

LITERATURE REVIEW

1. Cerium oxide

Cerium is an element of rare earth group which is called lanthanide series. It is found in the ores like monazite and xenotime which are the tailings of tin mines in the south of Thailand. Cerium compound exist in many forms, such as cerium nitrate, cerium chloride, cerium oxide and cerium sulfide. Among these compounds cerium oxide or ceria is the most widely used in many industries. In addition, its applications are increasing rapidly.

1.1 Physical and chemical properties of cerium oxide

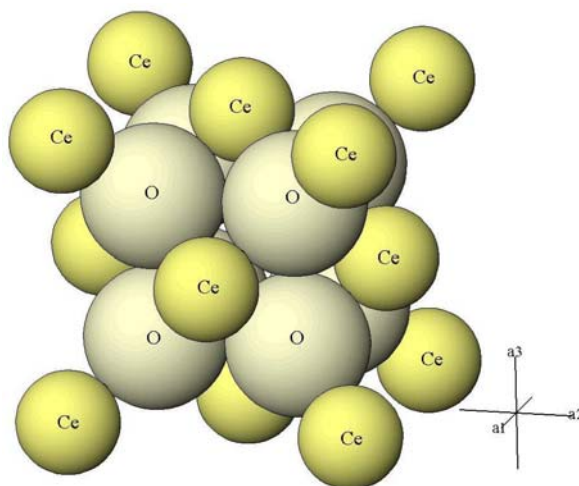
Cerium oxide has the formula of CeO_2 and the molecular weight of 172.12. The crystal structure of cerium oxide is shown in Figure 1 and the physical properties of CeO_2 are

Appearance	: Yellow powder
Melting point	: 2500°C
Specific gravity	: 7.3g/cm ³
Solubility	: Insoluble in water, moderately soluble in strong mineral acids.
Stability	: Slightly hygroscopic, will absorb small amount of moisture and CO_2 from the atmosphere.
Crystal structure	: Cubic, face centered

Table 1 Element analysis and oxidation number

Element	Amount (wt.%)	Formal oxidation state	Formal electronic configuration
Ce	81.14	4	[Xe]6s ² 4f ¹ 5d ¹
O	18.59	-2	[He]2s ² 2p ⁶

Source: Winter (2005)

**Figure 1** Crystal structure of cerium oxide.

Source: Numura (2006)

1.2 The method to synthesize nano-sized CeO₂

To date there are many methodologies available for synthesizing CeO₂ nanoparticles such as:

1.2.1 Flux method (Bondioli *et al.*, 1999).

CeO₂ powders were prepared by the flux method by adding cerium ammonium nitrate to an eutectic mixture of molten salts, followed by washing and drying. To evaluate the effect of the molten salts on the powders, three different fluxes were used, KOH/NaOH, NaNO₃/KNO₃, and LiCl/KCl eutectic mixtures.

Results showed the presence, in the reaction products, of homogeneously sized and shaped particles of a single nanosized CeO_2 phase. The powder obtained with chlorides out of molten salts had the finer particle size distribution, with a very narrow dimensional range of 10-20 nm.

1.2.2 Microemulsion method (Zhang, 2001).

The microstructure development of CeO_2 nanocrystal prepared by the microemulsion process, the cationic surfactant (CTAB) was dissolved in cyclohexane and butanol. This solution was stirred then cerium nitrate solution and ammonia was added to the solution with vigorous stirring. After the two solutions were mixed a transparent CeO_2 microemulsion was formed. The CeO_2 nanocrystal with a diameter of 6-8 nm appeared.

1.2.3 Glycothermal process (Bae *et al.*, 2002).

The cerium oxide nano-sized particles were prepared under mild temperature and pressure conditions by precipitation from metal nitrates with aqueous potassium hydroxide. Various types of cerium oxide powders were obtained at 200–230°C. The average size of synthesized particles was in the range of 10–50 nm and the phase of the synthesized particles was crystalline.

1.2.4 Mechanochemical reaction (Li *et al.*, 2003).

The preparation of nano-sized CeO_2 powder by mechanochemical reaction of hydrate cerium carbonate with sodium hydroxide and subsequent heat treatment can be divided into two steps. The first step is the multi-phases mechanochemical reaction of cerium carbonate with sodium hydroxide to form amorphous cerium hydroxide. And the second step is the crystallization of $\text{Ce}(\text{OH})_4$ to form crystalline $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ under a quasi-hydrothermal synthesis condition caused by the mechanical ball-milling. The CeO_2 powder obtained from as-milled $\text{Ce}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O} + \text{NaOH}$ following water washing and heat treatment at 800°C appears clearly separated monodisperse nano-sized particles. Their crystal sizes are from 10 to 20 nm and the medium size aggregated particles is 0.21 μm .

