MATERIALS AND METHODS

The experiment of this study is divided into three parts. First part is the preparation of CeO_2 by microemulsion method using different cerium sources and surfactants. The cerium sources include cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$, 98.5% purity assay from MERCK), ammonium cerium nitrate ($(NH_4)_2Ce(NO_3)_6$, 98.5% purity assay from Asia Pacific Specialty Chemicals Limited) and cerium chloride heptahydrate ($CeCl_3{\cdot}7H_2O$, from Rare Earth Research and Development Center). The surfactants are polyoxyethylene-4-lauryl ether (PE4LE, from SIGMA CHEMICAL CO.), polyoxy ethylene-10-oleyl ether (Brij96V from FLUKA CHEMIKA) and cetyl trimethyl ammonium bromine (CTAB from FLUKA CHEMIKA). When using CTAB, butanol ($CH_3(CH_2)_2CH_2OH$, 99.4 % assay from Asia Pacific Specialty Chemicals Limited) as a cosurfactant is needed in order to obtain microemulsion. Second part is to combine homogeneous precipitation method with microemulsion method. Cerium sources and methyl oxalate were used as starting materials and the last part is to prepare microemulsion from mixing two microemulsions obtained from cerium sources and ammonium hydroxide. The details of experiment are as follows.

1. <u>Microemulsion method</u>

Cerium nitrate hexahydrate (2 g) was dissolved in 0.1 ml of distilled water and then was added into 100 ml of n-hexane (C_6H_{14}, 95 % assay from Asia Pacific Specialty Chemicals Limited). Polyoxyethylene-4-lauryl ether was added dropwise to the solution under vigorous agitation until all cerium nitrate hexahydrate particles completely dissolved in the solution and transparent microemulsion (about 10 h) was obtained. The hydrazinium hydrate ($NH_2{\cdot}NH_2{\cdot}H_2O$, 99% assay from AJAX CHEMICALS) was then added into the solution to neutralize the cerium ions in the reverse micelles. The hydrazine in the amount of 5% of total volume is sufficient to ensure that reduction takes place without destroying the isotropic solution. The experiment flow chart of preparation is shown in Figure 13 and the formation mechanism is shown in Figure 14. Then the microemulsion was dried in an oven at

250°C for 2 h. Finally the precursor was calcined at 600°C for 1 h, CeO_2 powder was obtained. The experiment of microemulsion method with different cerium sources and surfactants are summarized in Table 2.

