

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Nanoparticles

Nanoparticles are defined as particles with diameters of about 100 nm or less. The technological significance of nanoparticles is that they can be used to fabricate, coating, and devices that have novel and useful properties due to the very small dimensions of their particulate constituents (Higgins and Goldsmith, 1999). Nanoparticles have been attracting extensive attention because of their unique and often improved mechanical, electrical, optical, and chemical properties as compared with conventional polycrystalline materials (Wu *et al.*, 1999).

There are several techniques for synthesizing nanoparticles, such as bulk precipitation, sol-gel processing, spray-drying, freeze-drying, hot-spraying, evaporation-condensation, matrix isolation, laser-induced vapor phase reactions, laser vaporization, vacuum synthesis technique for sputtering, hydrolysis, hydrothermal, and microemulsions (or reverse micelles).

Nanostructured powders have been synthesized by chemical methods in an aqueous solution. A typical procedure involves three sequential steps:

- (1) the preparation of a starting aqueous solution of mixed metal salts,
- (2) the reductive decomposition of the starting solution to obtain a colloidal suspension of the desired end-product phase, and
- (3) the separation of the end product powder by repeatedly washing and drying. The resulting dried powder products are in the form of loosely agglomerated nanoparticles (Xiao *et al.*, 2000).

These procedures have been developed to use in microemulsion technique by using the microemulsion as the microreactor. This makes it easier to control the growth of nanoparticle size and to prevent aggregation. The physical and chemical properties of nanoparticles depend on the shape and particle size of the particles.

Xiao *et al.* (2000) describes the quality of nanoparticles in many applications. In industrial coating applications, reduction to nanoscale is highly effective in increasing thermal impedance. For dense chemical coatings, nanostructured materials have the potential to provide high hardness combined with good fracture toughness and corrosion resistance. In catalytic applications (including pollution control such as nuclear waste mitigation, water purification, and air filtration) a high contact area for the oxidation and reduction with the surrounding environment is important; and thus the reduction of catalytic materials to nanoscale is clearly a distinct advantage. Nanostructured materials with high percolation rates are well suited for this application. In rechargeable batteries and fuel cells, the high surface area of the nanostructured materials promotes rapid interactions of active material with surrounding media.

In fuel cell applications, current fuel cells use expensive noble alloys, for example, platinum in a phosphoric acid cell, and platinum-ruthenium in a direct methanol cells. Using nanostructured fiber-containing manganese dioxide this innovative approach boost the power density of the fuel cells as well as extending their life times. In solid-state fuel cell application, the high-density active sites in nanostructured materials are utilized in the form of a nanoporous zirconia thin film fuel cell. This type of fuel cell is favorably regarded to provide state-of-the-art high temperature solid-state fuel cells.

In rechargeable battery applications, nanostructured fibrous lithium-doped manganese dioxide is ideal for use in this area due to the fact that the lithium cations can diffuse into and out of the molecular cages in the manganese dioxide defect structure. In general, such nanofibrous structures also make excellent cation-exchange materials. Moreover, with surface areas of greater than about 250 m²/g, they are outstanding catalytic materials for oxidative reactions, and excellent ionic/electronic conductors for high-energy storage batteries. This type of material also has applications in zinc-air battery systems.

The properties of final nanoparticles, such as size and shape, surface area, morphology, optical properties and any physical property can be investigated by various techniques including x-ray diffraction (XRD) which is used to study the

phase of the calcined powder and to estimate the crystallite size of each phase (Pillani and Shah, 1996; Quinlan *et al.*, 2000; and Kim and Hahn, 2001).

Transmission electron microscopy (TEM) is used to study the primary size, shape, and morphology of calcined particles (Pillani and Shah, 1996; Quinlan *et al.*, 2000; Kim and Hahn, 2001; and Fu and Qutubuddin, 2001). Scanning electron microscopy (SEM) is used to analyze particle size and morphology. SEM connected to energy dispersive x-ray analysis (SEM-EDX) is used for semi-quantitative elemental analysis of TiO₂ coatings (Fu and Qutubuddin, 2001).