1.2.5 Hydrothermal process (Lee, 2004).

Homogeneous and well-crystallized nano CeO_2 powders were produced by hydrothermal synthesis using a mixture of H_2O_2 as the oxidizer, NH_4OH as the mineralizer and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as starting materials. The precipitates were prepared by mixing ligands of $-\text{OH}$ and $-\text{OOH}$ derived from NH_4OH and H_2O_2 . The hydrothermal synthesis was conducted at 200°C . The particle sizes of CeO_2 ranging from 6 to 12 nm in diameter.

1.2.6 Homogeneous precipitation (Chen, 2004)

The CeO_2 nanoparticles were prepared via homogeneous precipitation technique starting from cerium nitrate solution. Firstly, cerium nitrate was dissolved in alcohol/water mixed solvent. Six alcohols were used, including methanol, ethanol, n-propanol, iso-propanol, tert-butanol and ethylene glycol. They were separately mixed with water as the solvents. The reaction was carried out at 50°C with vigorous stirring rate of 500 rpm, which began as ammonia was added. Finally, the precipitate was centrifuged and dried at 60°C overnight. The size of CeO_2 is about 15 nm.

1.3 The applications of CeO_2

CeO_2 is a useful material for chemical, catalysts, glasses and ceramics industries. It was used in many applications.

- Phototropic lens contains some CeO_2 particles. The lens has light color in shade but when exposed to light it turns to deep color.
- Glass polishing material, CeO_2 is used for scrubbing glass to prevent scratching.
- Cosmetic material, CeO_2 is used in cosmetic to protect ultraviolet.
- Catalyst, CeO_2 is used as a catalyst to decrease temperature in chemical reaction.
- Ultraviolet absorbent, CeO_2 is an important ingredient in a light sensitive glass bottle.

- Electrode materials, CeO_2 is used for solid oxide fuel cells (SOFCs).

2. Microemulsion method

Microemulsions are defined as mixtures of at least two immiscible liquids. Microemulsions are of two types, based on the nature of the dispersed phase: oil-in-water (O/W) and water-in-oil (W/O).

The O/W type is a dispersion of a water-immiscible liquid or solution, always called the oil (O), regardless of its nature, in an aqueous phase (W). The oil is in this case the “discontinuous” (inner) phase; the aqueous phase is the “continuous” (outer) phase as shown in Figure 2(a). The W/O type is a dispersion of water or an aqueous solution (W) in a water-immiscible liquid (O) as shown in Figure 2(b).

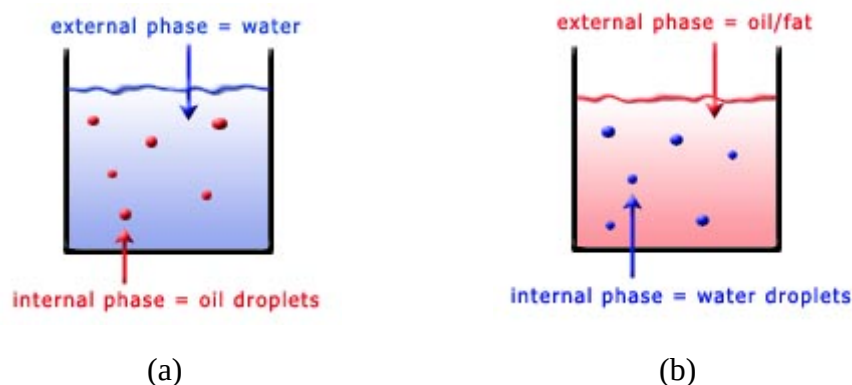


Figure 2 Diagram of microemulsion, (a) oil in water (O/W) (b) water in oil (W/O).

Source: Scaman (2005).

2.1 The formation mechanism of nano-sized particle

By adding an amount of surfactant into the mixed solution of organic solvent and aqueous solution, a uniform and transparent W/O microemulsion is formed. The metal ions take place inside the droplets. Since the water droplets contains the identical solution, located in the similar surroundings, the size of water droplets, the stability of water droplets itself and the particles formed in them are nearly same, the formation mechanism is shown in Figure 3.

