RESULTS AND DISCUSSION

1. Characterizations of Ce particles in microemulsion

The TEM images of Ce particles in microemulsion after reduction are shown in Figures 19 to 39. The Ce particles in microemulsion are good dispersed and spherical in shape. The particle sizes are very small in the nanometer range (≈ 1 nm). The average particle sizes of Ce prepared by different cerium sources and surfactants but the same method are nearly the same. Consider the particle sizes of Ce using different methods it was found that the particle sizes obtained from mixing of two microemulsions (≈ 0.3 nm) are smaller than those from other methods and the particle sizes obtained from the combined methods of homogeneous precipitation and microemulsion (≈ 0.5 nm) are smaller than that from the microemulsion method (≈ 1 nm).

Ce particles in microemulsion was detected by energy dispersive spectroscope (EDS). EDS spectra of the Ce particles obtained from the preparation using $CeCl_3{\cdot}7H_2O$ as a cerium source are shown in Figure 40. In the Figure, EDS spectra at the dark spot show Ce, Cl and O peaks. The presence of Cl and O peaks was due to the incomplete reduction of cerium compound to cerium particle.

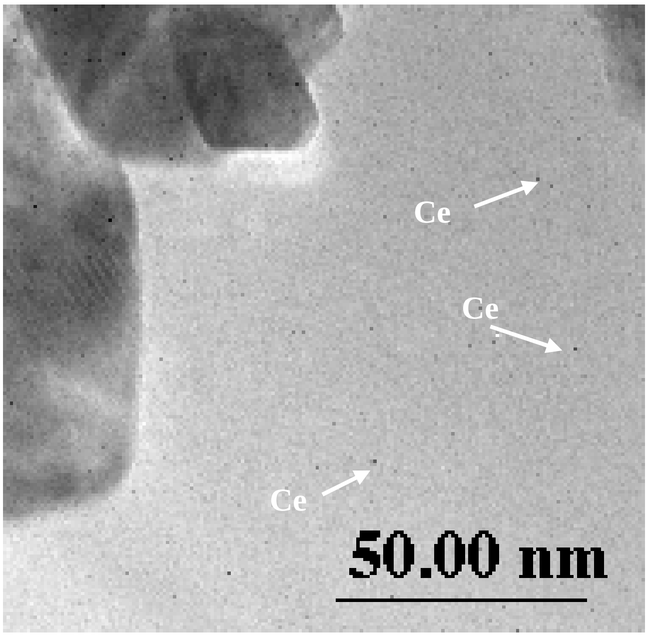


Figure 19 TEM Image of Ce particles in microemulsion obtained from $Ce(NO_3)_3 \cdot 6H_2O$ as a cerium source and PE4LE as a surfactant using microemulsion method (50,000x magnification).

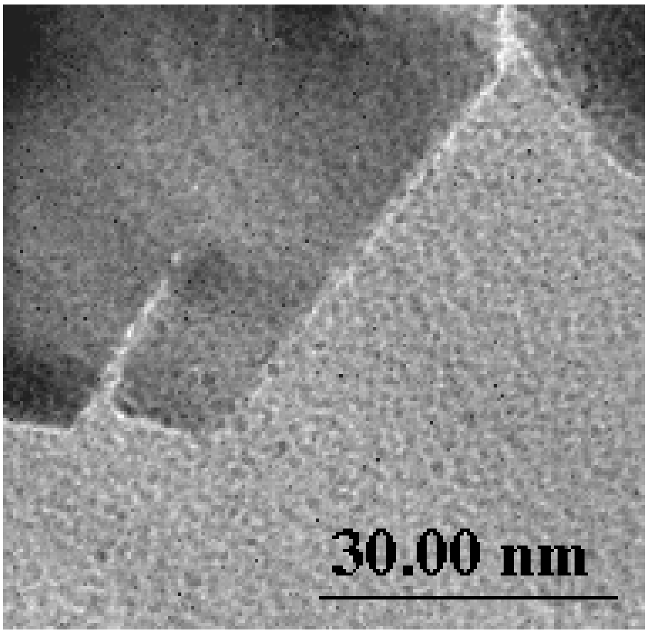


Figure 20 TEM Image of Ce particles in microemulsion obtained from $(NH_4)_2Ce(NO_3)_6$ as a cerium source and PE4LE as a surfactant using microemulsion method (100,000x magnification).

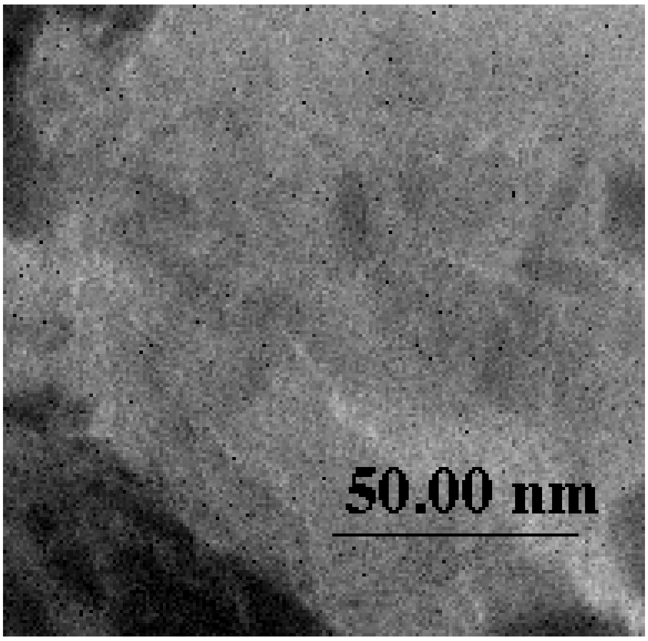


Figure 21 TEM Image of Ce particles in microemulsion obtained from $CeCl_3{\cdot}7H_2O$ as a cerium source and PE4LE as a surfactant using microemulsion method (20,000x magnification).

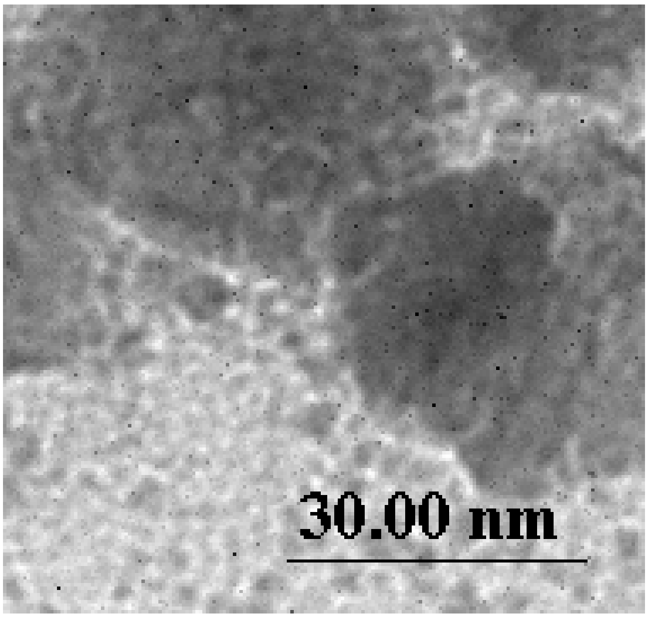


Figure 22 TEM Image of Ce particles in microemulsion obtained from $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source and Brij96V as a surfactant using microemulsion method (100,000x magnification).

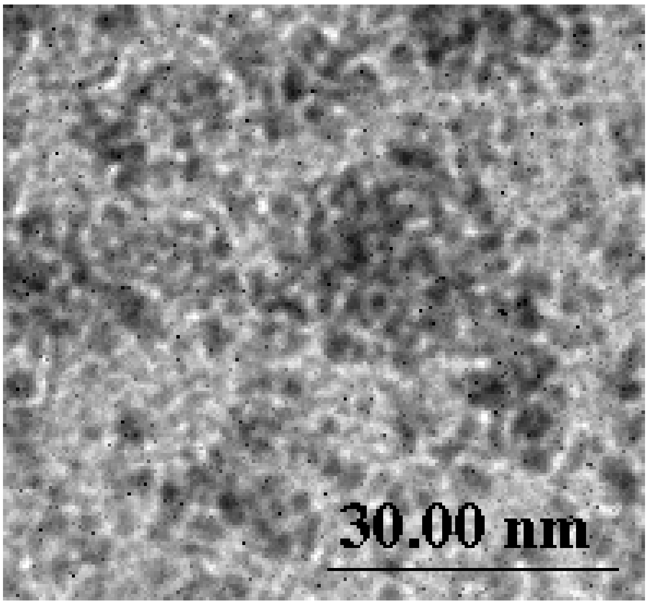


Figure 23 TEM Image of Ce particles in microemulsion obtained from $(NH_4)_2Ce(NO_3)_6$ as a cerium source and Brij96V as a surfactant using microemulsion method (100,000x magnification).

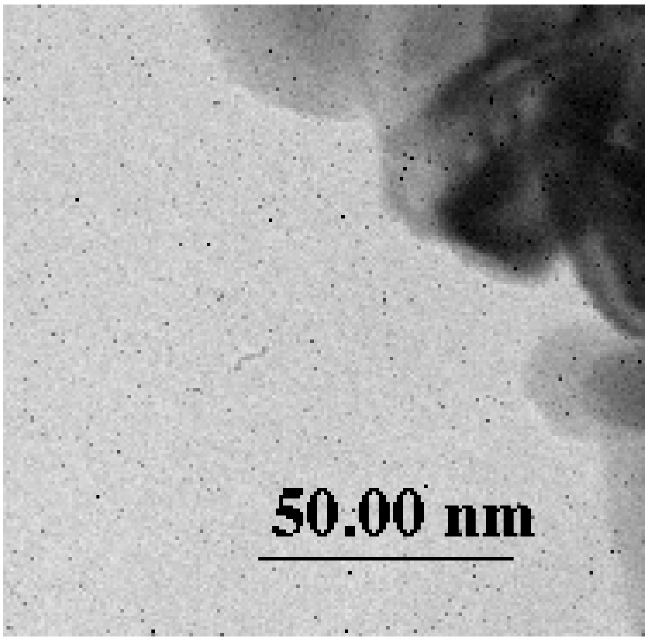


Figure 24 TEM Image of Ce particles in microemulsion obtained from $CeCl_3 \cdot 7H_2O$ as a cerium source and Brij96V as a surfactant using microemulsion method (50,000x magnification).

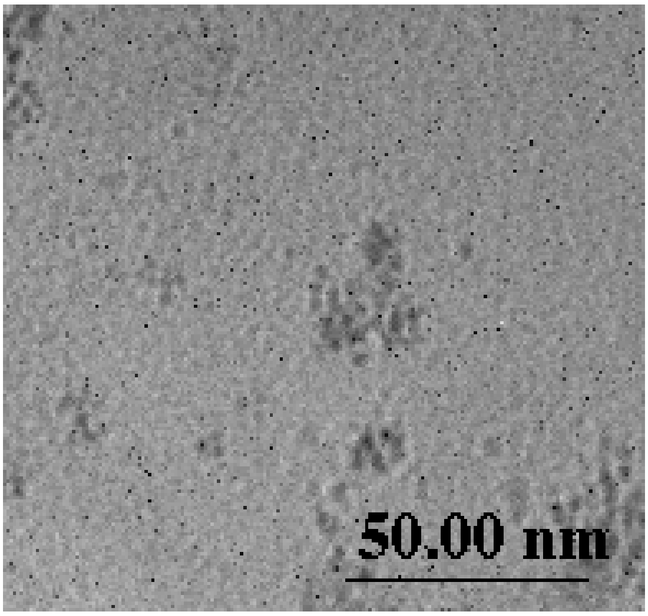


Figure 25 TEM Image of Ce particles in microemulsion obtained from $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using microemulsion method (50,000x magnification).

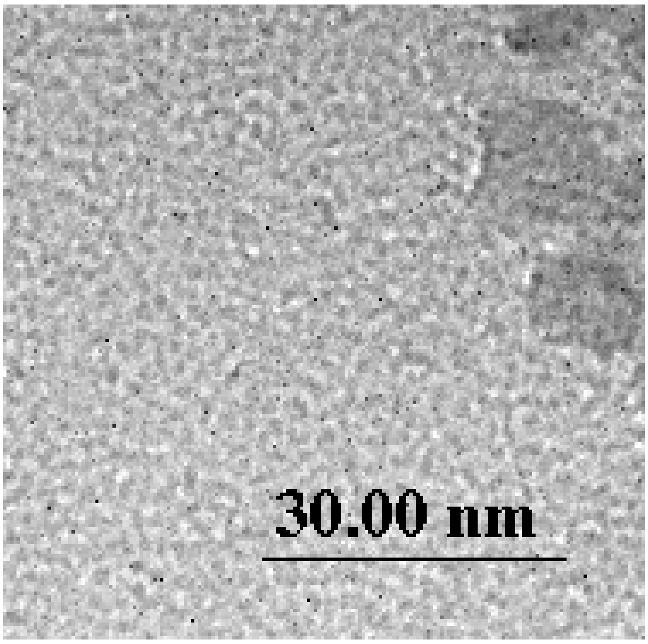


Figure 26 TEM Image of Ce particles in microemulsion obtained from $(NH_4)_2Ce(NO_3)_6$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using microemulsion method (100,000x magnification).

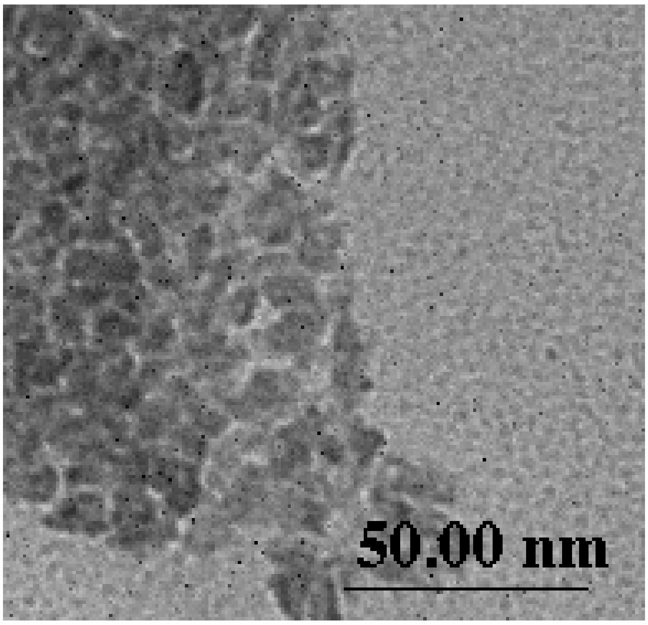


Figure 27 TEM Image of Ce particles in microemulsion obtained from $CeCl_3 \cdot 7H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using microemulsion method (50,000x magnification).

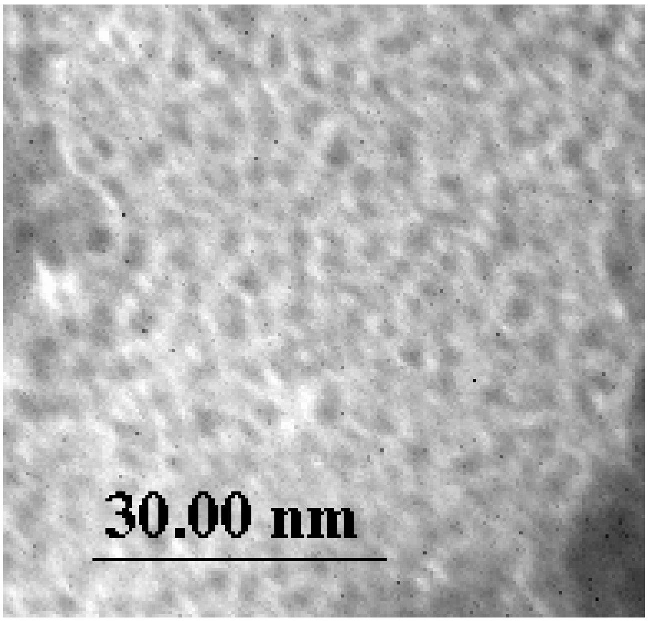


Figure 28 TEM Image of Ce particles in microemulsion obtained from $Ce(NO_3)_3 \cdot 6H_2O$ as a cerium source and PE4LE as a surfactant using combined methods of homogeneous precipitation and microemulsion (100,000x magnification).