Small angle neutron scattering (SANS), small angle x-ray scattering (SAXS), and dynamic light scattering (DLS) and static light scattering, are used to characterize particle size and morphology in microemulsions and thereby to monitor the kinetics of particle growth (Quinlan *et al.*, 2000 and Fu and Qutubuddin, 2001).

UV-visible spectroscopy and photoluminescence are used to study optical properties and absorption spectra of nanoparticles solutions (Calandra *et al.*, 1999 and Quinlan *et al.*, 2000). Time-resolved luminescence quenching (TRLQ) is used to investigate droplet exchange rates (Lade *et al.*, 2000). Raman spectroscopy is used to determine the crystallinity and structure of nanoparticles (Zhou *et al.*, 2000).

X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectrophotometry (FTIR) are used to investigate the surface chemical composition and to examine the chemical structure of the particles (Zhou *et al.*, 2000 and Kim and Hahn, 2001). Vibrating sample magnetometer (VSM) is used for the magnetization measurements (Pillai and Shah, 1996). Thermogravimetry (TG) and differential scanning calorimetry (DSC) are used to examine the thermal behavior of the synthesized particles (Kim and Hahn, 2001).

2.2 Microemulsions

Microemulsion is defined as a thermodynamically stable, optically isotropic dispersion of two immiscible liquids stabilized by an interfacial film of surface-active molecules. Microemulsions are usually classified as either water-in-oil (w/o) or oil-in-water (o/w), depending on which is the dispersed phase. More generally, microemulsions of two non-aqueous liquids of differing polarity with negligible

mutual stability can also be prepared. In addition certain systems that contain comparable amounts of two immiscible fluids will have a bi-continuous structure. When a dispersed oil phase is present in an aqueous phase, it will consist of monodispersed droplets usually in the size range of 2 to 50 nm. These droplets are also known as micelles. In water-in-oil microemulsions, the aqueous droplets are also known as reverse micelles.

Reverse microemulsions are of special interest because a variety of reactants can be introduced into the nanometer-sized aqueous domains to get reactions confined within the reverse micelles, leading to materials with controlled size and shape (Zarur *et al.*, 2000). The droplet sizes are usually determined by the surfactants used for the microemulsions and are known to be very uniform. Because of its size uniformity, microemulsion is considered a lucrative way to synthesize nanosize particles with a narrow size distribution.

Microemulsions are used in various fields, such as pharmaceuticals, cosmetics, and chemical engineering. A new application of water-in-oil microemulsions is the synthesis of inorganic nanoparticles, which is a versatile way of producing them (Lade *et al.*, 2000). Microemulsions can be used as microreactors to carry out chemical reactions in confined geometries. Although progress in this field has been extremely important, much has yet to be done to understand the properties of monodisperse particle systems, and to obtain better control of the nanostructure of these materials (Tojo *et al.*, 1998).

As the physical properties of nanoparticle change by changing the particle size, these nanoparticles provide an enormous interest in chemistry and material sciences. Various types of nanoparticles can be obtained from reverse micelles such as in semiconductors (CdS, CdSe, TiO₂), metals (Pt, Pd, Fe), and magnets (Ni, FeNi). Moreover, interesting developments are the formation of mixed materials, nonstoichiometric compounds, and superconductors.

2.3 Nanoparticles Synthesis from Microemulsions

Boutonet *et al.* first used the microemulsion synthesis technique for ultra-fine catalyst production in 1982. They obtained monodispersed metal particles (in

size range 3-5 nm) of Pt, Pd, Rh, and Ir by reducing the corresponding salts in water pools of water-in-oil microemulsions with hydrazine or hydrogen gas. Compounds that have been produced successfully with these techniques include rare metal catalysts (Pt, Pd, Rh, and Ir), carbonates (including calcium carbonate, an important motor oil additive), silver halides, and magnetic oxides (Fe_2O_3 , barium ferrite), zinc oxide, and multi-cation high-temperature superconductors (Y-Ba-Cu-O and Bi-Pb-Sr-Ca-Cu-O systems)

Higgins and Goldsmith (1999) described many advantages of the microemulsion synthesis technique in comparison to alternative methods for the formation of nanoparticles.