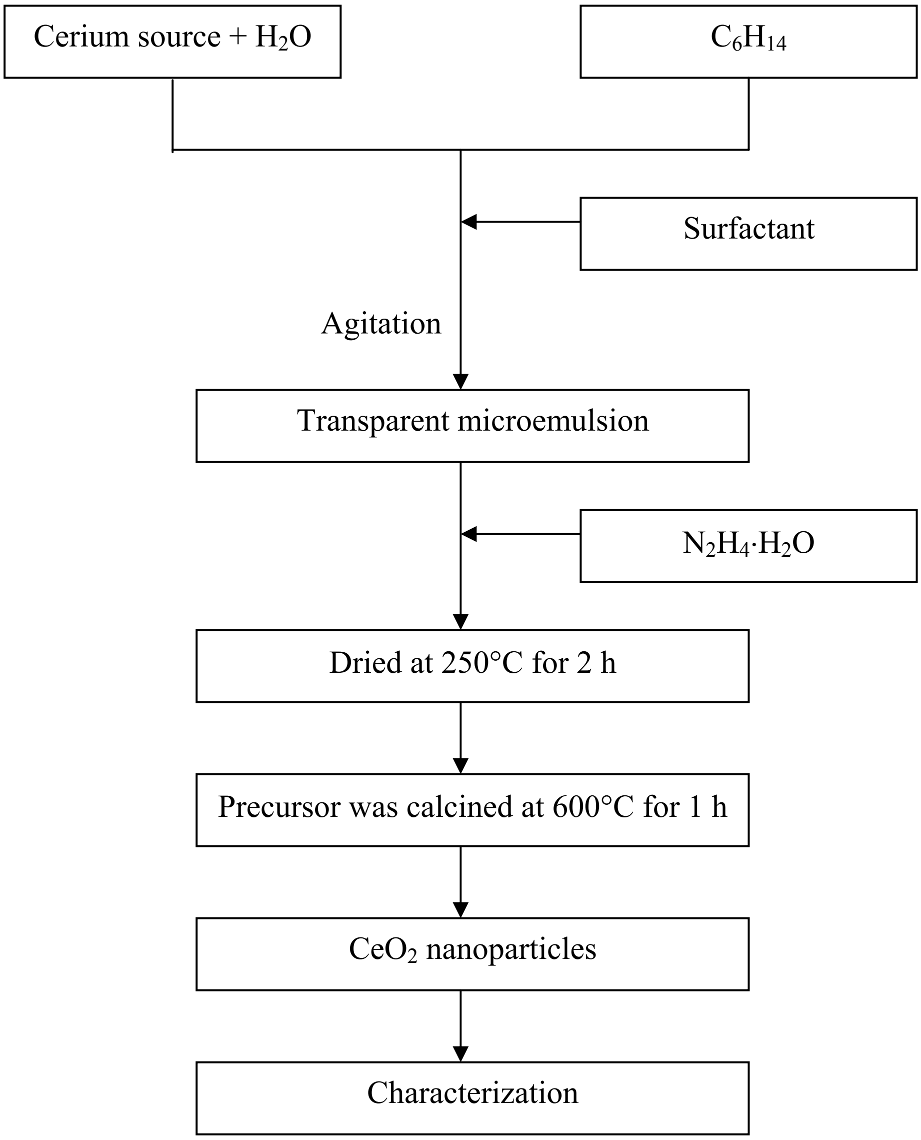

Figure 13 Experiment flow chart of preparation of nano-sized CeO_2 by microemulsion method.

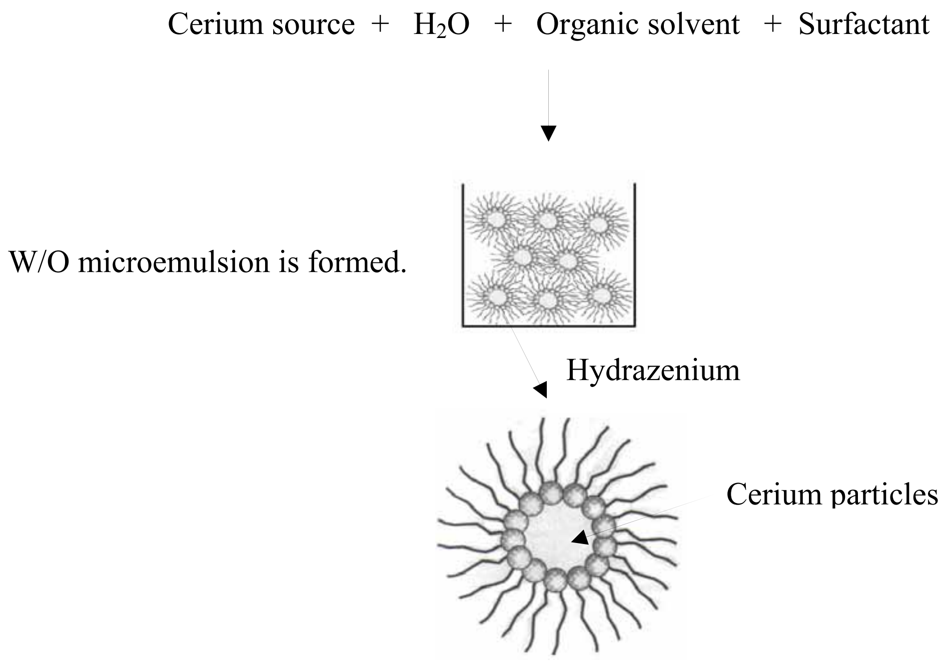

Figure 14 The formation mechanism of nano-sized cerium particle obtained from microemulsion method.

Table 2 The experiment of microemulsion method with different cerium sources and surfactants.