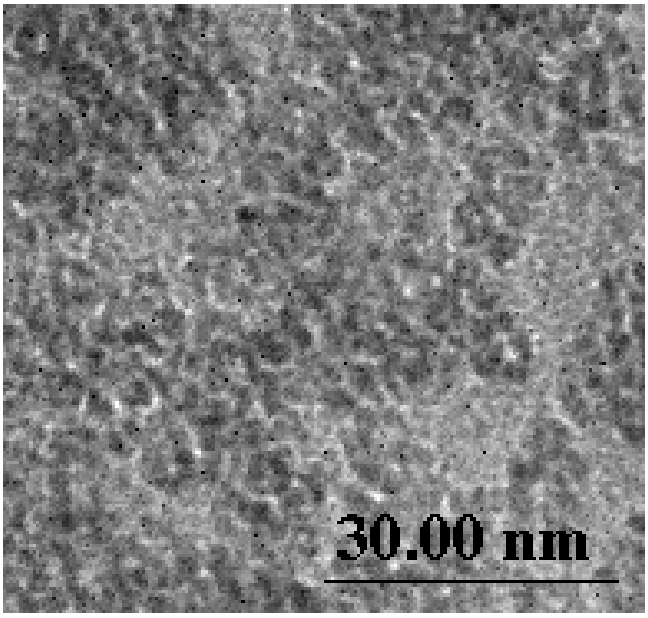


Figure 29 TEM Image of Ce particles in microemulsion obtained from $(NH_4)_2Ce(NO_3)_6$ as a cerium source and PE4LE as a surfactant using combined methods of homogeneous precipitation and microemulsion (100,000x magnification).

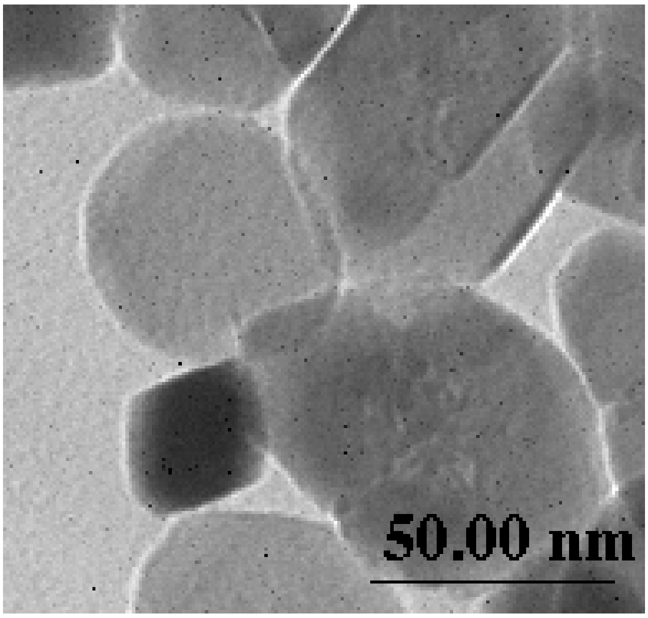


Figure 30 TEM Image of Ce particles in microemulsion obtained from $CeCl_3{\cdot}7H_2O$ as a cerium source and PE4LE as a surfactant using combined methods of homogeneous precipitation and microemulsion (50,000x magnification).

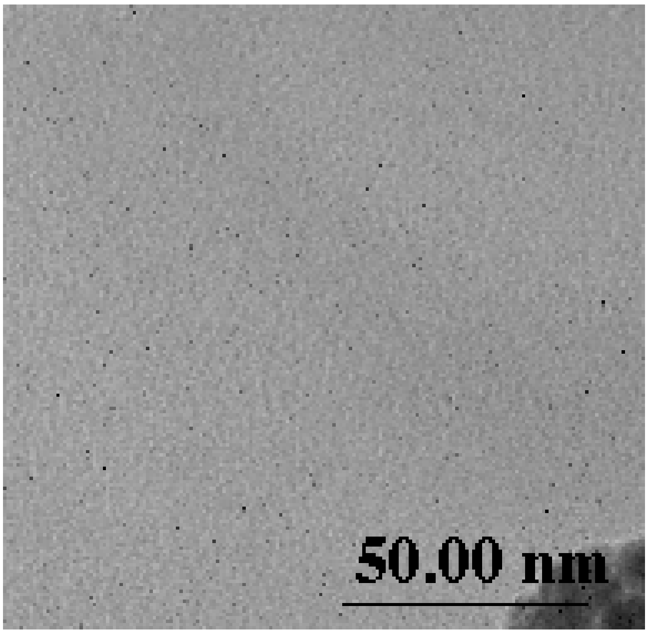


Figure 31 TEM Image of Ce particles in microemulsion obtained from $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using combined methods of homogeneous precipitation and microemulsion (50,000x magnification).

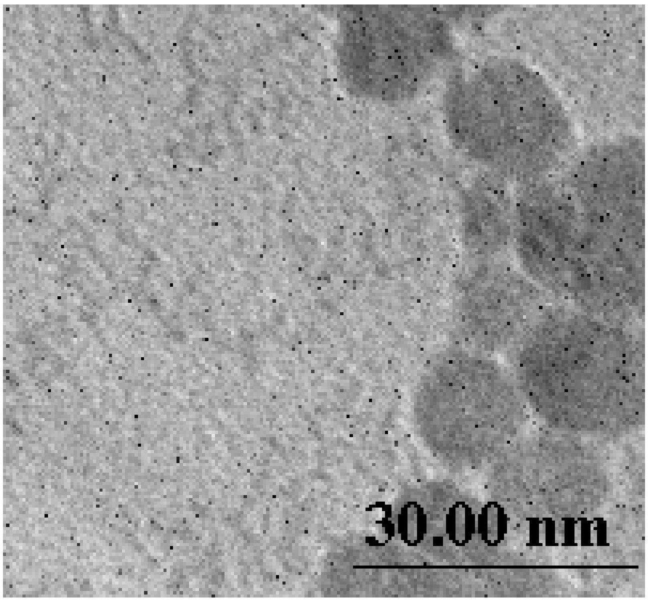


Figure 32 TEM Image of Ce particles in microemulsion obtained from $(NH_4)_2Ce(NO_3)_6$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using combined methods of homogeneous precipitation and microemulsion (100,000x magnification).

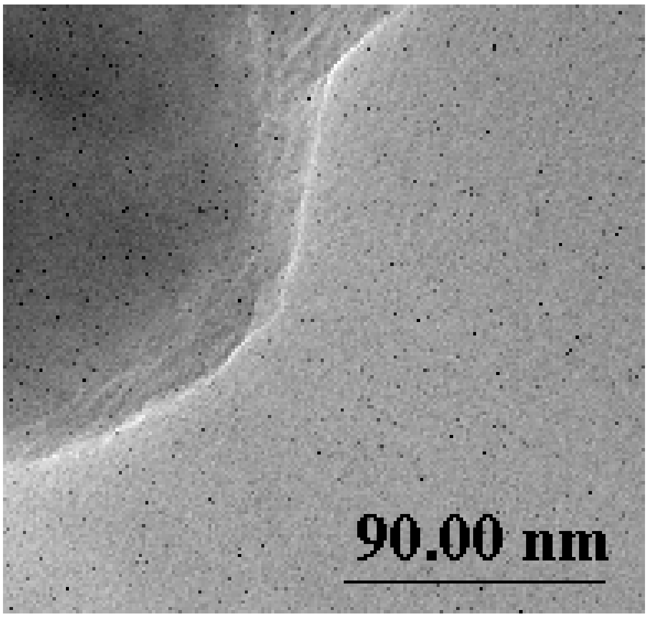


Figure 33 TEM Image of Ce particles in microemulsion obtained from $CeCl_3{\cdot}7H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using combined methods of homogeneous precipitation and microemulsion (30,000x magnification).

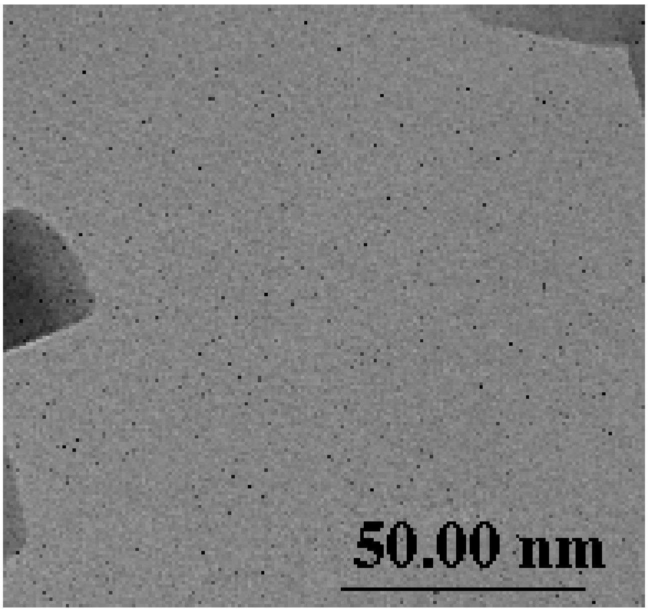


Figure 34 TEM Image of Ce particles in microemulsion obtained from $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source and PE4LE as a surfactant by mixing of two microemulsions (50,000x magnification).

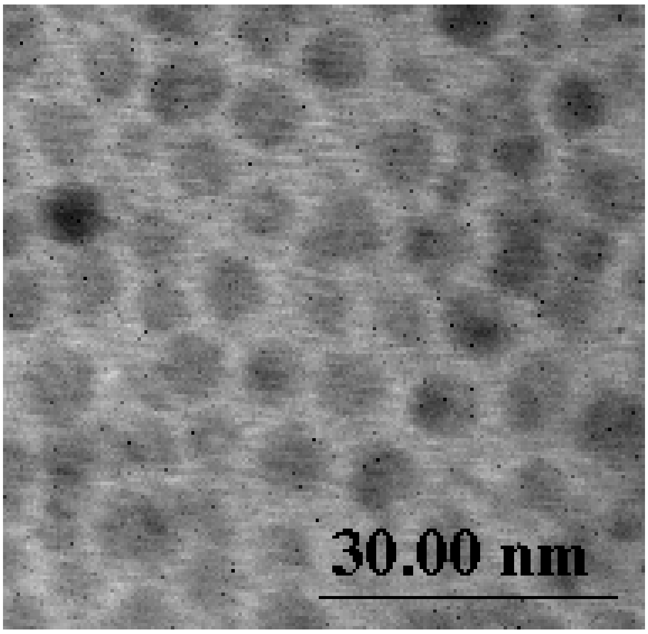


Figure 35 TEM Image of Ce particles in microemulsion obtained from $(NH_4)_2Ce(NO_3)_6$ as a cerium source and PE4LE as a surfactant by mixing of two microemulsions (100,000x magnification).

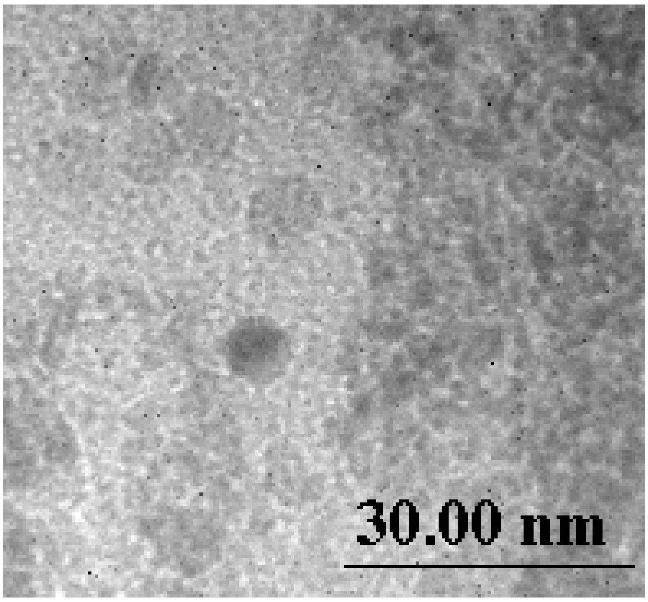


Figure 36 TEM Image of Ce particles in microemulsion obtained from $CeCl_3{\cdot}7H_2O$ as a cerium source and PE4LE as a surfactant by mixing of two microemulsions (100,000x magnification).

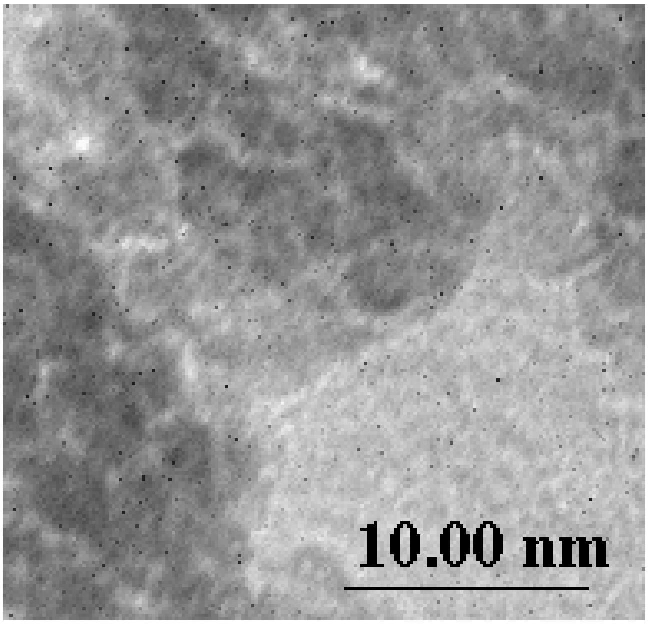


Figure 37 TEM Image of Ce particles in microemulsion obtained from $Ce(NO_3)_3 \cdot 6H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant by mixing of two microemulsions (250,000x magnification).

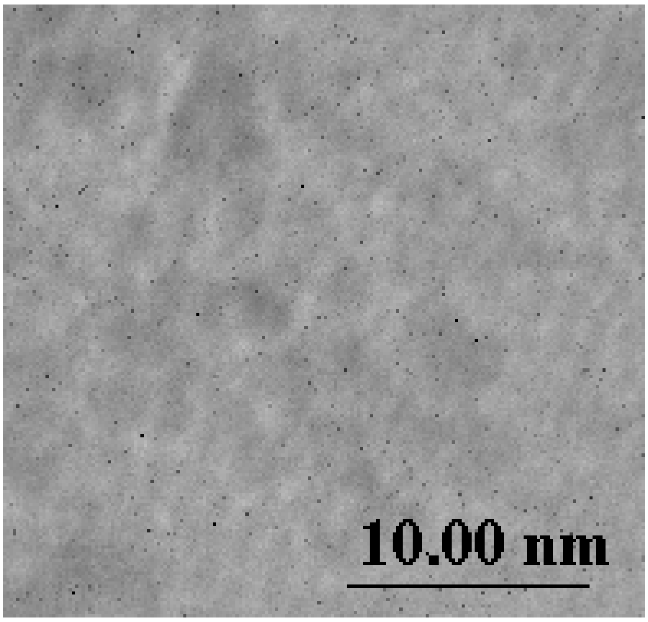


Figure 38 TEM Image of Ce particles in microemulsion obtained from $(NH_4)_2Ce(NO_3)_6$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant by mixing of two microemulsions (250,000x magnification).