- (1) It utilizes inexpensive and common reactants (water-soluble salts).
- (2) For production of liquid-dispersed nanoparticulate products, only simple and inexpensive hardware is required.
- (3) It is a generic method for the precipitation of nanoparticles of any type, including metals, oxides, borides, and semiconductors. It is also readily available for the production of coated nanoparticles.
- (4) It allows for a very high degree of control over the chemical and physical characteristics and homogeneity of the particles. Very narrow-sized-distribution powders are prepared and their average size can be readily tailored. For multi-cationic compositions in particular, the microemulsion process allows a degree of control of chemical homogeneity that is not attainable in nearly all other nanoparticle synthesis methods.

The use of microemulsions as nano-reactors for ultra-fine particle formation by dissolving a water-soluble reactant in a w/o microemulsion and allowing it to reach equilibrium distribution in each micelle. After this, there are two general methods used to form nanoparticles within the aqueous micelles (Li and Park, 1999):

- (1) single microemulsions method and
- (2) double or multiple microemulsions method.

The first is a single microemulsion method, in which nanoparticles are produced in a microemulsion by adding a reducing or precipitating agent in the form of gas or liquid, to a microemulsion containing the primary reactant dissolved in its

aqueous droplets as show in Figure 2.1. The particles produced by this type of process could be much larger than the original droplet size. One of the precipitations involves the subsequent addition of a reducing agent (e.g., hydrazine or hydrogen) to the microemulsion while the other involves addition of a precipitating agent (e.g., O₂, CO₂, and NH₃). The nanoparticles are formed by chemical reduction in a microemulsion with a non-continuous phase containing a reducible salt of a metal. The metal salt may be selected from the group containing platinum, iridium, gold, silver, palladium, rhodium, ruthenium, osmium, rhenium, copper, nickel, cobalt, iron, neodymium, and boron as well as combinations of the above metals.

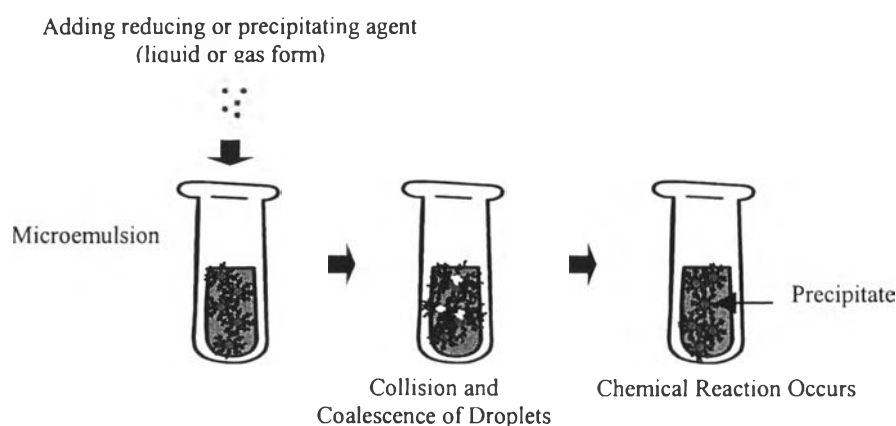


Figure 2.1 Single microemulsion technique (Li and Park, 1999).

The second is the double or multiple microemulsion type, in which two or more w/o microemulsions, each containing respective reactants are mixed together. The droplets of the mixed microemulsion that go through numerous collisions and thereby the reactants are mixed and ready to form solid particles or nanosized precipitates as a product of the chemical reaction as show in Figure 2.2. Experimental data indicate that the particles formed by this type are generally smaller than the original droplets.