Cerium source	Surfactant /cosurfactant		
	PE4LE (ml)	Brij96V (ml)	CTAB / butanol (g) / (ml)
$Ce(NO_3)_3{\cdot}6H_2O$ 2.00 g	8.0	8.4	5.0/13.0
$(NH_4)_2Ce(NO_3)_6$ 2.52 g	12.6	12.5	5.0/11.0
$CeCl_3{\cdot}7H_2O$ 1.71 g	12.0	15.0	5.0/14.4

2. Combined method of homogeneous precipitation and microemulsion

An approximately 13 ml of a surfactant, polyoxy ethylene-4-lauryl ether was added into 100 ml of n-hexane under agitation. Then 10 ml of aqueous solution, in which the concentration of cerium source, cerium nitrate hexahydrate, and a homogeneous precipitation, methyl oxalate ($C_4H_6O_4$, 99% purity assay from FLUKA CHEMIKA), was 0.06 and 0.09 mol/l, respectively, was injected into the hexane mixture under vigorous agitation until the microemulsion is transparent (about 8 h). The experiment flow chart of preparation is shown in Figure 15 and the formation mechanism is shown in Figure 16. The microemulsion was dried in an oven at 250°C for 2 h. Finally the precursor was calcined at 600°C for 1 h, CeO_2 powder was obtained. The experiment of combined method with different cerium sources and surfactants are summarized in Table 3.

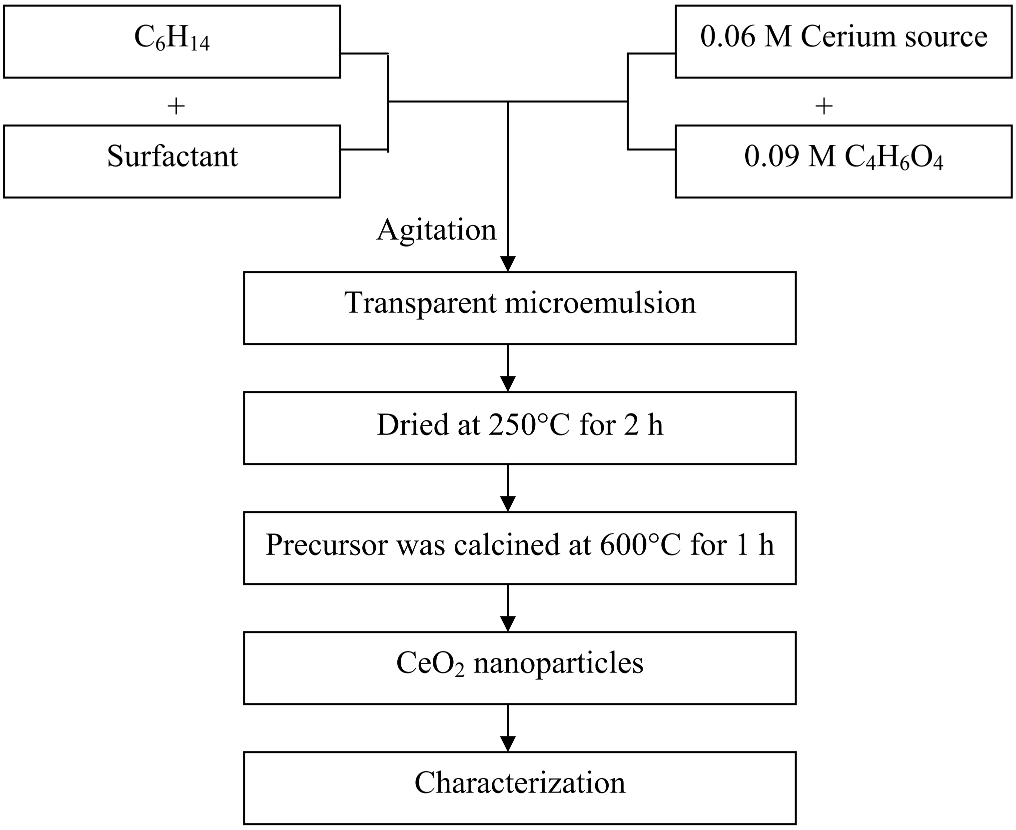

Figure 15 Experiment flow chart of preparation of nano-sized CeO_2 by combined methods of homogeneous precipitation and microemulsion.