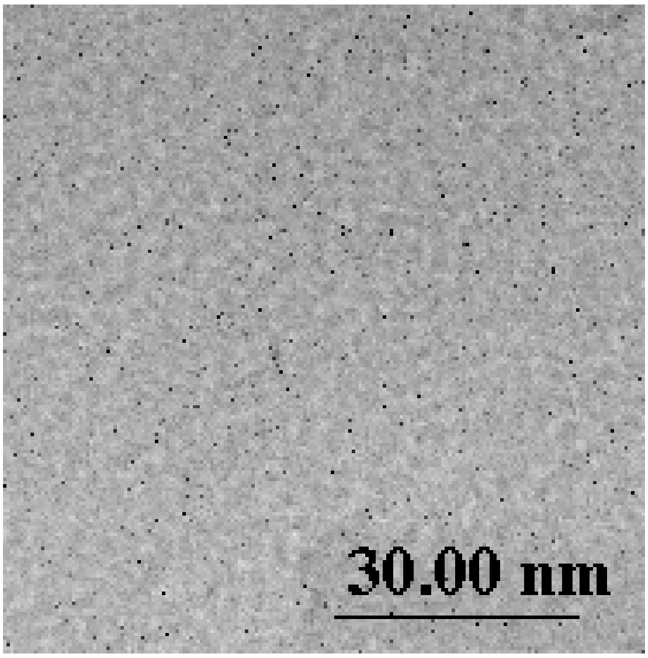


Figure 39 TEM Image of Ce particles in microemulsion obtained from $CeCl_3{\cdot}7H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant by mixing of two microemulsions (80,000x magnification).

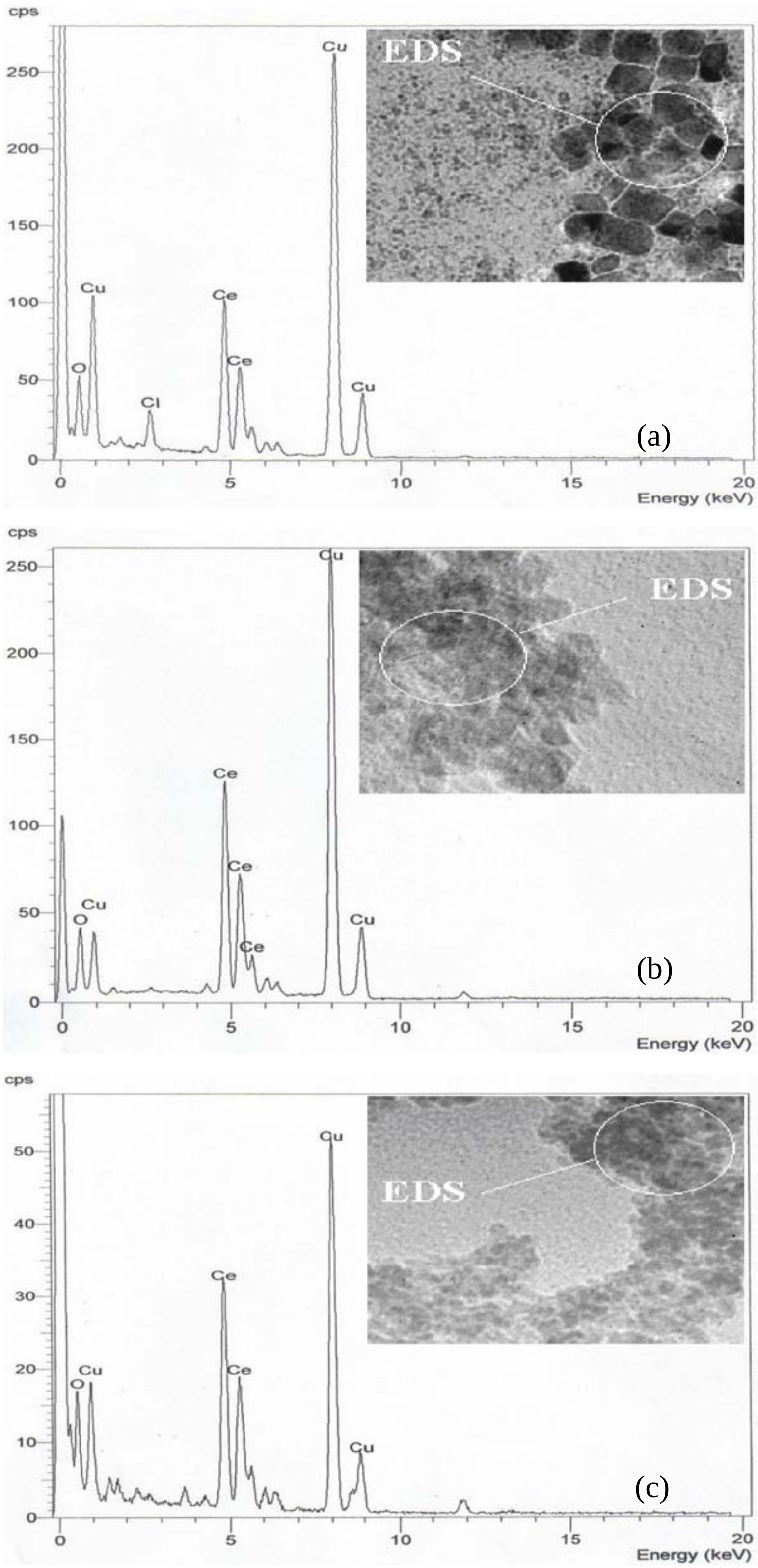


Figure 40 EDS spectrum of microemulsion obtained from different methods (a) microemulsion method (b) combined methods of homogeneous precipitation with microemulsion and (c) mixing of two microemulsions

2. Characterizations of nano-sized CeO_2

2.1 Microemulsion method

For water-in-oil microemulsion reactant A dissolves in the aqueous phase of the microemulsion and was confined in the interior of the microemulsion droplets. The small sizes of the water droplets confine the sizes of the particles and this is the main principle utilized in producing nanoparticles with microemulsions. Ratio of water to surfactant, types of surfactant and metal sources may affect the sizes of water droplets and as a consequence, the sizes of the particles.

In this study three types of surfactant are used. The effect of two types of nonionic surfactant with different hydrocarbon chain lengths and a cationic surfactant were compared and the effect of types of cerium source is investigated.

2.1.1 Nonionic surfactant: polyoxyethylene-4-laurylether(PE4LE)

The TEM image of CeO_2 obtained from $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source and PE4LE as a surfactant is shown in Figure 41. The particles are spherical in shape and agglomerated. The average particle size is 11.1 ± 0.4 nm and the particle size distribution is quite broad as shown in Figure 42.

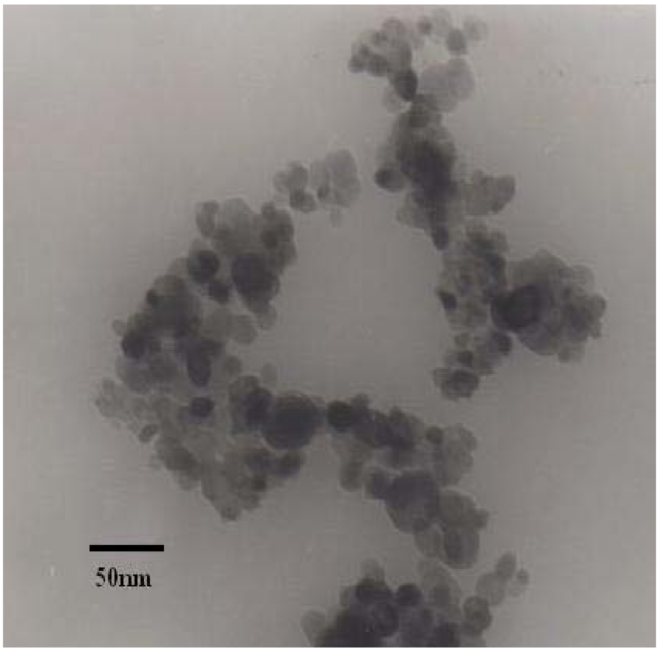


Figure 41 TEM Image of CeO_2 obtained from $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source and PE4LE as a surfactant using microemulsion method (120,000x magnification).

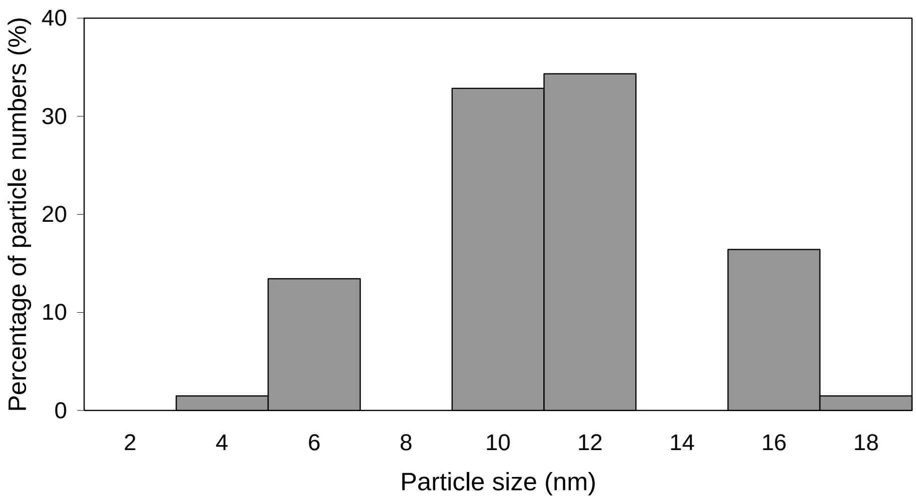


Figure 42 TEM Histograms of CeO_2 particles: $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source, PE4LE as a surfactant using microemulsion method (120,000x magnification).

The TEM image of CeO_2 obtained from $(NH_4)_2Ce(NO_3)_6$ as a cerium source and PE4LE as a surfactant is shown in Figure 43. The particles are spherical in shape the same as that from the $Ce(NO_3)_3{\cdot}6H_2O$ source. The average particle size is 9.4 ± 0.3 nm, smaller than that from the $Ce(NO_3)_3{\cdot}6H_2O$ source, and the particle size distribution is quite narrow as shown in Figure 44.

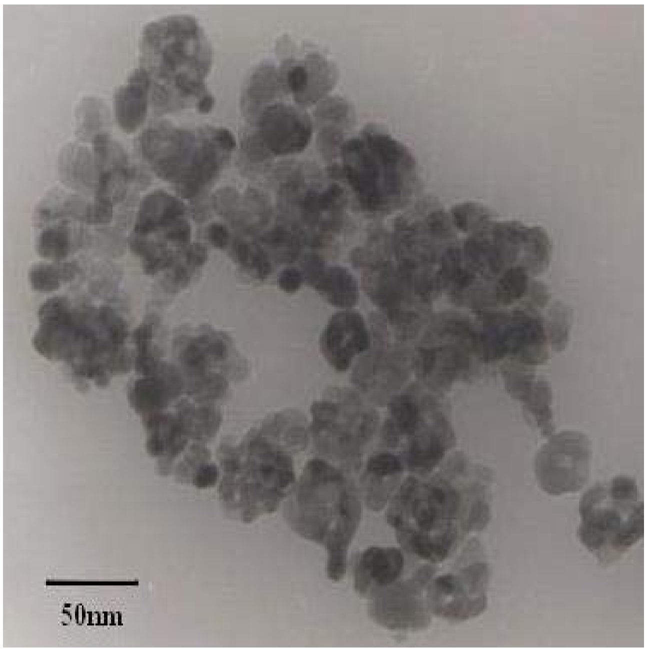


Figure 43 TEM Image of CeO_2 obtained from $(NH_4)_2Ce(NO_3)_6$ as a cerium source and PE4LE as a surfactant using microemulsion method (120,000x magnification).

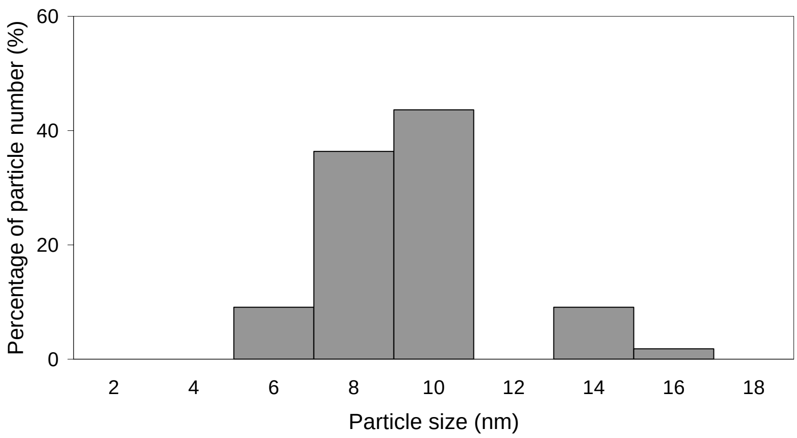


Figure 44 TEM Histograms of CeO_2 particles: $(NH_4)_2Ce(NO_3)_6$ as a cerium source, PE4LE as a surfactant using microemulsion method (120,000x magnification).

The TEM image of CeO_2 obtained from $CeCl_3{\cdot}7H_2O$ as a cerium source and PE4LE as a surfactant is shown in Figure 45. The particles are also spherical in shape the same as that from the $Ce(NO_3)_3{\cdot}6H_2O$ and $(NH_4)_2Ce(NO_3)_6$ sources. The average particle size is 11.5 ± 0.3 nm, bigger than those from the $Ce(NO_3)_3{\cdot}6H_2O$ and $(NH_4)_2Ce(NO_3)_6$ sources, and the particle size distribution is quite broad as shown in Figure 46.

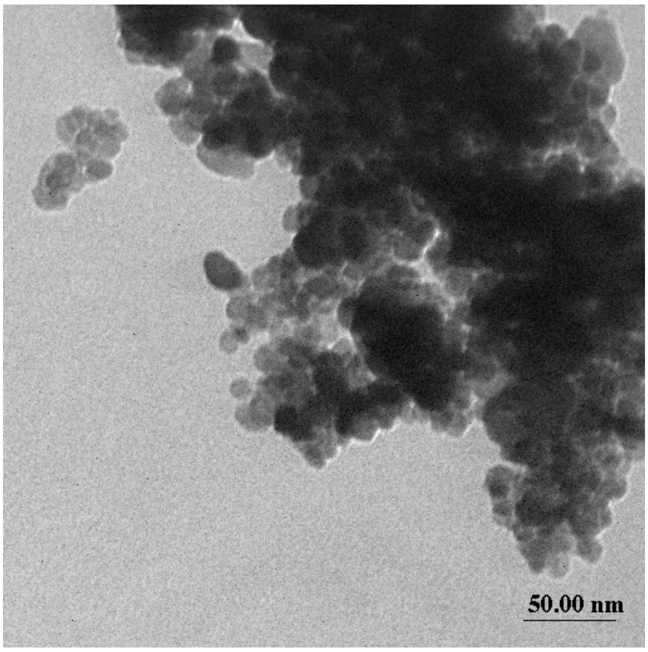


Figure 45 TEM Image of CeO_2 obtained from $CeCl_3{\cdot}7H_2O$ as a cerium source and PE4LE as a surfactant using microemulsion method (50,000x magnification).

