 171 |

2.8 Silver/Polymer Nanocomposites

Ag/polymer nanocomposite comprised of Ag nanoparticles incorporated into a polymer. In the past decade, synthetic polymers have been widely used due to its protective ability and/or the special property. For instance, epoxy with its excellent adhesion property is applied as the binder in electrical conductive adhesives