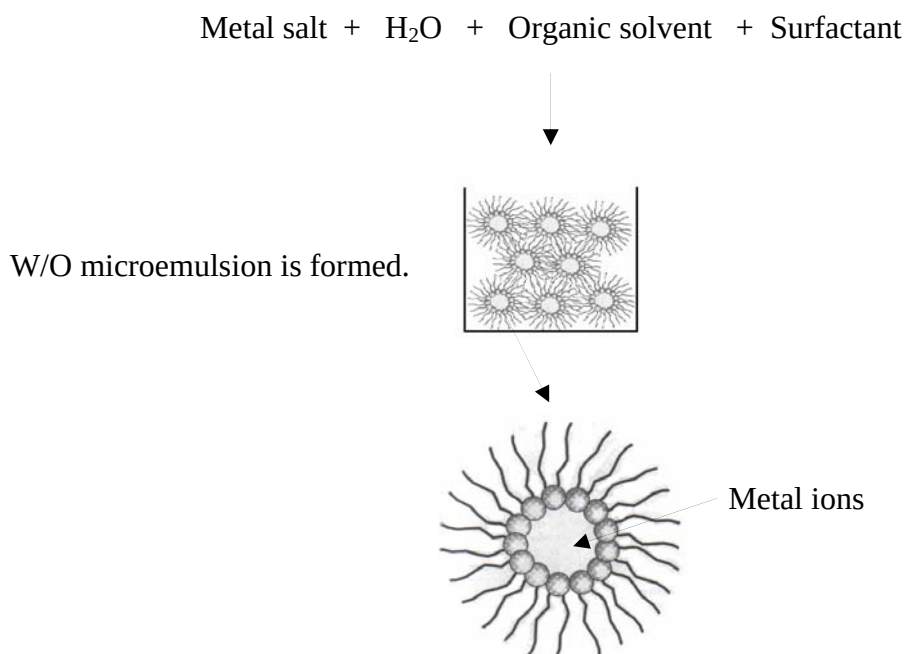


Figure 3 The formation mechanism of nano-sized metal particle obtained from microemulsion method.

2.2 Reaction in microemulsion

A microemulsion may be defined as a thermodynamically stable isotropic dispersion of two immiscible liquids consisting of microdomains of one or both liquids in the other, stabilized by an interfacial film of surfactant-active molecules. In water-in-oil microemulsion, the aqueous phase is dispersed as nano-size droplets (typically 5 to 25 nm in diameter) surrounded by a monolayer of surfactant molecules in the continuous hydrocarbon phase. These aqueous droplets continuously collide, coalesce, and break apart, resulting in a continuous exchange of solution content. The collision process depends on the diffusion of the aqueous droplets in the continuous medium (i.e., oil) and the exchange process depends on the attractive interactions between the surfactant tails and the rigidity of the interface, as the aqueous droplets approach close to each other (Pillai, 1997).

For reaction in water-in-oil microemulsions, reactant species are totally confined within the dispersed water droplets. A necessary step prior to their chemical

reaction is the exchange of reactants by the coalescence of two droplets. When chemical reaction is fast, the overall reaction rate is likely to be controlled by the rate of coalescence of droplets. Therefore, properties of the interface such as interfacial rigidity are of major importance. A relatively rigid interface decreases the rate of coalescence and hence leads to a low precipitation rate. On the other hand, a substantially fluid interfacial in the microemulsion enhances the rate of precipitation. Thus, by controlling the structure of the interface, one can change the reaction kinetics in microemulsions by an order of magnitude. It has been further shown that the structure of oil, the alcohol and the ionic strength of the aqueous phase can significantly influence the rigidity of the interface and the reaction kinetics.

Conceptually, if one takes two identical water-in-oil microemulsions and dissolves reactant A and B respectively in the aqueous phases of these two microemulsions, upon mixing, due to collision and coalescence of the droplets, reactant A and B come into contact with each other and form precipitate AB. This precipitate is confined in the interior of the microemulsion droplets. This is the main principle utilized in producing nanoparticles with microemulsions. Figure 3 shows a schematic representation of this process. However, nanoparticles can also be produced in microemulsions by adding a reducing or precipitating agent, in the form of a liquid or a gas, to a microemulsion containing the primary reactant dissolved in its aqueous core.