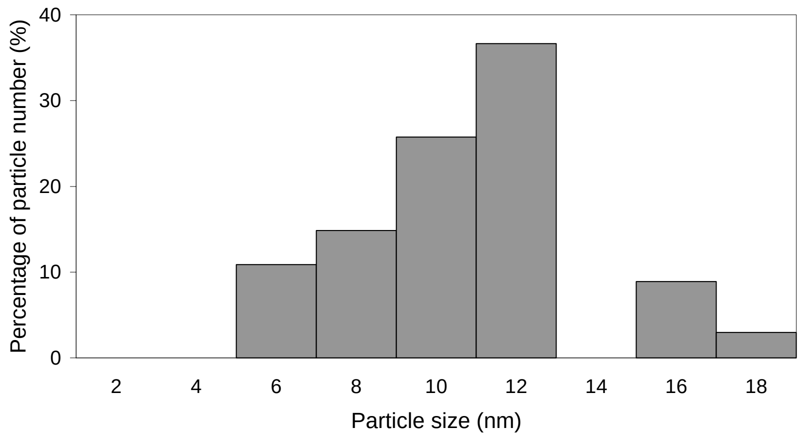


Figure 46 TEM Histograms of CeO_2 particles: $CeCl_3{\cdot}7H_2O$ as a cerium source, PE4LE as a surfactant using microemulsion method (50,000x magnification).

The average sizes of the particles prepared from microemulsion method using PE4LE are summarized in Table 5.

Table 5 Average particle sizes from TEM images of CeO_2 prepared from microemulsion method using PE4LE as a surfactant.

Method 1	Cerium source	Surfactant	Average particle size (nm)
Microemulsion	$Ce(NO_3)_3{\cdot}6H_2O$	PE4LE	11.1 ± 0.4
	$(NH_4)_2Ce(NO_3)_6$		9.4 ± 0.3
	$CeCl_3{\cdot}7H_2O$		11.5 ± 0.3

2.1.2 Nonionic surfactant: polyoxy ethylene-10-oleylether (Brij96V)

The TEM images of CeO_2 obtained from $Ce(NO_3)_3{\cdot}6H_2O$, $(NH_4)_2Ce(NO_3)_6$, and $CeCl_3{\cdot}7H_2O$ as cerium sources and Brij96V as a surfactant are shown in Figures 47, 49 and 51, respectively and the size distributions are in Figures 48, 50 and 52, respectively. The particle sizes are quite disperse. The average particle sizes from the $Ce(NO_3)_3{\cdot}6H_2O$, $(NH_4)_2Ce(NO_3)_6$, and $CeCl_3{\cdot}7H_2O$ sources are 10.2 ±

0.3, 8.2 ± 0.3, and 11.2 ± 0.4 nm, respectively as summarized in Table 6. Cerium oxide from the $(NH_4)_2Ce(NO_3)_6$ as cerium source has the smallest size, and from the $CeCl_3{\cdot}7H_2O$ is the biggest. The trend is consistent with those using PE4LE as a surfactant. The crystalline structure is also observed.

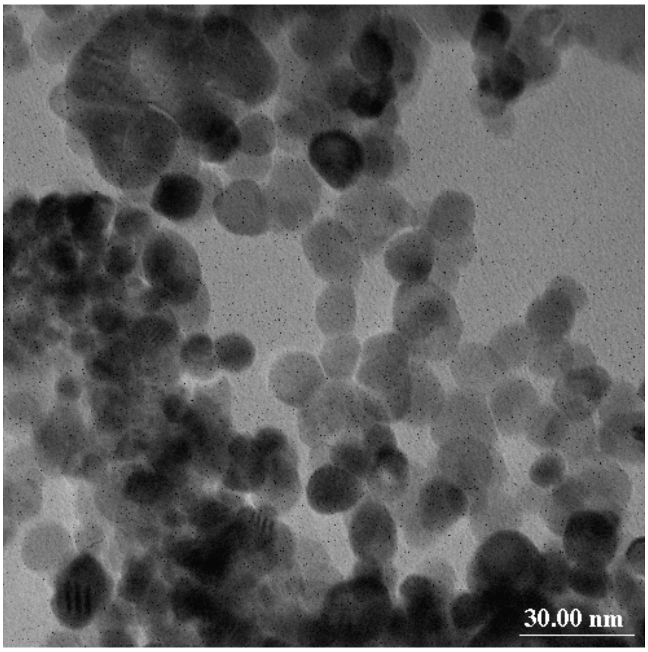


Figure 47 TEM Image of CeO_2 obtained from $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source and Brij96V as a surfactant using microemulsion method (100,000x magnification).

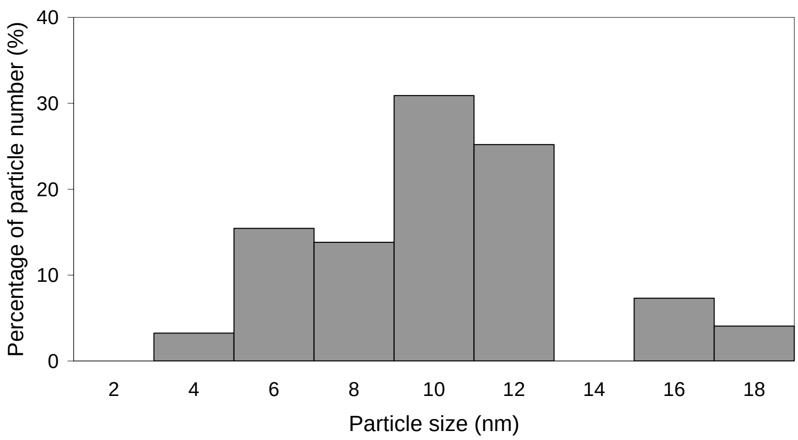


Figure 48 TEM Histograms of CeO_2 particles: $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source, Brij96V as a surfactant using microemulsion method (100,000x magnification).

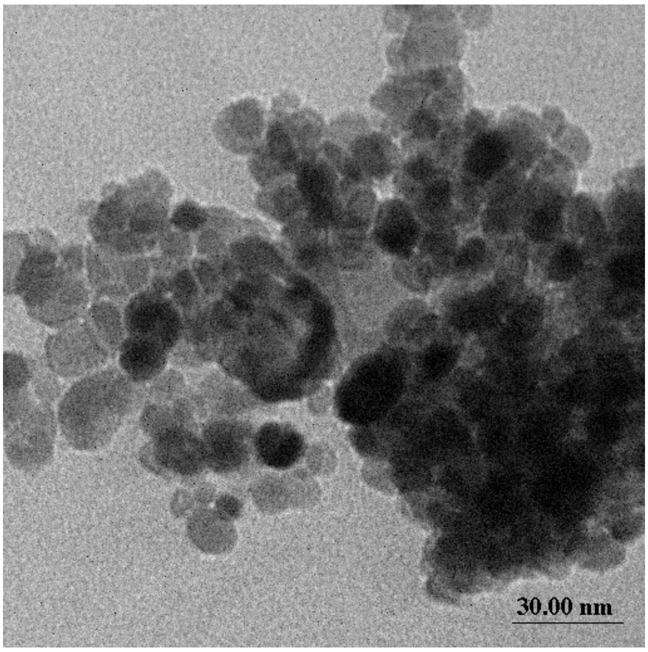


Figure 49 TEM Image of CeO_2 obtained from $(NH_4)_2Ce(NO_3)_6$ as a cerium source and Brij96V as a surfactant using microemulsion method (100,000x magnification).

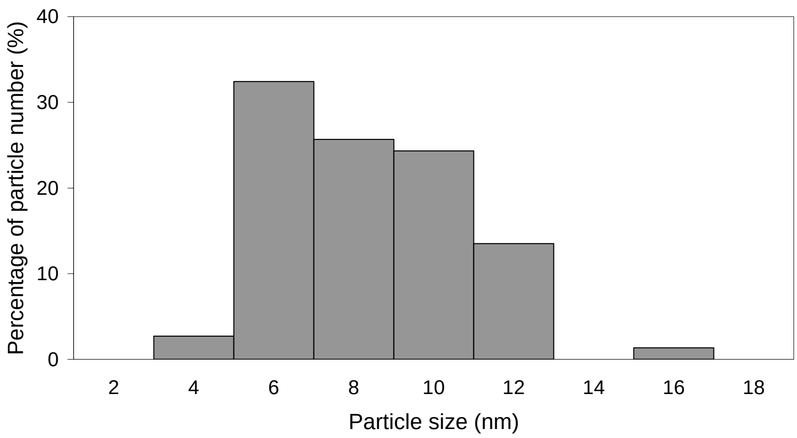


Figure 50 TEM Histograms of CeO_2 particles: $(NH_4)_2Ce(NO_3)_6$ as a cerium source, Brij96V as a surfactant using microemulsion method (100,000x magnification).

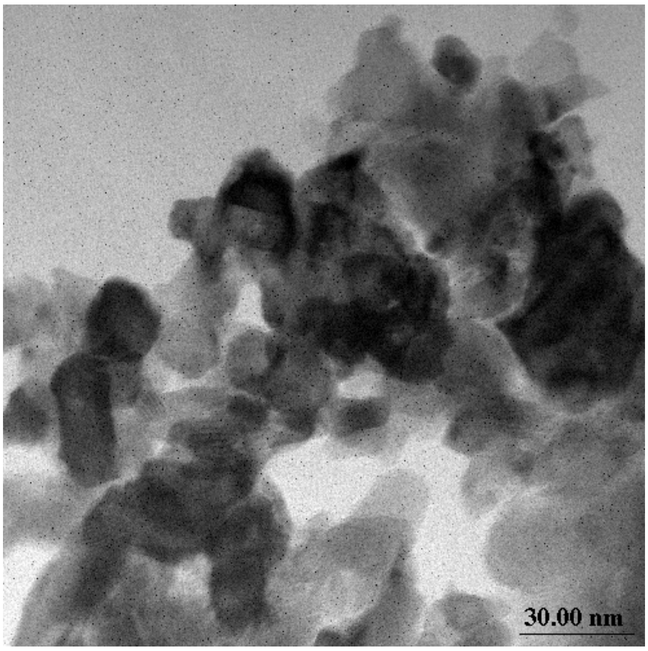


Figure 51 TEM Image of CeO_2 obtained from $CeCl_3{\cdot}7H_2O$ as a cerium source and Brij96V as a surfactant using microemulsion method (100,000x magnification).

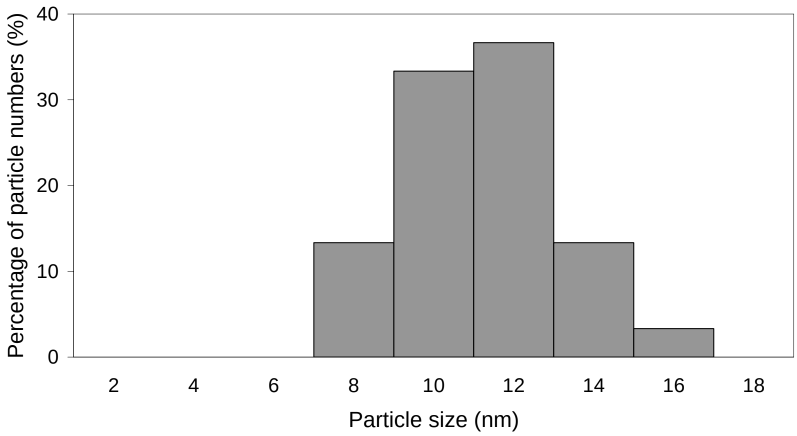


Figure 52 TEM Histograms of CeO_2 particles: $CeCl_3{\cdot}7H_2O$ as a cerium source, Brij96V as a surfactant using microemulsion method (100,000x magnification).

Table 6 Average particle sizes from TEM images of CeO_2 prepared from microemulsion method using Brij96V as a surfactant.

Method 1	Cerium source	Surfactant	Average particle size (nm)
Microemulsion	$Ce(NO_3)_3{\cdot}6H_2O$	Brij96V	10.2 ± 0.3
	$(NH_4)_2Ce(NO_3)_6$		8.2 ± 0.3
	$CeCl_3{\cdot}7H_2O$		11.2 ± 0.4

2.1.3 Cationic surfactant: cetyltrimethylammoniumbromine (CTAB)

Figures 53, 55 and 57 show TEM images of CeO_2 obtained from $Ce(NO_3)_3{\cdot}6H_2O$, $(NH_4)_2Ce(NO_3)_6$, and $CeCl_3{\cdot}7H_2O$ as cerium sources and CTAB as a surfactant, respectively and butanol as a cosurfactant using microemulsion method, and the size distributions are in Figures 54, 56 and 58 respectively.

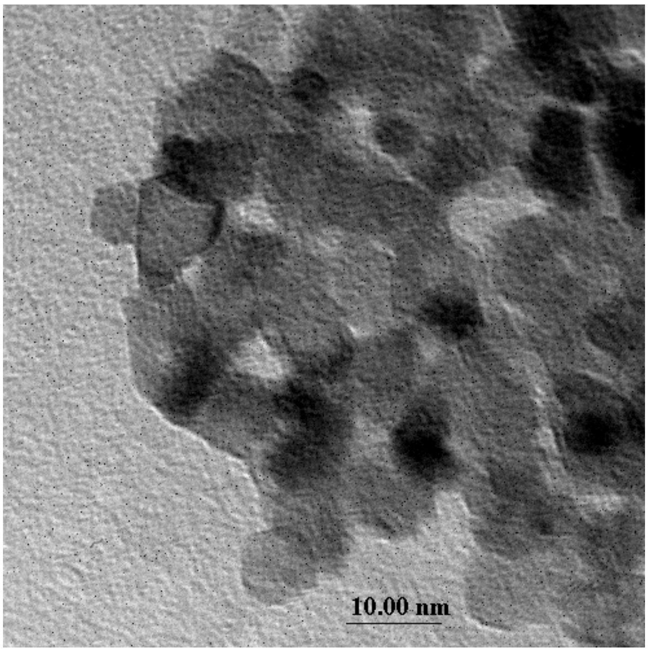


Figure 53 TEM Image of CeO_2 obtained from $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using microemulsion method (100,000x magnification).

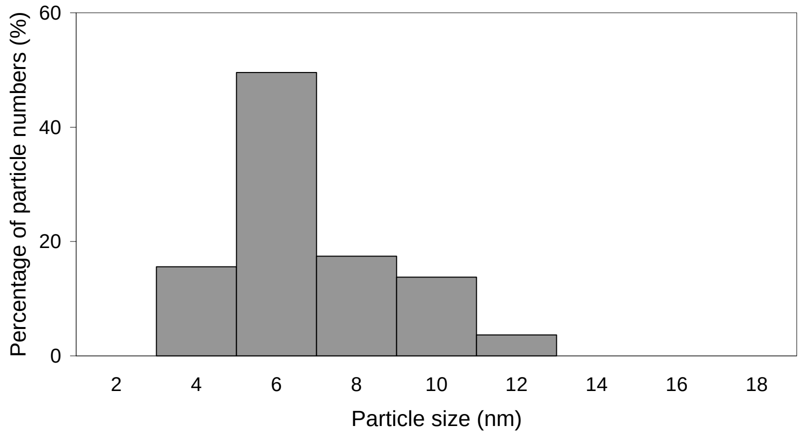


Figure 54 TEM Histograms of CeO_2 particles: $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using microemulsion method (100,000x magnification).