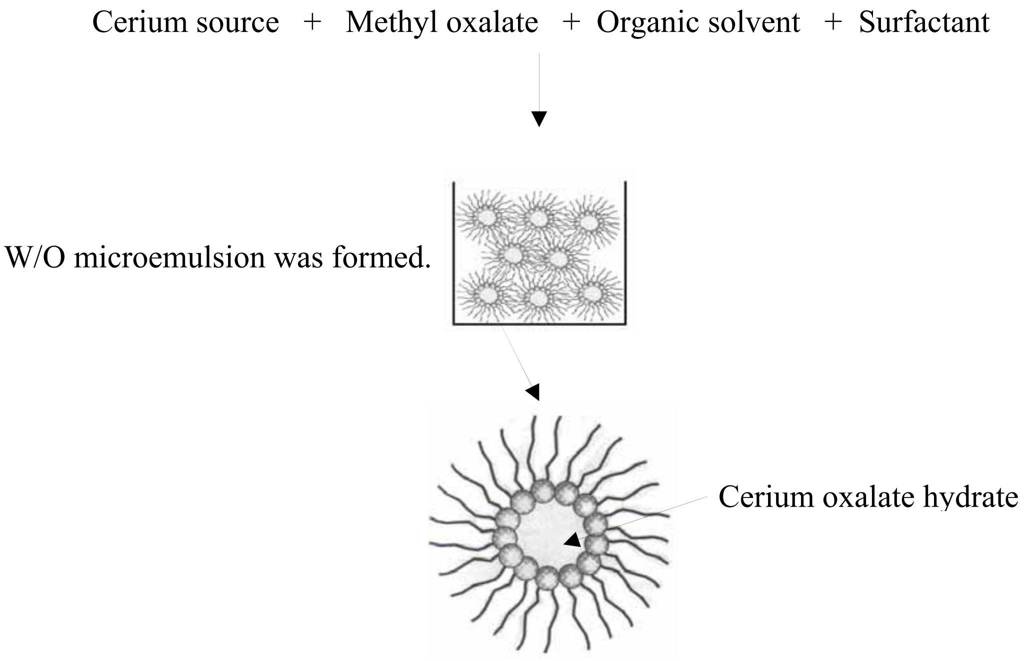

Figure 16 The formation mechanism of cerium oxalate hydrate obtained from combined methods of homogeneous precipitation and microemulsion.

Table 3 The experiment of combined method of homogeneous precipitation and microemulsion with different cerium sources and surfactants.

Cerium source	Surfactant /cosurfactant	
	PE4LE (ml)	CTAB / butanol (g) / (ml)
0.06 M $Ce(NO_3)_3 \cdot 6H_2O$ 10 ml	13.0	5.0/11.0
0.06 M $(NH_4)_2Ce(NO_3)_6$ 10 ml	10.6	5.0/8.8
0.06 M $CeCl_3 \cdot 7H_2O$ 10 ml	15.2	5.0/13.2

3. Mixing of two microemulsions

Cerium nitrate hexahydrate, ammonium cerium nitrate and cerium chloride heptahydrate (cerium sources) and ammonium hydroxide (NH_4OH, 30% as NH_3 assay from Mallinckrodt CHEMICALS) were used as starting materials.

First, two bottles of mixture of 13 ml polyoxy ethylene-4-lauryl ether and 75 ml of n-hexane were prepared. Then 10 ml of 0.1 M cerium nitrate solution was added into a bottle and 2 ml of 10% ammonium hydroxide was added into the other bottle under vigorous agitation until the transparent microemulsions were formed (about 30 min). The two microemulsions were mixed and stirred for 1 h. The mixed microemulsion was aged for 2 days at room temperature. The experiment flow chart of preparation is shown in Figure 17 and the formation mechanism is shown in Figure 18. After aging the microemulsion was dried in an oven at 250°C for 2 h. Finally the precursor was calcined at 600°C for 1 h, and CeO_2 powder was obtained. The experiment of mixing of two microemulsions with different cerium sources and surfactants are summarized in Table 4.