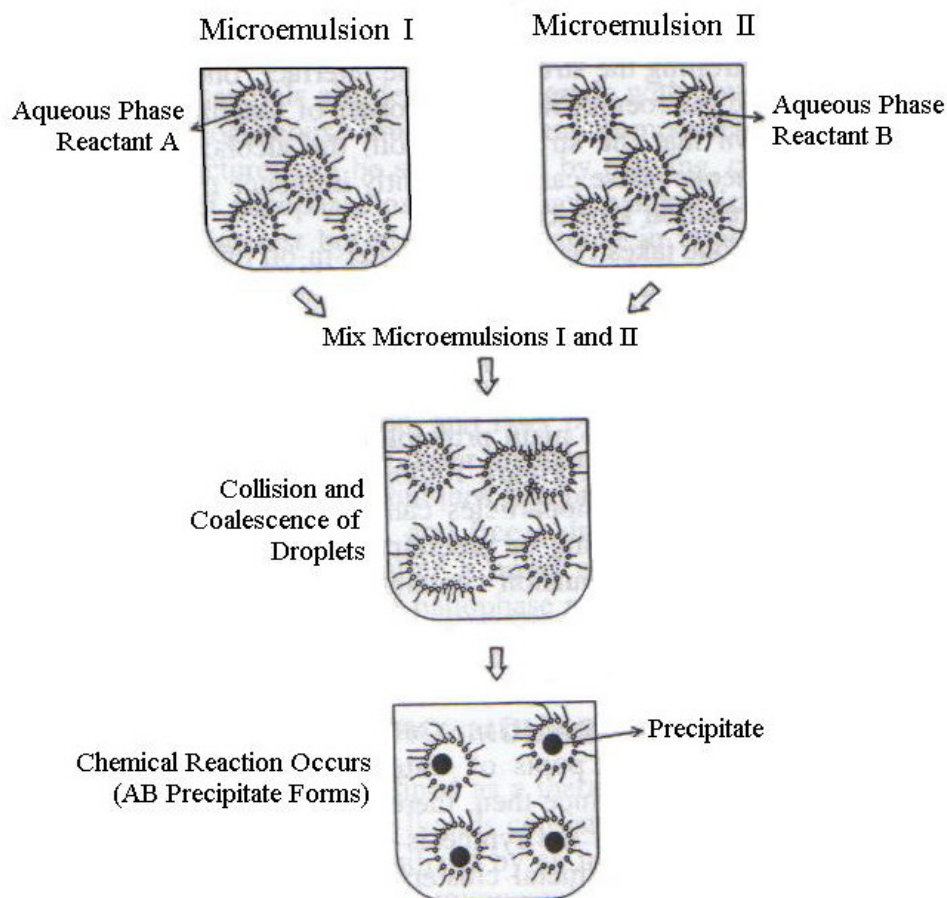


Figure 4 Schematic representation of synthesis of nanoparticles in microemulsion.
Source: Pillai (1997).

2.3 Microemulsion stability

During the formation of small dispersed droplets in a microemulsion, the interfacial area between the two liquids become enormously large. For example, when 1 ml of oil is dispersed as 1 mm diameter particles in water, 1.9×10^{12} droplet globules formed and the total interfacial area is 6 m^2 . The resulting heterogeneous system is therefore thermodynamically unstable. Surfactant is needed to stabilize the system through one of the following actions.

2.3.1 Interfacial tension

At the liquid interface, interfacial tension is the force required to reduce the actual contact between the two phases. Molecules in bulk phase are attracted to each other in all directions. The diagram of interfacial tension in a bulk phase is shown in Figure 5 (a). No net force is applying to any one particular molecule. However, at the boundary between phases, molecules are in contact with other molecules and experience unequal forces from the different phases. The diagram of interfacial tension at liquid/liquid interface is shown in Figure 5 (b). When a microemulsion is formed, the diagram is shown in Figure 5 (c), surface contact area increases, thus increases the total interfacial tension. As a result, molecules tend to migrate from the interface into the bulk phase and reduce the actual contact area between dissimilar molecules. And Figure 6 shows the diagram of addition surfactant to the liquid/liquid interface.

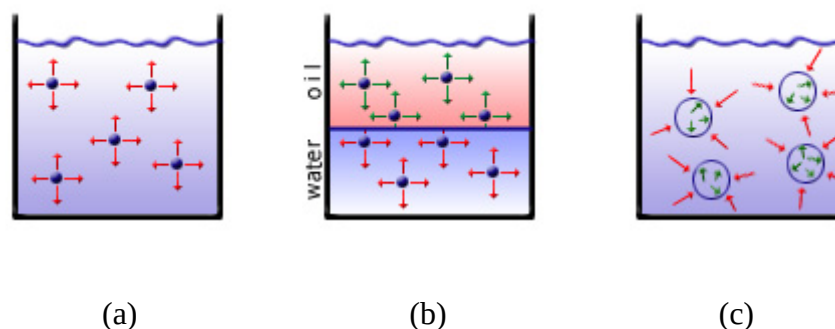


Figure 5 Diagram of interfacial tension, (a) in a bulk phase (b) at liquid/liquid interface and (c) when a microemulsion is formed.

Source: Scaman (2005).

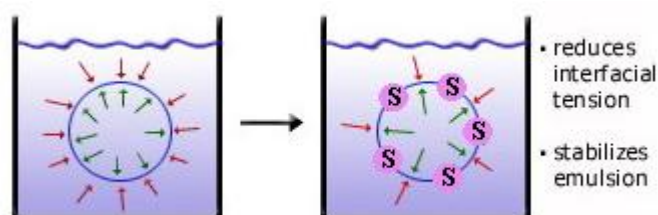


Figure 6 Addition of surfactant (S) to the liquid/liquid interface.

Source: Scaman (2005)

2.4 Microemulsion destabilization

Microemulsion system can be destabilized through one of the following mechanisms depending on the phase volume, droplet size, and the physical environment of the system (Scaman, 2005).

2.4.1 Creaming

The rate of creaming can be lowered by reducing the droplet size, lowering the density difference between oil and the aqueous phase, and increasing the viscosity of the medium, diagram of creaming is shown in Figure 7. In addition, the creaming rate is dependent on the volume fraction of the dispersed phase, and is usually slow in concentrated microemulsion.

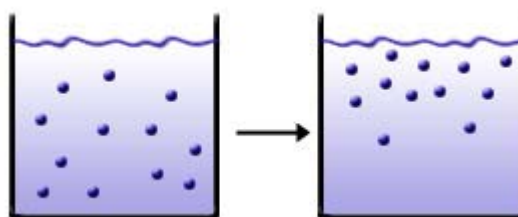


Figure 7 Diagram of creaming.