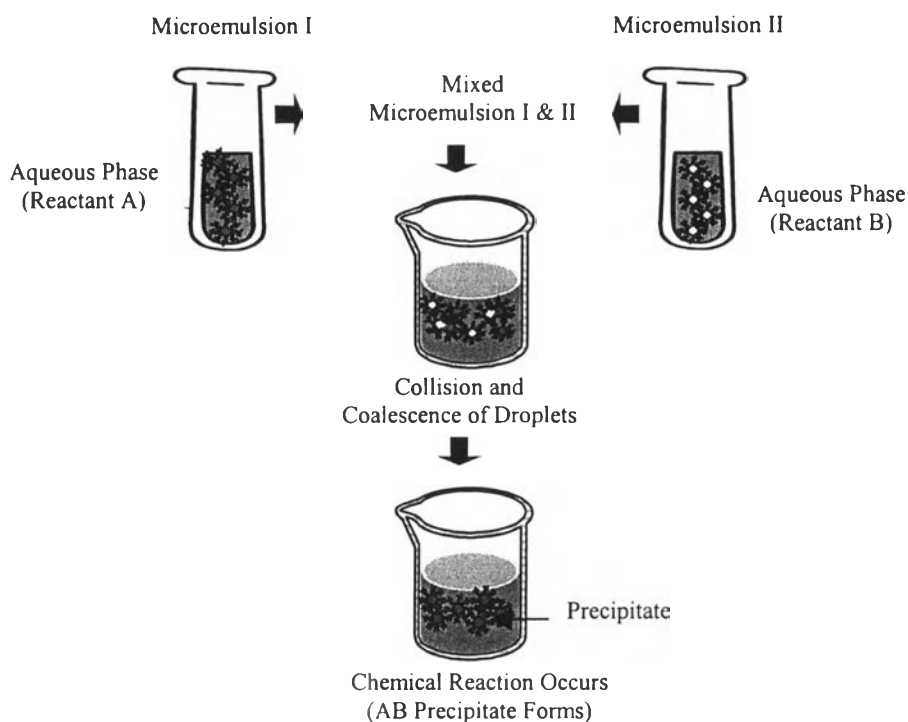


Figure 2.2 Double or multiple microemulsions technique (Li and Park, 1999).

This precipitate is confined to the interior of the microemulsion droplets and the shape of the particle formed reflects the interior of the droplet. In this process, the overall reaction rate will be controlled by the rate of coalescence of the droplets if the intrinsic chemical reaction rate is fast.

Because of this, properties of the microemulsion interface such as interfacial rigidity, as determined by specific surfactant chemistry, can strongly influence the measured reaction rates. Relatively rigid interfaces decrease the rates of droplet coalescence and overall reaction while substantially fluid interfaces enhance these rates. The properties of the continuous oil phase and ionic strength and pH of the aqueous phase can also be manipulated to control reaction kinetics. Therefore, this reaction method provides a great degree of control over the nanoparticle formation process.

Chemical precipitation arising from mixing a first microemulsion having a non-continuous micellar phase containing a dissolved metallic salt and a second microemulsion having a non-continuous micellar phase containing a dissolved

precipitating agent or reactant forms the nanoparticles. The dissolved metallic salt may be selected from the group containing metallic salts of zinc, titanium, aluminum, iron, chromium, yttrium, copper, tin, calcium, silicon, cerium, magnesium, vanadium, cobalt, nickel, strontium, zirconium, cadmium, barium, lithium, lead, bismuth, silver, manganese, antimony, and lanthanum, and mixtures thereof. The dissolved precipitating agent or reactant may be selected from the groups containing soluble hydroxides, carbonates, mineral acids, organic acids, sulfides, halides, borohydrides, and chalcogenides, and combinations thereof.

The second method has been used for the production of metallic particles, while the first method has been employed for the formation of nanoparticle oxides, oxide precursors and carbonates.

The precipitated nanoparticles are further processed (by rinsing, drying, calcinating and/or annealing) to yield a final dry product with desired chemical composition. The calcination is operated at high temperature for the complete removal of water and any impurity that can cause breaking in pores or structure of nanoparticle. Therefore, Soxhlet extraction technique can be applied to remove impurities at lower temperature conditions. Such compositions would include a crystalline, thermally stable method suitable for a wide range of technological uses. To concentrate the nanoparticles for recovery, the semipermeable membrane employed for ultrafiltration is a ceramic membrane. The ceramic membrane may be composed of materials selected from the group containing alumina, zirconia, titania, silica, or other ceramic oxides, single or in combination.

The synthesis of nanoparticles in microemulsions is only performed on a laboratory scale. Since nanotechnology is regarded as a major future technology, methods for scaling-up nanoparticle synthesis are required. For not only a successful particle design but also for a scale-up we need detailed knowledge of the particle formation mechanism. To date there are only a few qualitative ideas about this mechanism. It is commonly accepted that the droplet size and the droplet exchange rate are important parameters, which determine the properties of the produced particles (Lade *et al.*, 2000).