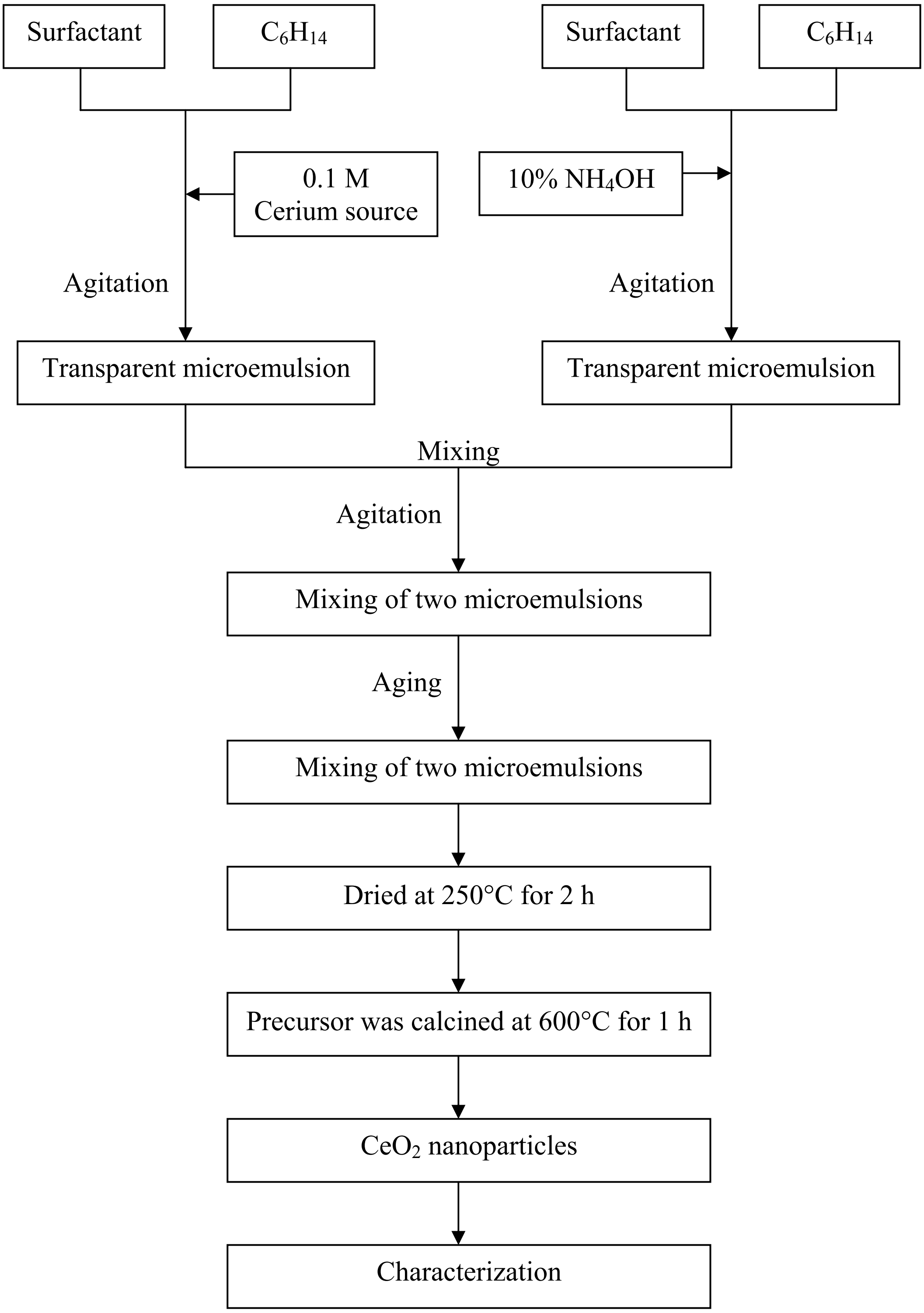

Figure 17 Experiment flow chart of preparation of nano-sized CeO_2 by microemulsion method.