Source: Scaman (2005).

2.4.2 Flocculation

Flocculation is defined as a process by which two or more droplets aggregate without losing their individual identities, the diagram of flocculation is shown in Figure 8. Microemulsion droplets flocculate through interaction of the adsorbed macromolecules between droplets. Bridging flocculation is a very complex phenomenon and greatly depends on the size, type and amount of the macromolecules used in the system. In addition, rate of flocculation can be affected by the pH and ionic strength of the aqueous environment.

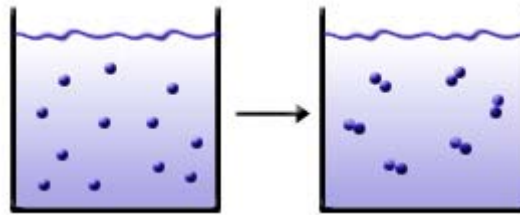


Figure 8 Diagram of flocculation.

Source: Scaman (2005).

2.4.3 Coalescence

Coalescence is the process when two or more droplets collide to each other and results in the formation of one larger droplet, the diagram of coalescence is shown in Figure 9. Coalescence involves breaking the interfacial film and is irreversible. At extreme, a planar interface exists between the homogeneous lipid phase and the homogeneous aqueous phase. Various factors, such as solubility of surfactant, pH, salts, surfactant concentration, phase-volume ratio, temperature and properties of the film, affect coalescence stability of microemulsion.

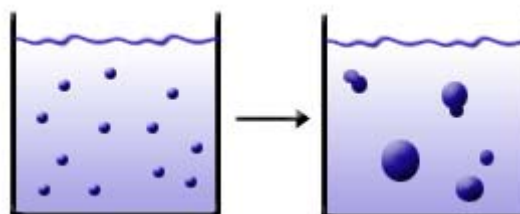


Figure 9 Diagram of coalescence.

Source: Scaman (2005).

2.4.4 Ostwald ripening

Ostwald ripening occurs in microemulsions with polydispersed droplets. Collisions between two droplets may lead to one bigger droplet and one smaller droplet, the diagram of Ostwald ripening is shown in Figure 10. As a result, small droplets become smaller. Eventually, the small droplets become very small and become solubilized in the continuous medium.

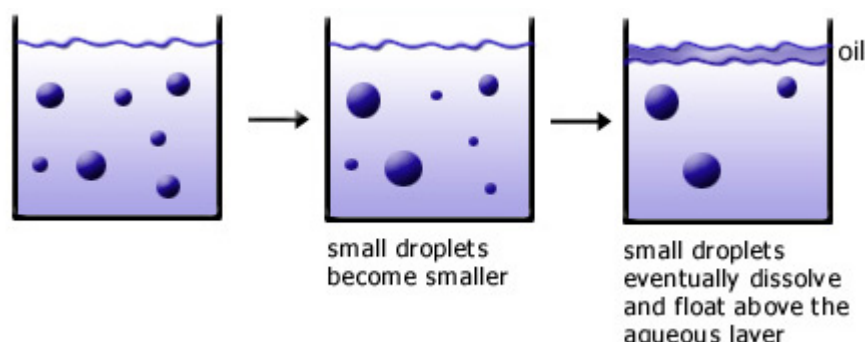


Figure 10 Diagram of Ostwald ripening.

Source: Scaman (2005).

2.5 General structural features and behavior of surfactant

The molecules at a surface have higher potential energies than those in the interior. This is because they interact more strongly with the molecules in the interior of the substance than they do with the widely spaced gas molecules above it. Work is therefore required to bring a molecule from the interior of the surface (Rosen, 2004).

Surfactants have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as a lyophobic group, together with a group that has strong attraction for the solvent, called the lyophilic group. This is known as an amphipathic structure. When a molecule with an amphipathic structure is dissolved in a solvent, the lyophobic group may distort the structure of the solvent, increasing the free energy of the system. When that occurs, the system responds in some fashion in order to minimize contact between the lyophobic group and the solvent. In the case of the surfactant dissolved in aqueous medium, the lyophobic (hydrophobic) group distorts the structure of the water (by breaking hydrogen between the water molecules and by structuring the water in the vicinity of the hydrophobic group). As a result of this distortion, some of the surfactant molecules are expelled to the interfaces of the system, with their hydrophobic groups oriented so as to minimize contact with the water molecules. The surface of the water becomes covered with a single layer of surfactant molecules with

their hydrophobic groups oriented predominantly toward the air. Since air molecules are essentially nonpolar in nature, as are they hydrophobic group, this decrease in the dissimilarity of the two phases contacting each other at the surface results in a decrease in the surface tension of the water. On the other hand, the presence of the lyophilic (hydrophilic) group prevents the surfactant from being expelled completely from the solvent as a separate phase, since that would require dehydration of the hydrophilic group. The amphipathic structure of the surfactant therefore causes not only concentration of the surfactant at the surface and reduction of the surface tension of the water, but also orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it.