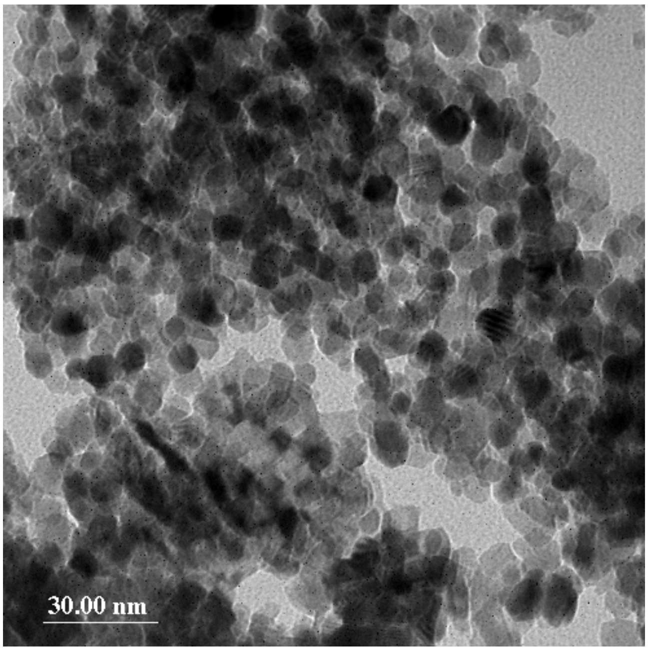


Figure 55 TEM Image of CeO_2 obtained from $(NH_4)_2Ce(NO_3)_6$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using microemulsion method (100,000x magnification).

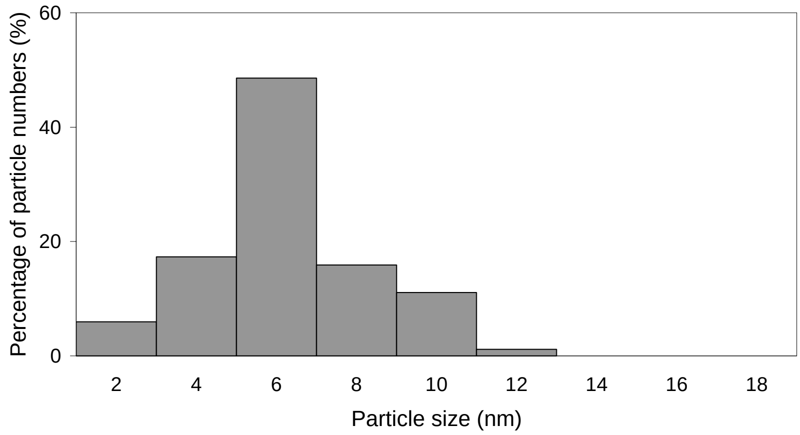


Figure 56 TEM Histograms of CeO_2 particles: $(NH_4)_2Ce(NO_3)_6$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using microemulsion method (100,000x magnification).

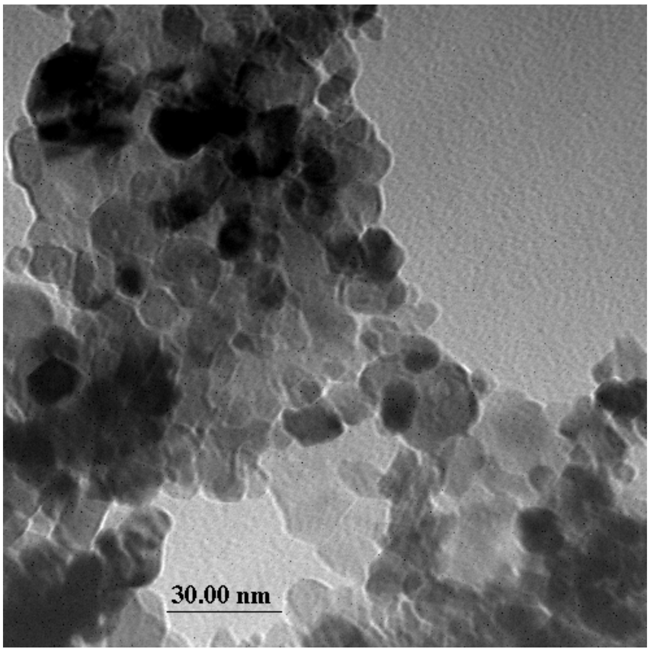


Figure 57 TEM Image of CeO_2 obtained from $CeCl_3{\cdot}7H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using microemulsion method (100,000x magnification).

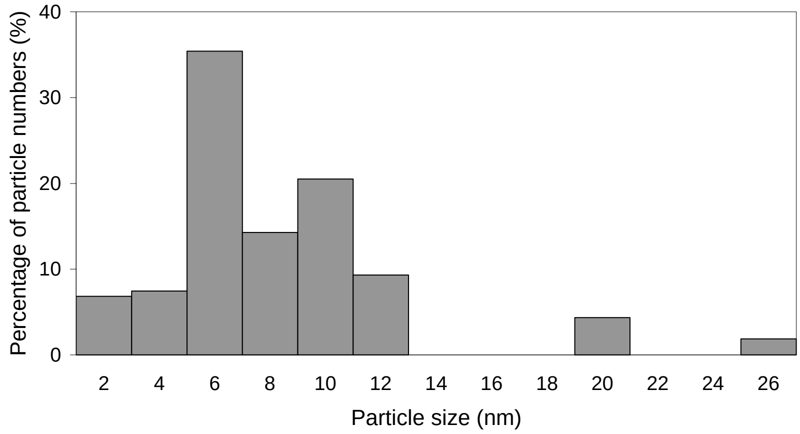


Figure 58 TEM Histograms of CeO_2 particles: $CeCl_3{\cdot}7H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using microemulsion method (100,000x magnification).

The average particle sizes from the $Ce(NO_3)_3{\cdot}6H_2O$, $(NH_4)_2Ce(NO_3)_6$, and $CeCl_3{\cdot}7H_2O$ sources are 6.7 ± 0.2, 6.1 ± 0.1, and 8.1 ± 0.4 nm, respectively, as summarized in Table 7. Cerium oxide from the $(NH_4)_2Ce(NO_3)_6$ source has the smallest size, and from the $CeCl_3{\cdot}7H_2O$ is the biggest one. The trend is consistent with those using PE4LE and Brij96V as surfactants.

Table 7 Average particle sizes from TEM images of CeO_2 prepared from microemulsion method using CTAB as a surfactant and butanol as a cosurfactant.

Method 1	Cerium source	Surfactant	Average particle size (nm)
Microemulsion	$Ce(NO_3)_3{\cdot}6H_2O$	CTAB (using butanol as a cosurfactant)	6.7 ± 0.2
	$(NH_4)_2Ce(NO_3)_6$		6.1 ± 0.1
	$CeCl_3{\cdot}7H_2O$		8.1 ± 0.4

With the processing of calcination CeO_2 particles was confirmed by the analytical results of x-ray diffraction spectroscopy (XRD) and energy dispersive spectroscopy (EDS). The XRD analysis of the CeO_2 obtained from the preparation are shown in Figure 59. It was found that the powders showed the same crystalline structure for both $Ce(NO_3)_3{\cdot}6H_2O$ and $(NH_4)_2Ce(NO_3)_6$ sources that were used (note: CeO_2 obtained from $CeCl_3{\cdot}7H_2O$ as a cerium source is not suffice to analyze by XRD). Peaks were attributed to crystalline of CeO_2 with a cubic fluorite structure. EDS spectra of the CeO_2 obtained from the preparation are shown in Figure 60. In Figures, Ce and O peaks are clearly seen.

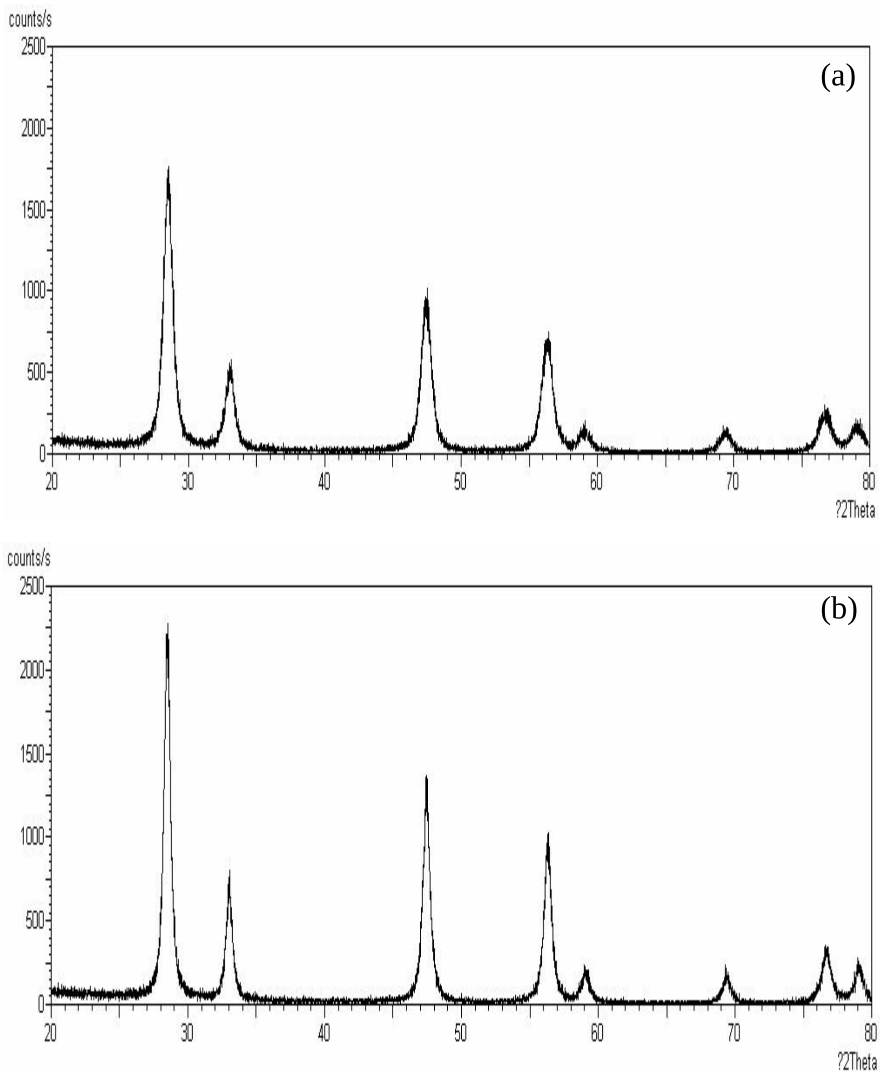


Figure 59 X-Ray diffraction pattern of CeO_2 powders obtained from microemulsion method (a) $Ce(NO_3)_3{\cdot}6H_2O$ (b) $(NH_4)_2Ce(NO_3)_6$ as a cerium source.

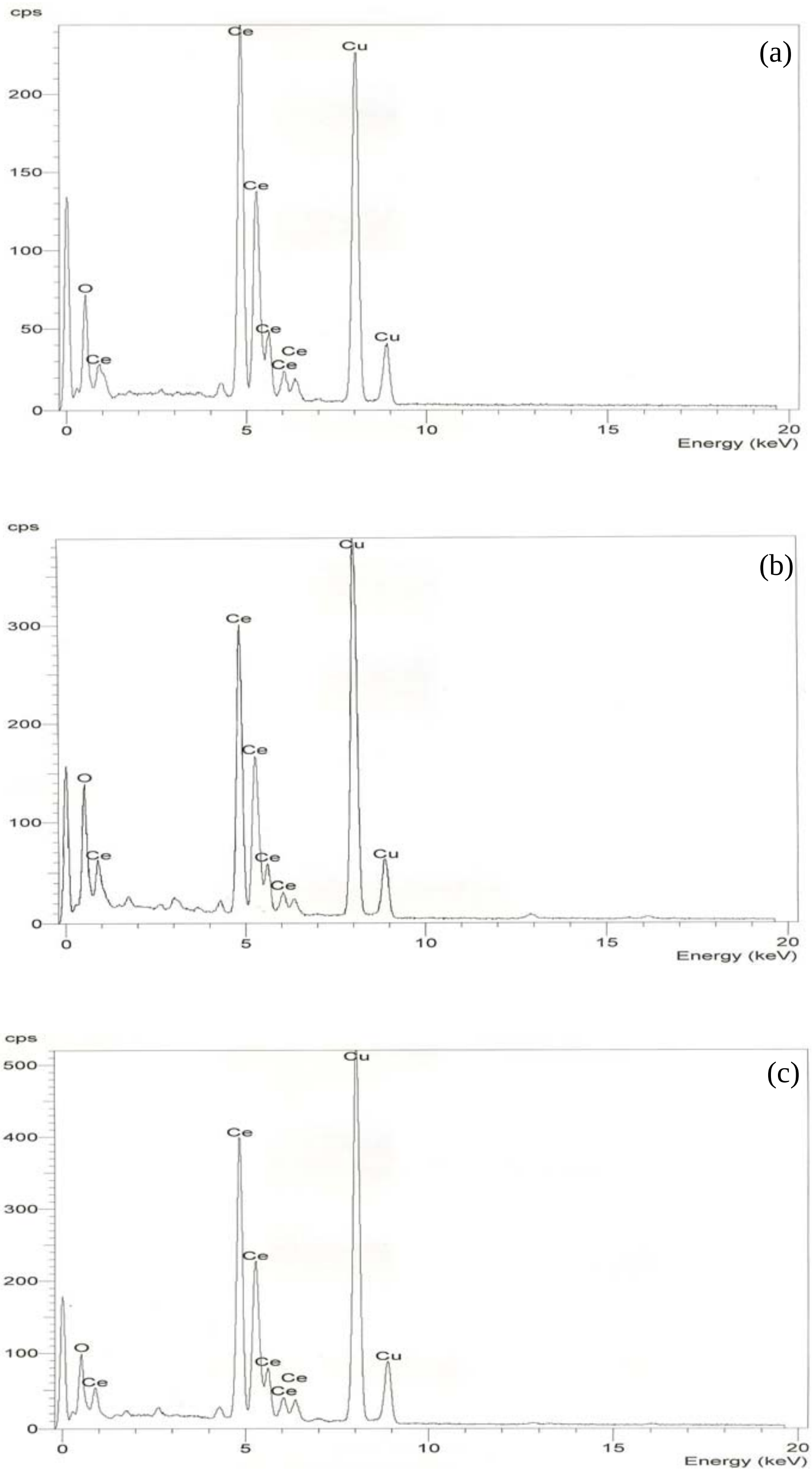


Figure 60 EDS spectrum of CeO_2 powders obtained from microemulsion method (a) $Ce(NO_3)_3{\cdot}6H_2O$ (b) $(NH_4)_2Ce(NO_3)_6$ and (c) $CeCl_3{\cdot}7H_2O$as a cerium source.

2.2 Combined methods of homogeneous precipitation and microemulsion

2.2.1 Nonionic surfactant: polyoxyethylene-4-lauryl ether (PE4LE)

By adding an amount of surfactant into the mixed solution of organic solvent and aqueous solution containing methyl oxalate and cerium source, the uniform and transparent W/O microemulsion was prepared first. The homogeneous precipitation of methyl oxalate with cerium source takes place within them. Since the water droplets contained the identical solution, located in the similar surroundings, and went through the same reactions in them, the size of water droplets, the stability of water droplets itself and the particles formed in them were nearly the same.

On the other hand, when the stable nucleus of cerium oxalate hydrate was formed, it enlarged through the growth and aggregation of primary particles. As the particle size reached the water droplets, the surfactants would cover the particles surface and hinder further particle growing, which also restricted the size of particles.

TEM images and particle sizes distribution of CeO_2 obtained from $Ce(NO_3)_3{\cdot}6H_2O$, $(NH_4)_2Ce(NO_3)_6$, and $CeCl_3{\cdot}7H_2O$ as cerium sources and PE4LE as a surfactant using combined methods of homogeneous precipitation and microemulsion are shown in Figures 61 to 66.