2.4 Particles Design and Method of Control

The microemulsions technique has the ability to control the size and form of the particle. In preparation technique, there are several factors or parameters that influence the nanoparticle size. They are operating conditions (reaction temperature and time, calcination temperature and time) and intermicellar exchange rate. The intermicellar exchange rate changes by changing the organic solvent, organic additive, surfactant, and water content (molar ratio of water to surfactant). The effect of adding another substance into microemulsions is apparent, such as adding a cationic to a nonionic surfactant to form a mixed surfactant, and adding a substance to coat metallic nanoparticle to improve magnetic property. The most useful parameter for the study of the effect on particle size is water content, which causes a change in nanoreactor size and can be used to control the growth of nanoparticle inside the nanoreactor.

Lisiecki *et al.* (1995) synthesized copper nanoparticles in reverse micelles containing water/AOT/isooctane and using hydrazine as the reducing agent. They controlled the particle size by varying the water content of anionic reverse micelles AOT. They also found that in the presence of CTAC cationic surfactant, depending on the concentration, the size of particles is strongly affected. A decrease in size is observed at higher CTAC concentration because a random distribution of the positively charged surfactant takes place and the decrease in the size could be due to a decrease in the intermicellar attraction.

Calandra *et al.* (1999) controlled the particle size by using the same water content parameter as that of Lisiecki *et al.* (1995). They studied the growth of ZnS nanoparticles in water/AOT/n-heptane microemulsion and did the characterization by UV-VIS spectroscopy. They found that the water content was the suitable external parameter to control the nanoparticle size.

Later, in 2000, Bagwe and Khilar studied the effect of many parameters that were important for the use of microemulsions. They reported the effects of the intermicellar exchange rate on the absorption spectra and particle size of silver nanoparticles synthesized in reverse micelles of AOT. The silver nanoparticles were prepared by mixing two microemulsions, one containing silver nitrate and the other

containing sodium borohydride. The intermicellar exchange rate was varied by changing the organic solvent (decane, heptane, cyclohexane), surfactant (SDS anionic, NP-5 nonionic, and DTAB cationic), and organic additive (benzyl alcohol and toluene). The higher intermicellar exchange rate resulted in smaller particle size. An interesting and potentially useful effect observed is that the addition of a small amount of a nonionic surfactant significantly reduced the particle size. When varying the organic solvent, the smallest particle size was found when using cyclohexane and the highest when using heptane because an increase in the chain length of the oil resulted in an increase in the value of intermicellar exchange rate. The addition of organic additive both benzyl alcohol and toluene resulted in a decrease in particle size by decreasing the growth rate. The addition of DTAB and SDS did not bring about any change in particle size but adding NP-5 decreased the particle size with corresponding increase in the number of particles formed.

Lade *et al.* (2000) presented well-characterized Marlipal nonionic surfactant/water/cyclohexane microemulsions as a suitable reaction media for the synthesis of nanoparticles. They determined the phase behavior, the viscosity, the droplet size, and the interdroplet exchange rates. The retardation caused a particle growth, which was not accompanied by aggregation of nuclei. Therefore, a higher number of nuclei were maintained during the precipitation that grew to smaller sizes when compared to using the precipitation in a homogeneous solution. The application of a microemulsion as the precipitation medium yielded much smaller particles than those obtained from homogeneous solutions.

The research that used the other parameter to control particle growth was done by Debuigne *et al.* (2000). They synthesized organic nanoparticles of cholesterol, rhovanil, and rhodiarome used a different microemulsion (AOT/heptane/water and Triton/decanol/water) with direct precipitation of the active compound in an aqueous core under continuous ultrasound treatment. Different solvents were used to solubilize the organic molecule, but the average diameter of the particles did not change. The solvents were considered as a carrier vector for organic molecules and did not influence the precipitation in a significant way. They discussed the influence of the concentration of the organic compound (number of particle per aqueous core), the equipment used for stirring the solutions (magnetic

stirring and ultrasonication), volume of solution, the addition of the organic compound, the time after injection organic solution, and the comparison with the mixture of two microemulsion techniques.