The chemical structures of groupings suitable as the lyophobic and lyophilic portions of the surfactant molecule vary with the nature of the solvent and the conditions of use. In highly polar solvent such as water, the lyophobic group may be a hydrocarbon or fluorocarbon or siloxane chain of proper length, whereas in a less polar solvent only some of these may be suitable (e.g., fluorocarbon or siloxane chain in polypropylene glycol). In a polar solvent such as water, ionic or highly polar groups may act as lyophilic groups, whereas in a nonpolar solvent such as heptane they may act as lyophobic groups. As the temperature and use conditions (e.g., presence of electrolyte or organic additives) vary, modifications in the structure of the lyophobic and lyophilic groups may become necessary to maintain surface activity at a suitable level. Thus, for surface activity in a particular system the surfactant molecule must have a chemical structure that is amphipathic in that solvent under the conditions of use.

The hydrophobic group is usually a long-chain hydrocarbon residue, and less often a halogenated or oxygenated hydrocarbon or siloxane chain; the hydrophilic group is an ionic or highly polar group, depending on the nature of the hydrophilic group.

2.5.1 Classification of surfactant (Lange, 1999).

- Anionics surfactant.

The surface-active portion of the molecule bears a negative charge, for example, $RCOO^-Na^+$ (soap), $RC_6H_4SO_3^-Na^+$ (alkylbenzene).

- Cationic surfactant.

The surface-active portion of the molecule bears a positive charge, for example, $RNH_3^+Cl^-$ (salt of a long-chain amine), $RN(CH_3)_3^+Cl^-$ (quaternary ammonium chloride).

- Zwitterionic surfactant.

Both positive charge and negative charge may be present in the surface-active portion, for example, $RN^+H_2CH_2COO^-$ (long-chain amino acid), $RN^+(CH_3)_2CH_2CH_2SO_3^-$ (sulfobetaine).

- Nonionic surfactant.

The surface-active portion of the molecule bears no apparent ionic charge, for example, $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long-chain fatty acid), $RC_6H_4(OC_2H_4)_xOH$ (polyoxyethylenated alkylphenol), $R(OC_2H_4)_xOH$ (poly oxyethylenated alcohol).

2.5.2 General use of charge types.

Most natural surfaces are negatively charged. Therefore, if the surface is to be made hydrophobic (water-repellent) by use of a surfactant, then the best type of surfactant will adsorb onto the surface with its positively charged hydrophilic head group oriented toward the negatively charged surface (because of electrostatic attraction) and its hydrophobic group oriented away from the surface, making the surface water-repellent. On the other hand, if the surface is to be made hydrophilic (water-wettable), then cationic surfactants should be avoided. If the

surface should happen to be positively charged, however, then anionics will make it hydrophobic and should be avoided if the surface is to be made hydrophilic (Rosen, 2004).

Nonionic adsorb onto surface with either the hydrophilic or the hydrophobic group oriented toward the surface, depending upon the nature of the surface. If polar group capable of H-bonding with the hydrophilic group of the surfactant are present on the surface, then the surfactant will probably be adsorbed with its hydrophilic group oriented toward the surface, making the surface more hydrophobic; if such groups are absent from the surface, then the surfactant will probably be oriented with its hydrophobic group toward the surface, making it more hydrophilic.

Zwitterionics, since they carry both positive and negative charges, can adsorb onto both negatively charged and positively charged surface without changing the charge of the surface significantly. On the other hand, the adsorption of a cationic onto a negatively charged surface reduces the charge on the surface and may even reverse it to a positive charge (if sufficient cationic is adsorbed). In similar fashion, the adsorption of an anionic surfactant onto a positively charged surface reduces its charge and may reverse it to a negative charge. The adsorption of a nonionic onto a surface generally does not affect its charge significantly, although the effective charge density may be reduced if the adsorbed layer is thick.

2.5.3 General effects of the nature of the hydrophobic group.

- **Length of the hydrophobic group.** Increase in the length of the hydrophobic group:

- 1) Decreases the solubility of the surfactant in water and increases its solubility in organic solvents.
- 2) Causes closer packing of the surfactant molecules at the interface (provided that the area occupied by the hydrophilic group at the interface permits it).

3) Increases the tendency of the surfactant to adsorb at interface or to form aggregates, called micelles.

4) Increases the melting point of the surfactant and of the adsorbed film and the tendency to form liquid crystal phases in the solution.

5) Increases the sensitivity of the surfactant, if it is ionic, to precipitation from water by counterions.

- **Branching or unsaturation.** The introduction of branching or unsaturation into the hydrophobic group:

1) Increases the solubility of the surfactant in water or in organic solvents (compared to the straight-chain, saturated isomer).

2) Decreases the melting point of the surfactant and of the adsorbed film.

3) Causes looser packing of the surfactant molecules at the interface (the cis isomer is particularly loosely packed; the trans isomer is packed almost as closely as the saturated isomer) and inhibits liquid crystal phase formation in solution.