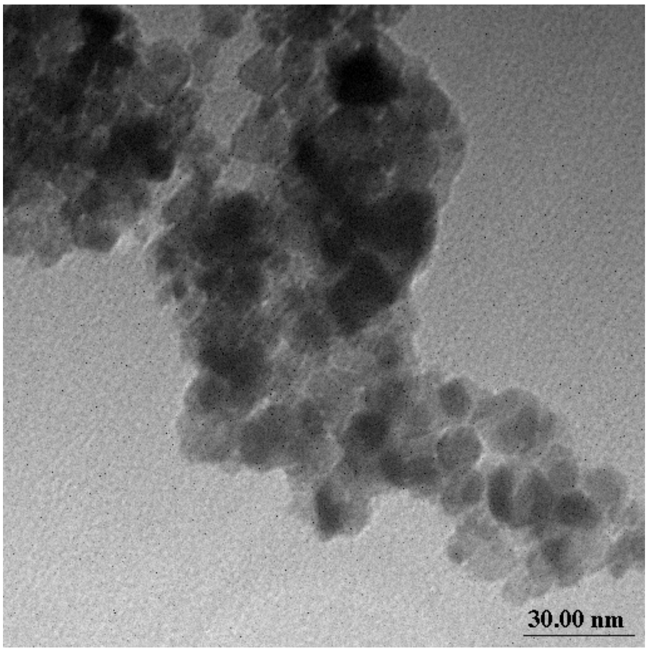


Figure 61 TEM Image of CeO_2 obtained from $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source and PE4LE as a surfactant using combined methods of homogeneous precipitation and microemulsion (100,000x magnification).

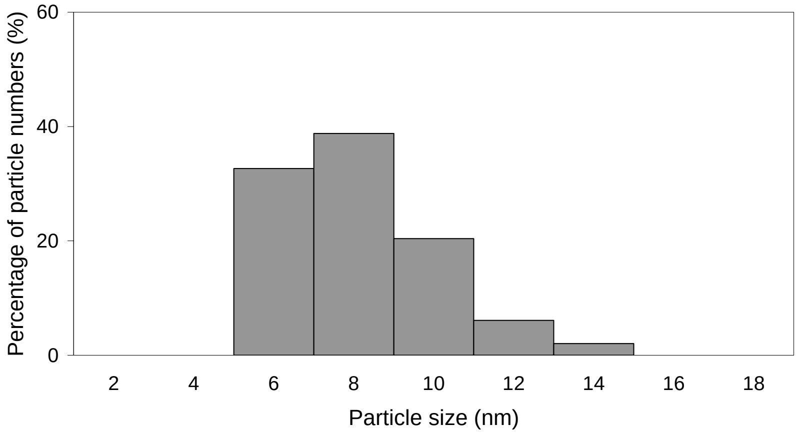


Figure 62 TEM Histograms of CeO_2 particles: $Ce(NO_3)_3{\cdot}6H_2O$ as cerium source, PE4LE as a surfactant using combined methods of homogeneous precipitation and microemulsion (100,000x magnification).

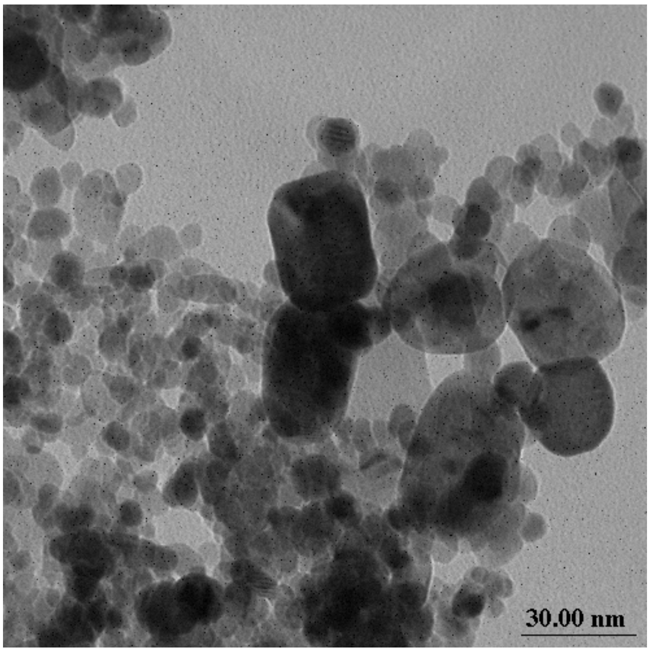


Figure 63 TEM Image of CeO_2 obtained from $(NH_4)_2Ce(NO_3)_6$ as a cerium source and PE4LE as a surfactant using combined methods of homogeneous precipitation and microemulsion (100,000x magnification).

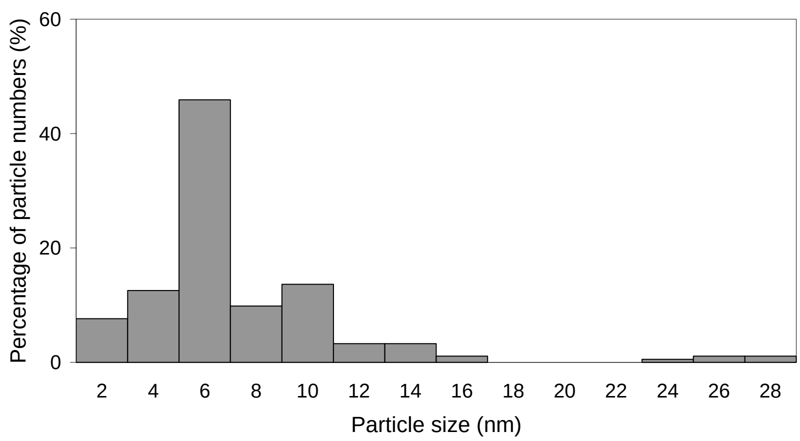


Figure 64 TEM Histograms of CeO_2 particles: $(NH_4)_2Ce(NO_3)_6$ as a cerium source, PE4LE as a surfactant using combined methods of homogeneous precipitation and microemulsion (100,000x magnification).

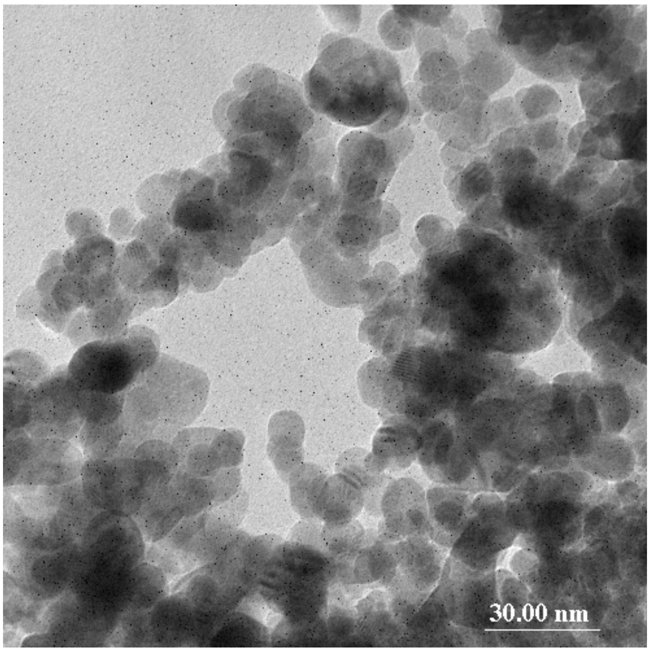


Figure 65 TEM Image of CeO_2 obtained from $CeCl_3{\cdot}7H_2O$ as a cerium source and PE4LE as a surfactant using combined methods of homogeneous precipitation and microemulsion (100,000x magnification).

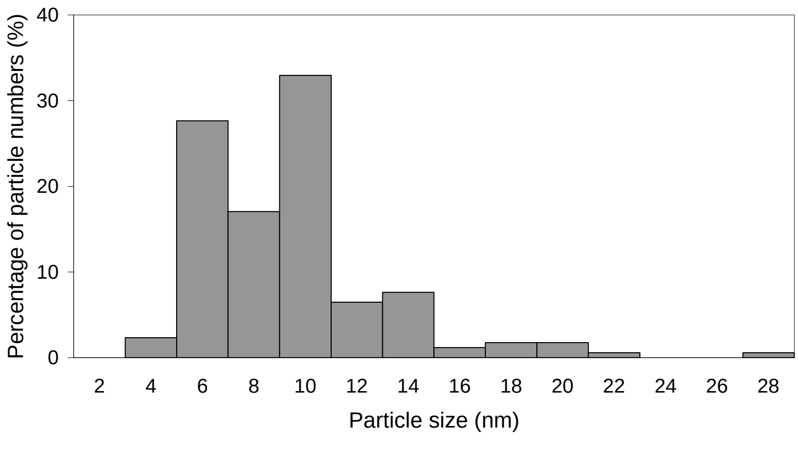


Figure 66 TEM Histograms of CeO_2 particles: $CeCl_3{\cdot}7H_2O$ as a cerium source, PE4LE as a surfactant using combined methods of homogeneous precipitation and microemulsion (100,000x magnification).

The average sizes of cerium oxide particles from $Ce(NO_3)_3{\cdot}6H_2O$, $(NH_4)_2Ce(NO_3)_6$, and $CeCl_3{\cdot}7H_2O$ are 7.9 ± 0.3, 7.2 ± 0.3, and 9.2 ± 0.3 nm, respectively and are summarized in Table 8.

Table 8 Average particle sizes from TEM images of CeO_2 prepared from combined methods of homogeneous precipitation and microemulsion using PE4LE as a surfactant.

Method 2	Cerium source	Surfactant	Average particle size (nm)
Homogeneous precipitation and microemulsion.	$Ce(NO_3)_3{\cdot}6H_2O$	PE4LE	7.9 ± 0.3
	$(NH_4)_2Ce(NO_3)_6$		7.2 ± 0.3
	$CeCl_3{\cdot}7H_2O$		9.2 ± 0.3

2.2.2 Cationic surfactant: cetyltrimethylammoniumbromine (CTAB)

TEM Images and particle sizes distributions of CeO_2 obtained from $Ce(NO_3)_3{\cdot}6H_2O$, $(NH_4)_2Ce(NO_3)_6$, and $CeCl_3{\cdot}7H_2O$ as cerium sources and CTAB as a surfactant and butanol as a cosurfactant using combined methods of homogeneous precipitation and microemulsion are shown in Figures 67 to 72.

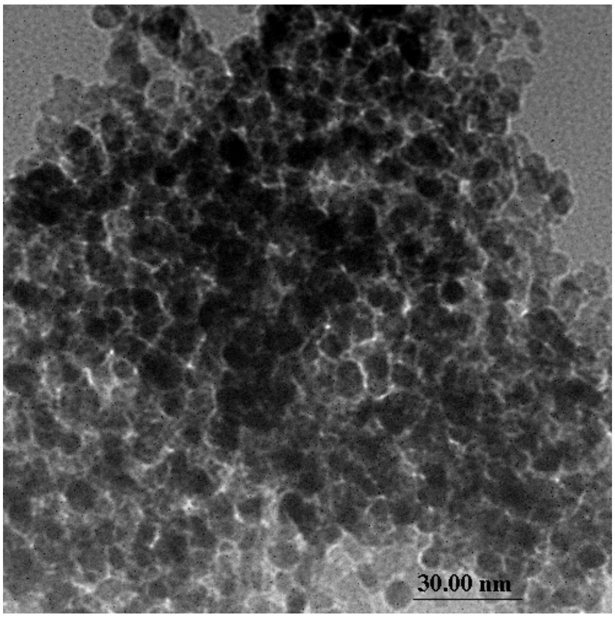


Figure 67 TEM Image of CeO_2 obtained from $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using combined methods of homogeneous precipitation and microemulsion (100,000x magnification).

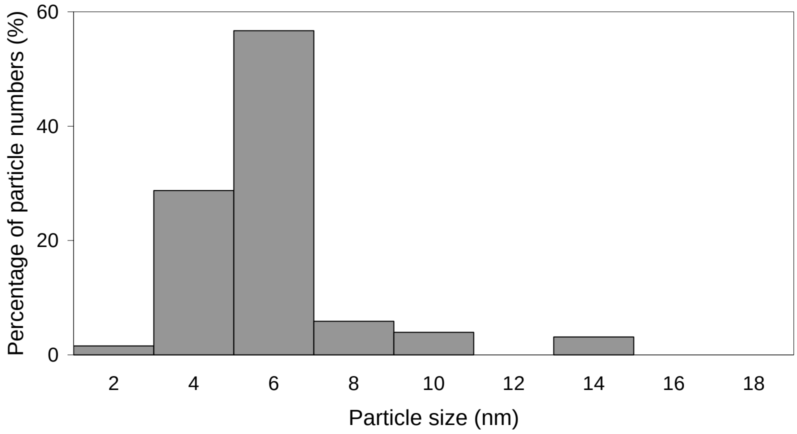


Figure 68 TEM Histograms of CeO_2 particles: $Ce(NO_3)_3 \cdot 6H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using combined methods of homogeneous precipitation and microemulsion (100,000x magnification).

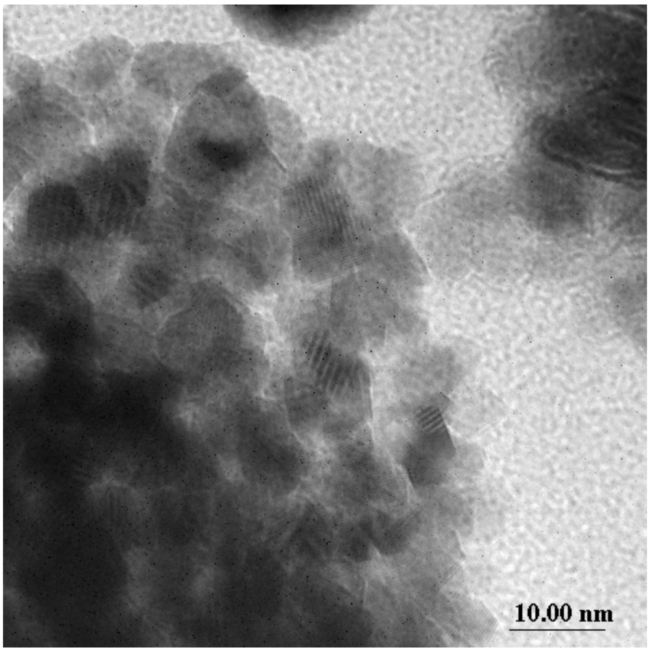


Figure 69 TEM Image of CeO_2 obtained from $(NH_4)_2Ce(NO_3)_6$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using combined methods of homogeneous precipitation and microemulsion (250,000x magnification).

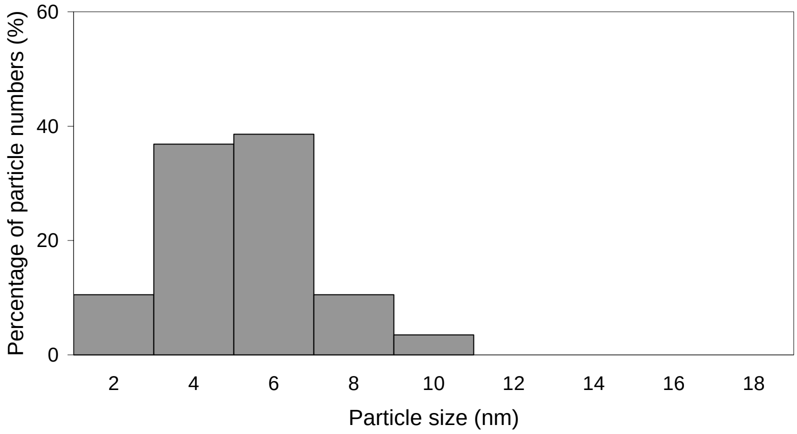


Figure 70 TEM Histograms of CeO_2 particles: $(NH_4)_2Ce(NO_3)_6$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using combined methods of homogeneous precipitation and microemulsion (250,000x magnification).