2.5 Titanium Dioxide Nanoparticles

Titanium dioxide occurs in nature in three crystalline forms: anatase, brookite, and rutile. The two most important are anatase and rutile. Rutile is more stable than anatase and the transformation of anatase to rutile is exothermic. The rate of transformation was critically dependent on the detailed environment and may be either promoted or retarded by the presence of other substances. Titanium dioxide is used as a ceramic sensor for oxygen in automotive exhaust systems, inorganic sun block, and catalysts or catalyst supports (selective oxidation catalyst). It is also used in photocatalytic degradation of pollutants to remove trace amounts of pesticide residues from water.

There are several studies in the synthesis of titanium dioxide or titania nanoparticle. In 1995, Zang *et al.* prepared TiO_2 in AOT-isooctane reverse micelles. Three dyes, eosin (EO), methyl thionine (MT), and rhodamine B (RB), with different net charges were chosen as probes solubilizing in the water phase to investigate the interaction with TiO_2 and AOT. It was found from the spectra characteristics of dyes that the three molecules were located at different places in reverse micelles. The different locations of dyes resulted in different efficiencies of photoinduced interfacial electron transfer from dyes to TiO_2 particles. They prepared TiO_2 by using simple injection technique, by rapidly adding cooled TiCl_4 into AOT/isooctane micellar solution with constant water content ratio. The colloid TiO_2 was prepared from the hydrolysis reaction of TiCl_4 .

François and Ginzberg (1998) synthesized titania particles and gels in reverse micelles with either anionic (AOT) or nonionic (Triton X-100) surfactants in alkanes with low water contents. Acids (HClO_4 , HNO_3 , and HCl) were, in some cases, dissolved in the aqueous phase. Titania gels were prepared by mixing reverse micelles formed by water, surfactant and organic solvent (cyclohexane and isooctane) with the solution of titanium butoxide diluted in organic solvent. They

controlled the kinetics by changing microemulsion parameters. They reported that the gelation time was longer in Triton X-100 than in AOT. The increasing in acidity yielded a decrease in rate of hydrolysis.

Stathatos *et al.* (1999) made titanium dioxide mesoporous films by dip coating in reverse micellar gels containing titanium isopropoxide. Reverse micelles were first made in cyclohexane and alkoxide was added last. Hydrolysis and inorganic polymerization produced composite organic/inorganic gels that were deposited on glass slides and gave uniform transparent films. Calcination yielded TiO₂ nanoparticle mesoporous films. Retaining water by hydration of the surfactant resulted in slow hydrolysis rates. The differences between films made by varying water content parameters were discussed.

The microemulsion mediated hydrothermal (MMH) method for synthesizing titania nanoparticles of rutile and anatase was presented by Wu *et al.* (1999). This method led to the formation of titania under much milder reaction conditions (calcination is not necessary). A solution formed by dissolving tetrabutyl titanate into HCl or HNO₃ hydrolysis inhibitor the aqueous core of water/Triton X-100/hexanol/cyclohexane microemulsions was used. The effect of changing variables of reaction conditions (type of acid used, concentration of acid, reaction temperature, and reaction time) on phase and morphology of titania are described. HCl was more favorable for the formation of rutile phase than HNO₃, and the formation of rutile phase favored the higher concentration of HCl. [HCl] higher than 1 M resulted in pure rutile phase and had needle morphology, [HCl] less than 1 M or [HNO₃] higher than 0.5 M resulted in a mixed phase of rutile and anatase, and [HNO₃] of 0.5 M resulted in pure anatase with spherular structure. The reaction temperature plays an important role in phase formation the fractions of rutile phase increasing with higher reaction temperature.

Kim and Hahn (2001) prepared titania particles by reacting TiOCl₂ with NH₄OH in water/Triton X-100/n-hexanol/cyclohexane microemulsions. The as-prepared particles were amorphous, but transformed into the anatase phase at 460°C, and further into the rutile phase at 850°C. With increasing calcination temperature, the specific surface area of particles decreased rapidly while the average pore radius

increased. The anatase phase formed at 500-700°C showed considerable photoactivity for degradation of phenol whereas both the amorphous phase at 300°C and the rutile phase at 900°C were inactive for this reaction. The anatase-rutile transformation temperature decreased as concentration of titanium solution reactant increased.