4) May cause oxidation and color formation in unsaturated compounds.

5) May decrease biodegradability in branched-chain compound.

6) May increase thermal instability.

- **Aromatic nucleus.** The presence of an aromatic nucleus in the hydrophobic group may:

1) Increases the adsorption of the surfactant onto polar surface.

2) Decreases its biodegradability.

3) Cause looser packing of the surfactant molecules at the interface.

- **Polyoxypropylene or polyoxyethylene units.** Polyoxypropylene units increase the hydrophobic nature of the surfactant, its adsorption onto polar

surfaces and its solubility in organic solvents. Polyoxyethylene units decrease the hydrophobic character of the surfactant.

3. The preparation of nano-sized CeO₂ by microemulsion method

Zhang *et al.* (2001) prepared CeO₂ nanocrystal using CTAB (cetyl trimethylamine bromide) as a surfactant, butanol as a cosurfactant and cyclohexane as an organic solvent. The starting materials are cerium nitrate and ammonia. The effect of annealing temperature in air on the formation of CeO₂ were studied. Combined with the HRTEM, the TG-DTA and the XRD patterns reveal that the CeO₂ annealed at 623 K is amorphous and the formation of CeO₂ nanocrystal occurs above 773 K. The HRTEM pictures of as-prepared sample annealed at different temperatures are shown in Figure 11. When the annealing temperature was 623 K, it was observed that there were many aggregates that were of spherical shape with a size of about 65 nm. In addition, there were some clusters having a spherical particle, which was amorphous from the electron diffraction (ED) pattern. On the other hand, the cerium oxide nanocrystal with a diameter of 6-8 nm appeared when the annealing temperature increased up to 873 K.

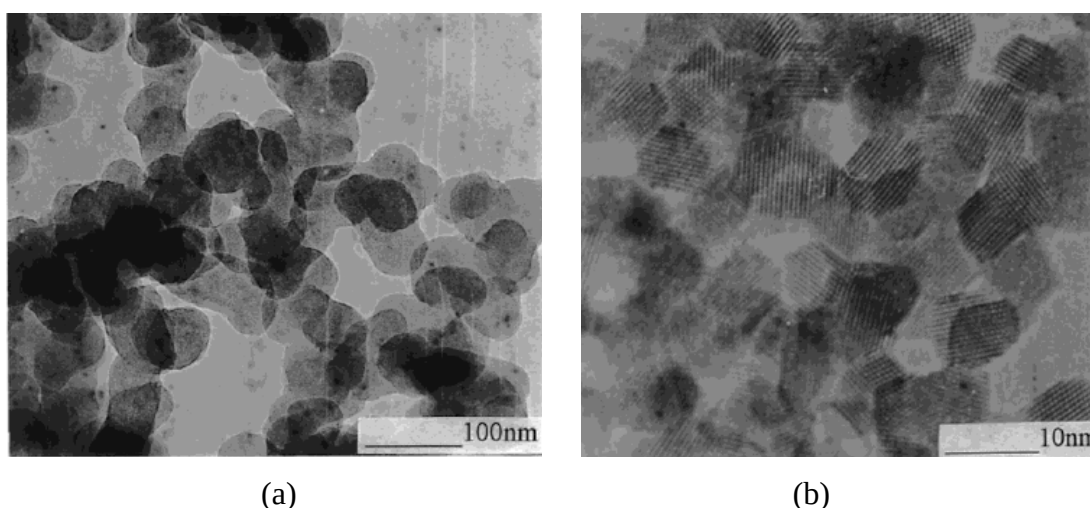


Figure 11 HRTEM of as-prepared samples annealed at (a) 623 K and (b) 873 K.

Source: Zhang *et al.* (2005).

From the ED pattern, the nanocrystal can be assigned to be the cubic phase of CeO_2 . Obviously, this observation is consistent with the result of XRD and supports the formation of the cerium oxide nanocrystal. And it was found that the phase structure changed from triclinic to cubic and the electronic structure changed from Ce^{3+} to Ce^{4+} upon increasing the annealing temperature.

Wu *et al.* (2002) studied the preparation of CeO_2 nanoparticles coated by CTAB (cetyl trimethylamine bromide) using reverse micelles and microemulsion method. The structural dependence on temperature and chemical transformation were investigated. The synthesis process can be divided into three steps, the first step CTAB and cerium nitrate solution were added into cyclohexane. After that butanol were added into the mixture and stirred until the transparent microemulsion was formed. The second step, CTAB and ammonia were added into cyclohexane. Then butanol were added into the mixture and stirred until the transparent microemulsion was formed. And the last step, the two microemulsions were mixed and stirred. The resultant mixture turned into a colloid solution with opalescence. The powder of CeO_2 nanoparticles was obtained from this colloid solution by rotary evaporation. The as-prepared sample (at 25°C) was further annealed at 200, 350, 500 and 700°C under air condition.