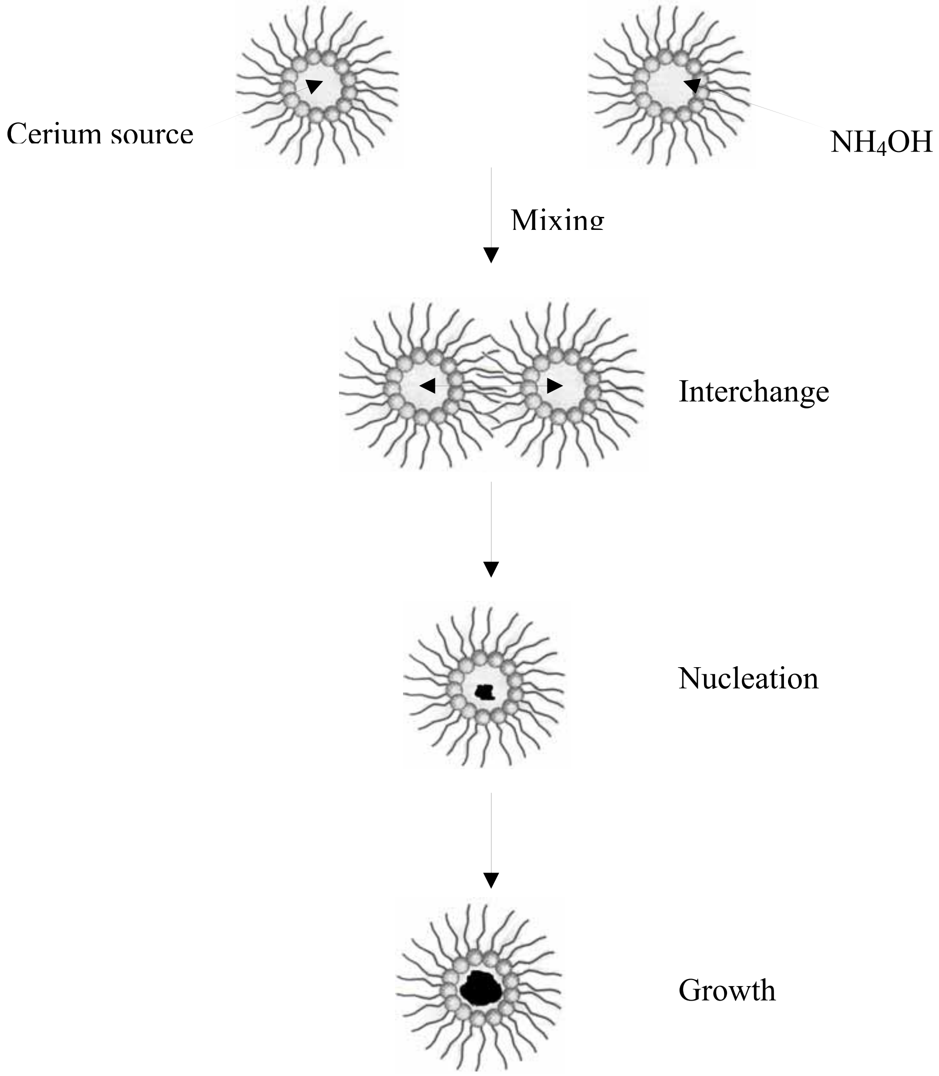

Figure 18 The formation mechanism of cerium hydroxide obtained from mixing of two microemulsions.

Table 4 The experiment of mixing of two microemulsions with different cerium sources and surfactants.

Starting materials	Surfactant /cosurfactant	
	PE4LE (ml)	CTAB / butanol (g) / (ml)
0.1 M $Ce(NO_3)_3 \cdot 6H_2O$ 10 ml	13.0	5.0/13.0
0.1 M $(NH_4)_2Ce(NO_3)_6$ 10 ml	12.6	5.0/8.2
0.1 M $CeCl_3 \cdot 7H_2O$ 10 ml	13.2	5.0/14.2
10% NH_4OH 2 ml	8.0	5/10.6

4. Product characterization

The products were characterized by the following methods.

- X-Ray diffraction spectroscopy (XRD, Phillips:X'Pert Model)
- Transmission electron microscopy (TEM, Jeol Model JEM-2010)
- Energy dispersive spectroscopy (EDS, Jeol Model JEM-2010)

4.1 X-Ray diffraction spectroscopy (XRD)

The crystalline phase of products was identified by x-ray diffraction spectroscopy (XRD) and recorded by X'Pert X-ray diffraction instrument using CuKα radiation.

4.2 Transmission Electron Microscopy (TEM)

The particle morphologies and the sizes of particles were observed by transmission electron microscopy (TEM).

4.2.1 Ce particle in microemulsion.

The cerium particles prepared by microemulsion method were deposited on a carbon coated grid. The grid was placed in a vacuum oven at temperature of 150°C to remove excess surfactant. TEM Images were taken by using transmission electron microscope operated at 160 kV. The particle size and shape were determined from the enlarged TEM images.

4.2.2 CeO_2 particles.

The CeO_2 particles prepared by microemulsion method was suspended in ethanol under ultrasonification for 30 minutes. The suspended sample was deposited on a carbon coated grid by slow evaporation at room temperature. TEM Images were taken by using transmission electron microscope operated at 160 kV. The particle sizes and shapes were determined from the enlarged TEM images.

4.3 Energy dispersive spectroscopy (EDS)

The elemental composition of products were identified by energy dispersive spectroscopy (EDS) operated at 10-50 kV and recorded by Jeol Model JEM-2010 instrument.