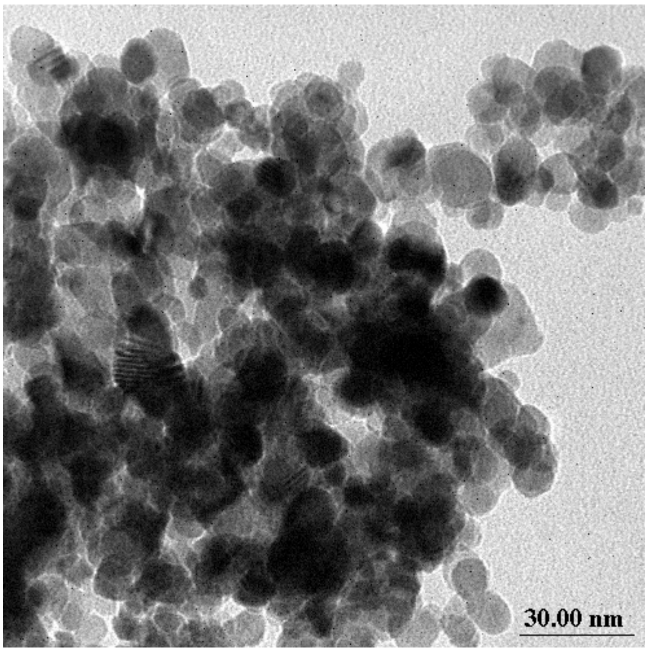


Figure 71 TEM Image of CeO_2 obtained from $CeCl_3{\cdot}7H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using combined methods of homogeneous precipitation and microemulsion (100,000x magnification).

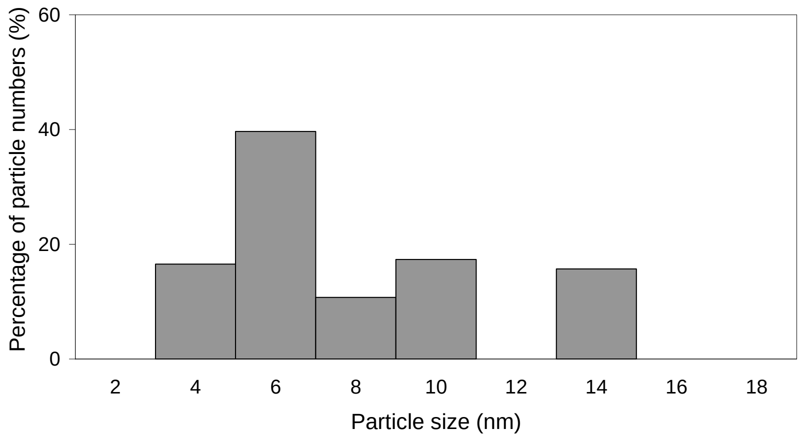


Figure 72 TEM Histograms of CeO_2 particles: $CeCl_3 \cdot 7H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant using combined methods of homogeneous precipitation and microemulsion (100,000x magnification).

The average sizes of cerium oxide particles from $Ce(NO_3)_3 \cdot 6H_2O$, $(NH_4)_2Ce(NO_3)_6$, and $CeCl_3 \cdot 7H_2O$ sources, CTAB as a surfactant and butanol as a cosurfactant using combined methods of homogeneous precipitation and microemulsion are 5.7 ± 0.1, 4.9 ± 0.2, and 7.7 ± 0.3 nm, respectively and are summarized in Table 9.

Table 9 Average particle sizes from TEM images of CeO_2 prepared from combined methods of homogeneous precipitation and microemulsion using CTAB as a surfactant and butanol as a cosurfactant.

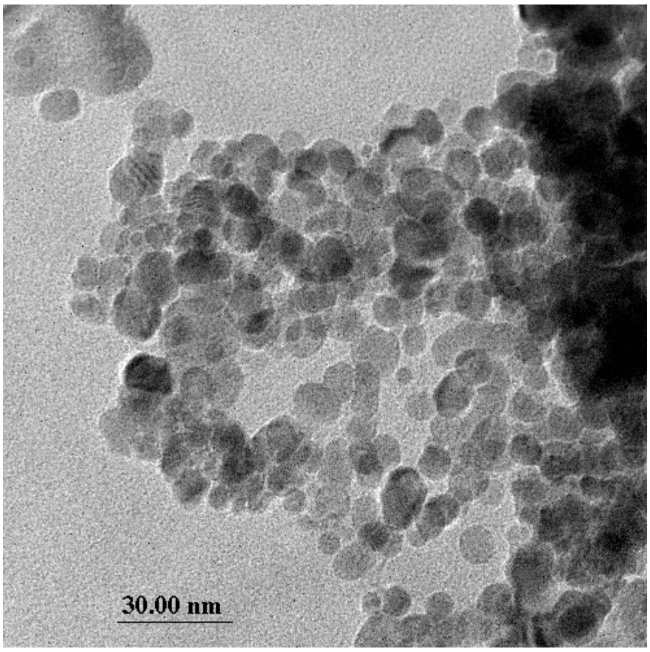
Method 2	Cerium source	Surfactant	Average particle size (nm)
Homogeneous precipitation and microemulsion.	$Ce(NO_3)_3 \cdot 6H_2O$	CTAB (using butanol as a cosurfactant)	5.7 ± 0.1
	$(NH_4)_2Ce(NO_3)_6$		4.9 ± 0.2
	$CeCl_3 \cdot 6H_2O$		7.7 ± 0.3

2.3 <u>Mixing of two microemulsions</u>

The method consists of mixing of two microemulsions carrying the appropriate reactants in order to obtain the desired particles. A schematic figure of this method is represented in Figure 18. It can be seen that after mixing both microemulsions containing the reactants, interchange of the reactant takes place during the collisions of the water droplets in the microemulsion. The reaction then takes place inside the droplets (nucleation and growth), which control the final size of the particles.

2.3.1 Nonionic surfactant: polyoxyethylene-4-lauryl ether (PE4LE)

TEM Images and particle sizes distributions of CeO_2 obtained from $Ce(NO_3)_3{\cdot}6H_2O$, $(NH_4)_2Ce(NO_3)_6$, and $CeCl_3{\cdot}7H_2O$ as cerium sources and PE4LE as a surfactant by mixing of two microemulsions are shown in Figures 73 to 78.



<u>Figure 73</u> TEM Image of CeO_2 obtained from $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source and PE4LE as a surfactant by mixing of two microemulsions (100,000x magnification).

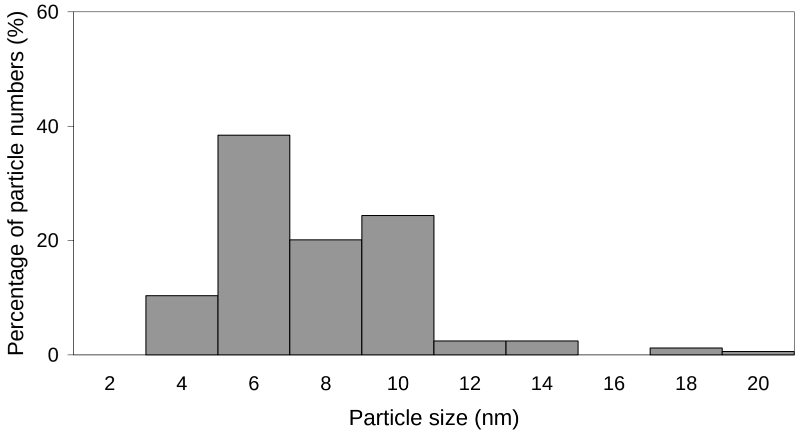


Figure 74 TEM Histograms of CeO_2 particles: $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source, PE4LE as a surfactant by mixing of two microemulsions (100,000x magnification).

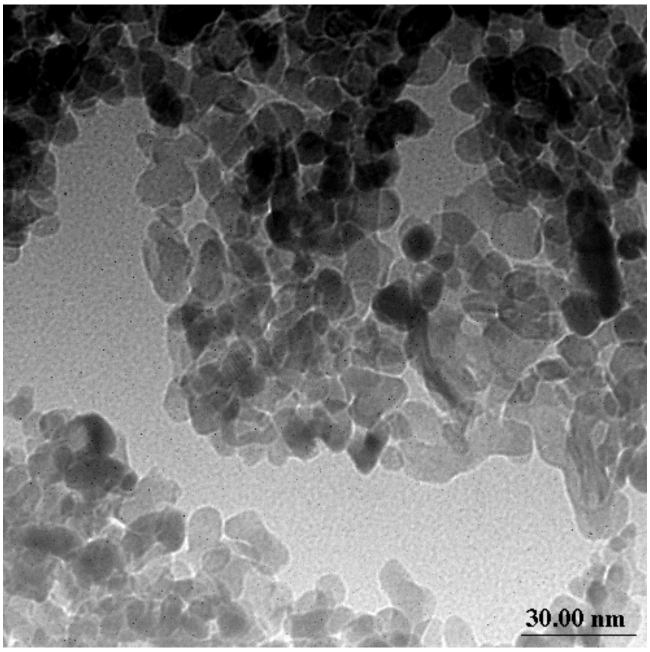


Figure 75 TEM Image of CeO_2 obtained from $(NH_4)_2Ce(NO_3)_6$ as a cerium source and PE4LE as a surfactant by mixing of two microemulsions (100,000x magnification).

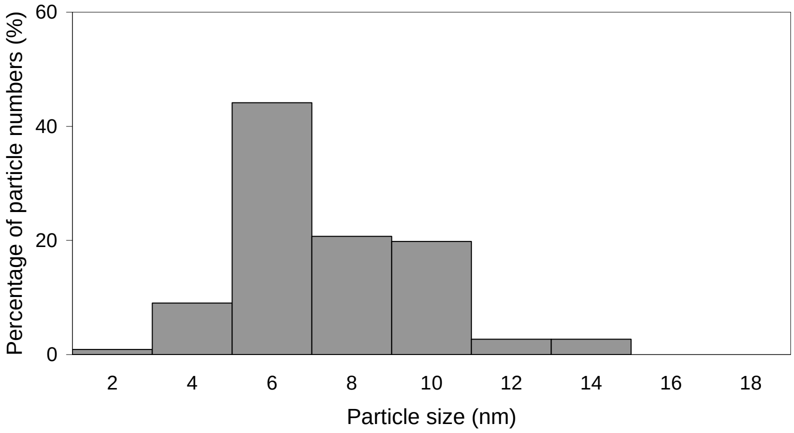


Figure 76 TEM Histograms of CeO_2 particles: $(NH_4)_2Ce(NO_3)_6$ as a cerium source, PE4LE as a surfactant by mixing of two microemulsions (100,000x magnification).

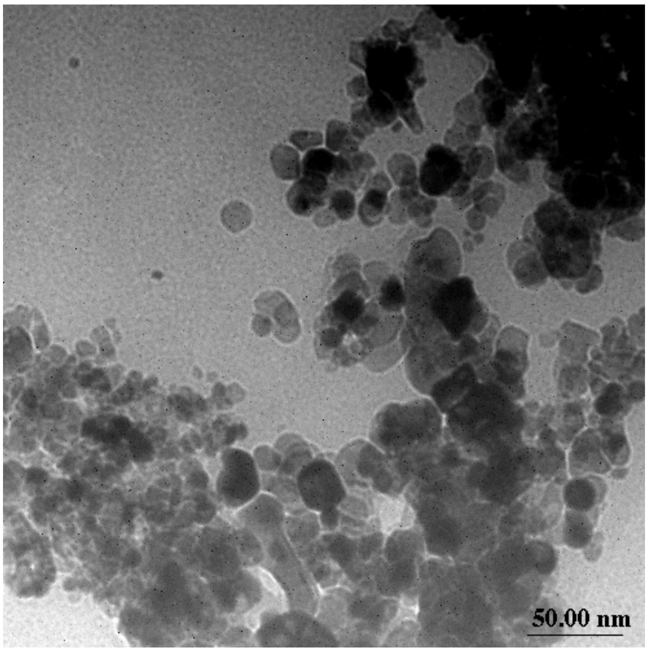


Figure 77 TEM Image of CeO_2 obtained from $CeCl_3{\cdot}7H_2O$ as a cerium source and PE4LE as a surfactant by mixing of two microemulsions (50,000x magnification).

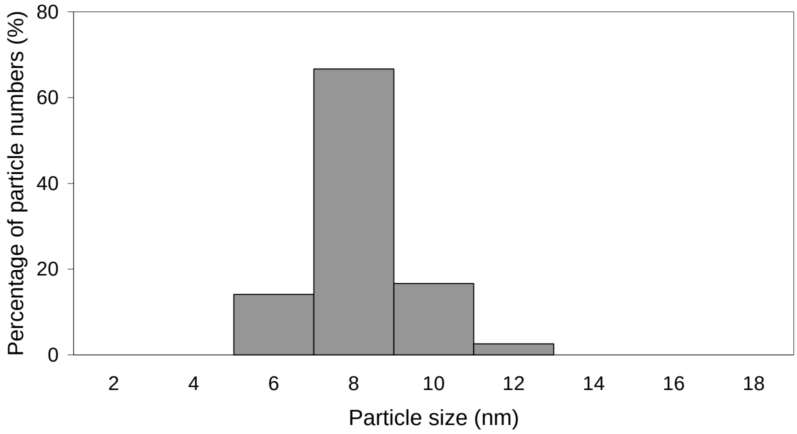


Figure 78 TEM Histograms of CeO_2 particles: $CeCl_3{\cdot}7H_2O$ as a cerium source, PE4LE as a surfactant by mixing of two microemulsions (50,000x magnification).

The average sizes of cerium oxide particles from $Ce(NO_3)_3{\cdot}6H_2O$, $(NH_4)_2Ce(NO_3)_6$, and $CeCl_3{\cdot}7H_2O$ sources, PE4LE as a surfactant by mixing of two microemulsions are 7.6 ± 0.3, 7.1 ± 0.2, and 8.8 ± 0.2 nm, respectively as summarized in Table 10.

Table 10 Average particle sizes from TEM images of CeO_2 prepared from mixing of two microemulsions using PE4LE as a surfactant.

Method 3	Cerium source	Surfactant	Average particle size (nm)
Mixing of two microemulsions	$Ce(NO_3)_3{\cdot}6H_2O$	PE4LE	7.6 ± 0.3
	$(NH_4)_2Ce(NO_3)_6$		7.1 ± 0.2
	$CeCl_3{\cdot}7H_2O$		8.8 ± 0.2

2.3.2 Cationic surfactant:cetyltrimethylammoniumbromine (CTAB)

TEM Images and particle sizes distributions of CeO_2 obtained from $Ce(NO_3)_3{\cdot}6H_2O$, $(NH_4)_2Ce(NO_3)_6$, and $CeCl_3{\cdot}7H_2O$ as cerium sources and CTAB as a surfactant and butanol as a cosurfactant by mixing of two microemulsions are shown in Figures 79 to 84.

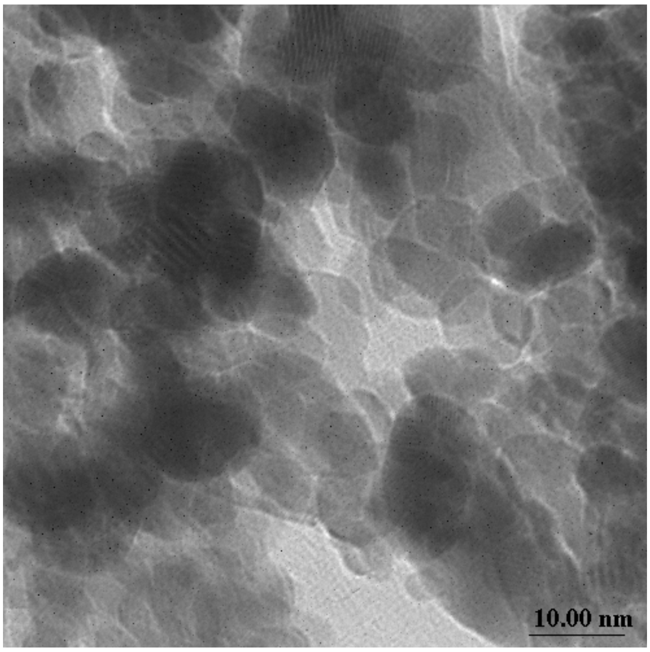


Figure 79 TEM Image of CeO_2 obtained from $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant by mixing of two microemulsions (250,000x magnification).