Figure 12 (a) shows the TEM micrograph of CTAB-coated CeO_2 nanoparticles annealed at 200°C with particle size of 50 nm. TEM diffraction pattern shown in the inset image demonstrates that these nanoparticles are in an amorphous form. Figure 12 (b) is the HRTEM photograph of CTAB-coated CeO_2 nanoparticles annealed at 500°C with particle size of 6 nm. The clear stripes in the image illustrate the nanoparticles are in a crystalline form. A chemical transformation from Ce^{3+} to Ce^{4+} components was found in about the temperature range of $200\text{--}400^\circ\text{C}$. After the annealing was performed at 500°C and 700°C , a single phase with Ce^{4+} oxidation state and CaF_2 type structures was obtained. The room temperature products are in amorphous state and present Ce^{3+} characteristics. The samples annealed at 200°C and 350°C are, respectively, a mixture of amorphous Ce^{3+} component and crystalline Ce^{4+} component. These nanoparticles consist of two parts, that is, the core part (Ce^{4+}) and

the surface part (Ce^{3+}). The surface parts change with the increase of annealing temperature. The core parts are always the same with bulk CeO_2 .

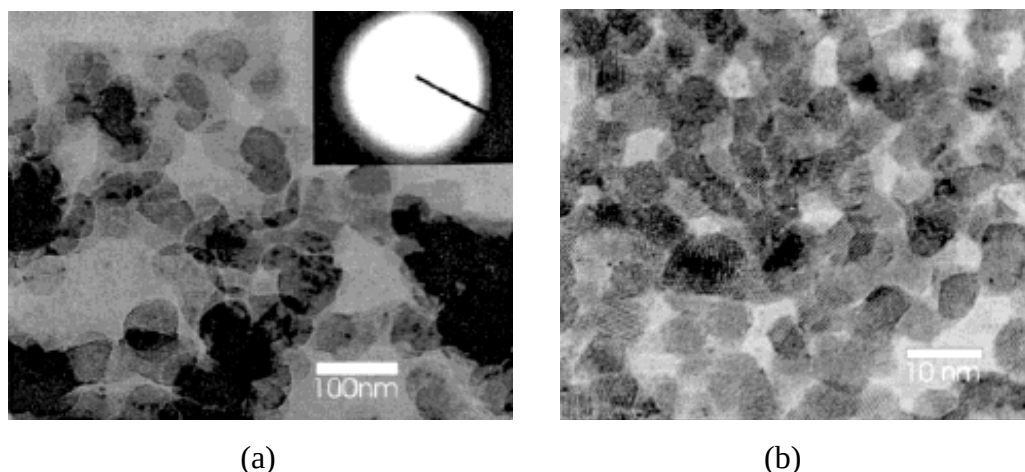


Figure 12 (a) TEM micrograph of CTAB-coated CeO_2 nanoparticles annealed at 200°C and (b) HRTEM photograph of CTAB-coated CeO_2 nanoparticles Annealed at 500°C .

Source: Wu *et al.* (2002).

He *et al.* (2003) synthesized CeO_2 by the combined methods of homogeneous precipitation with microemulsion. The effect of precipitation temperature, calcination temperature, the sort of surfactant and the sort of cosurfactant were investigated. The water droplets of W/O microemulsion were utilized as the constrained microreactors for the homogeneous precipitation of methyl oxalate with cerium nitrate. AOT (sodium bis(2-ethylhexyl)sulfosuccinate), CTAB (cetyl trimethylamine bromide) and NP-9 (poly(oxyethylene)₉ nonyl phenol ether) were used as surfactants, 1-hexyl alcohol, 1-amyl alcohol and 1-heptyl alcohol were used as cosurfactants, and cyclohexane was used as an organic solvent. The microemulsion was heated to 323, 333 and 343 K then dried in vacuum at 323 K. Finally the precursor was calcined at 973, 1073 and 1173 K. It was found that with the rise of precipitation temperature, the average size of CeO_2 nanoparticles increased. The sort of surfactant has correlative affections on the average size of products, while the influence of the sort of cosurfactants is not notable. Calcinations in higher temperature make the average size of products increased and the size distribution broadened.

Bumajdad *et al.* (2004) synthesized pure CeO_2 powders in heptane-microemulsified aqueous solution of CeCl_3 or $\text{Ce}(\text{NO}_3)_3$ stabilized by AOT, DDAB or DDAB+Brij 35 surfactant mixtures. Micellar DTAB and vesicular DDAB systems were also used as media for generating CeO_2 . It revealed that in the presence of surfactants almost agglomerate free nanosized crystallites (6-13 nm) of anionic vacancy-free cubic CeO_2 were produced. In the absence of surfactants the crystallites size of 21 nm were formed, comparing with the crystallites size of 85 nm when cubic CeO_2 was created via thermal decomposition of cerium oxalate.

In this thesis, preparation of nano-size CeO_2 powders by microemulsion method is studied. The technique of preparation, the type of cerium source and the sort of surfactant are investigated.