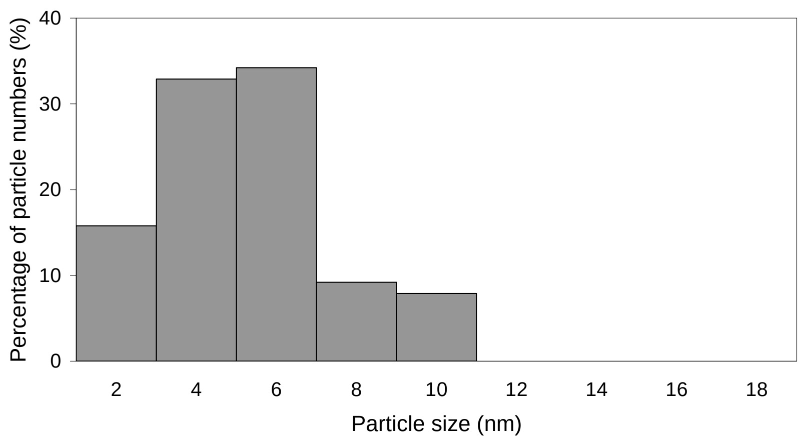


Figure 80 TEM Histograms of CeO_2 particles: $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant by mixing of two microemulsions (250,000x magnification).

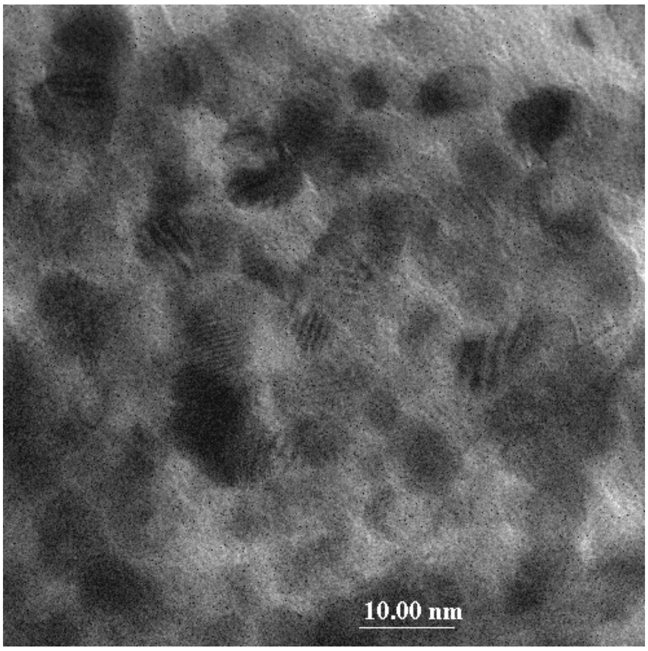


Figure 81 TEM Image of CeO_2 obtained from $(NH_4)_2Ce(NO_3)_6$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant by mixing of two microemulsions (100,000x magnification).

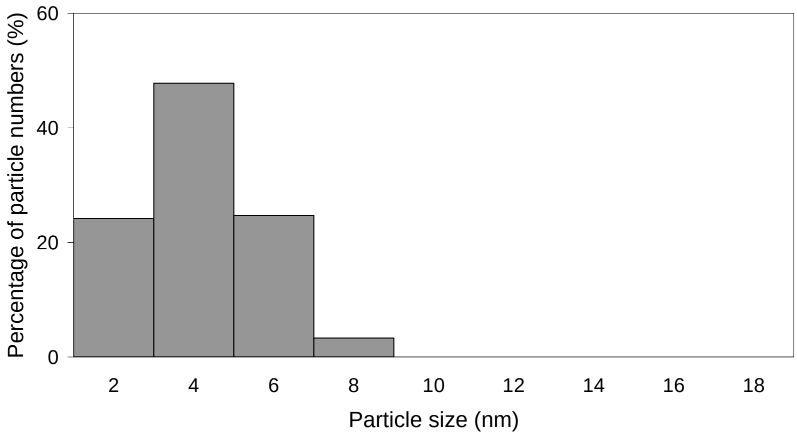


Figure 82 TEM Histograms of CeO_2 particles: $(NH_4)_2Ce(NO_3)_6$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant by mixing of two microemulsions (100,000x magnification).

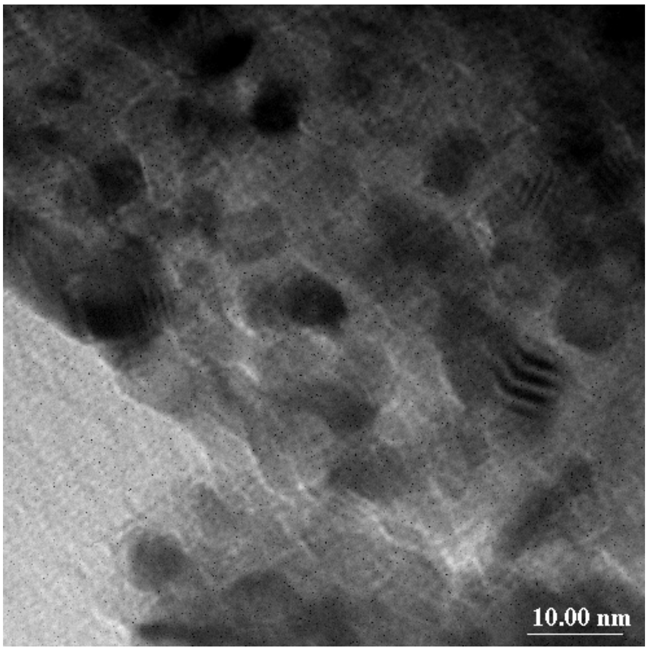


Figure 83 TEM Image of CeO_2 obtained from $CeCl_3{\cdot}7H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant by mixing of two microemulsions (100,000x magnification).

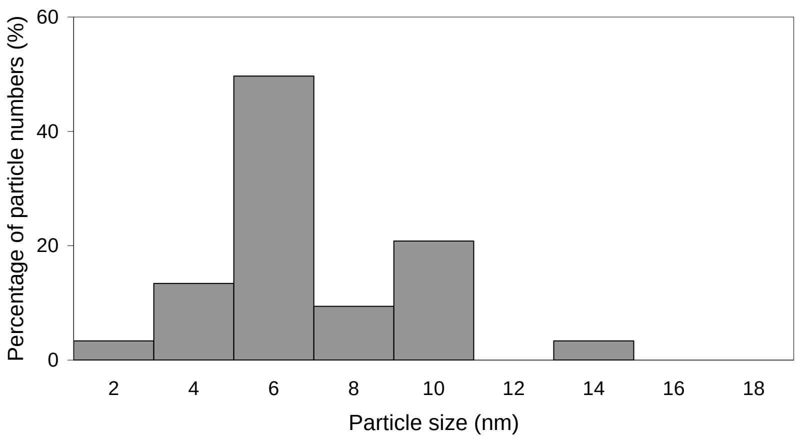


Figure 84 TEM Histograms of CeO_2 particles: $CeCl_3{\cdot}7H_2O$ as a cerium source, CTAB as a surfactant and butanol as a cosurfactant by mixing of two microemulsions (100,000x magnification).

The average sizes of cerium oxide particles from $Ce(NO_3)_3{\cdot}6H_2O$, $(NH_4)_2Ce(NO_3)_6$, and $CeCl_3{\cdot}7H_2O$ sources, CTAB as a surfactant and butanol as a cosurfactant by mixing of two microemulsions are 5.1 ± 0.3, 4.1 ± 0.1, and 6.7 ± 0.2 nm, respectively as summarized in Table 11.

Table 11 Average particle sizes from TEM images of CeO_2 prepared from mixing of two microemulsions using CTAB as a surfactant and butanol as a cosurfactant.

Method 3	Cerium source	Surfactant	Average particle size (nm)
Mixing of two microemulsions	$Ce(NO_3)_3 \cdot 6H_2O$	CTAB (using butanol as a cosurfactant)	5.1 ± 0.3
	$(NH_4)_2Ce(NO_3)_6$		4.1 ± 0.1
	$CeCl_3 \cdot 7H_2O$		6.7 ± 0.2

The average particle sizes of cerium oxide from all methods are summarized in Table 12.

Table 12 Average particle size from TEM images using different methods.
Method 1 Microemulsion method.
Method 2 Combined methods of homogeneous precipitation and microemulsion.
Method 3 Mixing of two microemulsions

Method	Cerium source	Surfactant	Average particle size (nm)
Method 1	$Ce(NO_3)_3{\cdot}6H_2O$	PE4LE	11.1 ± 0.4
	$(NH_4)_2Ce(NO_3)_6$		9.4 ± 0.3
	$CeCl_3{\cdot}7H_2O$		11.5 ± 0.3
	$Ce(NO_3)_3{\cdot}6H_2O$	Brij96V	10.2 ± 0.3
	$(NH_4)_2Ce(NO_3)_6$		8.2 ± 0.3
	$CeCl_3{\cdot}7H_2O$		11.2 ± 0.4
	$Ce(NO_3)_3{\cdot}6H_2O$	CTAB (used butanol as cosurfactant)	6.7 ± 0.2
	$(NH_4)_2Ce(NO_3)_6$		6.1 ±0.1
	$CeCl_3{\cdot}7H_2O$		8.1 ± 0.4
Method 2	$Ce(NO_3)_3{\cdot}6H_2O$	PE4LE	7.9 ± 0.3
	$(NH_4)_2Ce(NO_3)_6$		7.2 ± 0.3
	$CeCl_3{\cdot}7H_2O$		9.2 ± 0.3
	$Ce(NO_3)_3{\cdot}6H_2O$	CTAB (used butanol as cosurfactant)	5.7 ± 0.1
	$(NH_4)_2Ce(NO_3)_6$		4.9 ± 0.2
	$CeCl_3{\cdot}7H_2O$		7.7 ± 0.3
Method 3	$Ce(NO_3)_3{\cdot}6H_2O$	PE4LE	7.6 ± 0.3
	$(NH_4)_2Ce(NO_3)_6$		7.1 ± 0.2
	$CeCl_3{\cdot}7H_2O$		8.8 ± 0.2
	$Ce(NO_3)_3{\cdot}6H_2O$	CTAB (used butanol as cosurfactant)	5.1 ± 0.3
	$(NH_4)_2Ce(NO_3)_6$		4.1 ± 0.1
	$CeCl_3{\cdot}7H_2O$		6.7 ± 0.2

2.4 Effect of technique of preparation

The experiment of this study is divided into three techniques:

- Method 1: microemulsion method.
- Method 2: combined methods of homogeneous precipitation and microemulsion.
- Method 3: mixing of two microemulsions.

The advantages of microemulsion method are soft chemistry, demanding no extreme pressure or temperature control, easy to handle, requiring no special or expensive equipment and enable to restrict the size of particle. In method 2 it is known that the combined method of homogeneous precipitation and microemulsion not only eliminate the gradient of precipitants concentration, but also confine the space of precipitating reaction thus can restrict the growth and aggregation of grains and can control the size of particles. In method 3 each microemulsion can restrict the size of particles, after mixing both microemulsions containing the reactants, interchange of the reactant takes place during the collisions of the water droplets in the microemulsion. The reaction then takes place inside the droplets (nucleation and growth), which control the final size of the particles to small particles. The comparison of these methods are shown in Figures 85 to 87.

It can be seen that the average particle size of CeO_2 obtained from method 3 are smallest and the average particle size of CeO_2 obtained from method 2 are smaller than that from method 1 the trend are the same with different cerium sources and surfactants.

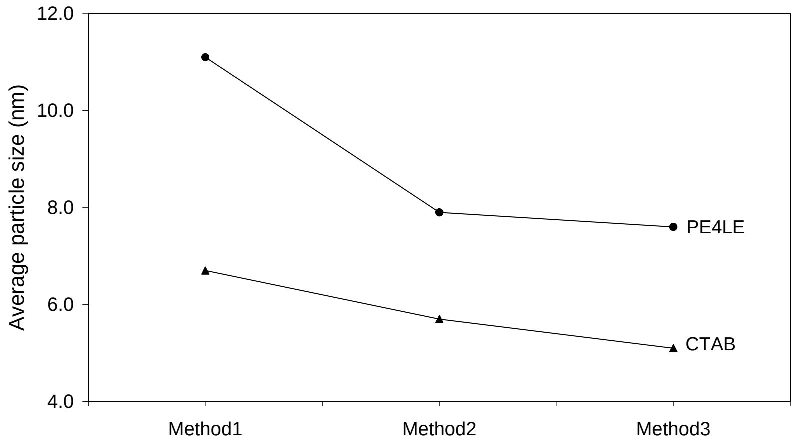


Figure 85 Variation of the average size of CeO_2 particles with different techniques using $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source.

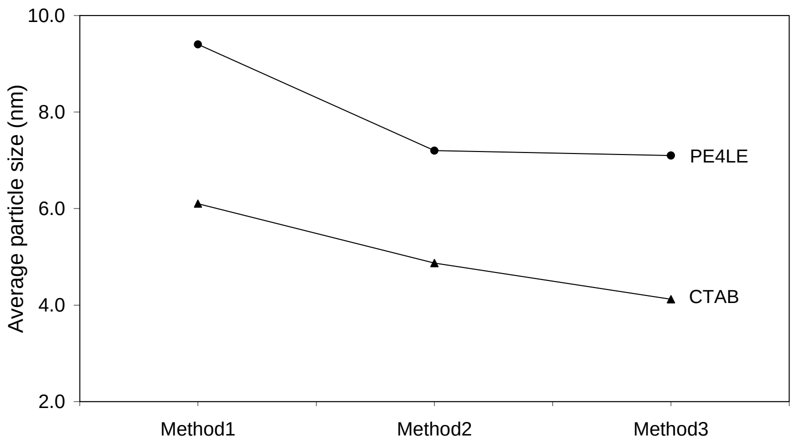


Figure 86 Variation of the average size of CeO_2 particles with different techniques using $(NH_4)_2Ce(NO_3)_6$ as a cerium source.

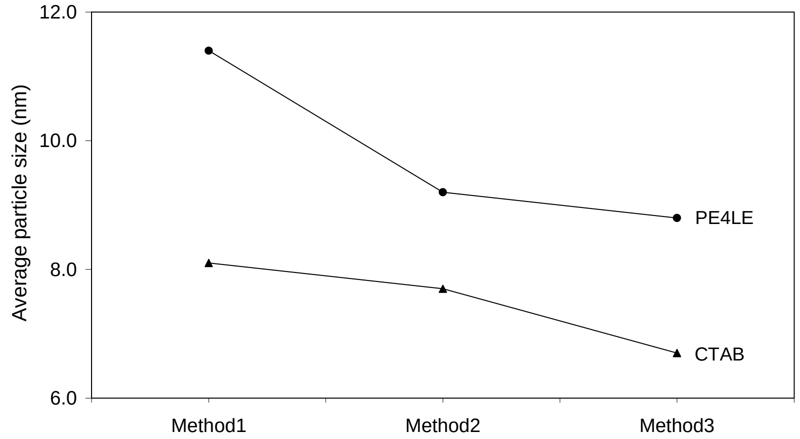


Figure 87 Variation of the average size of CeO_2 particles with different techniques using $CeCl_3 \cdot 7H_2O$ as a cerium source.

This results showed that the average size of CeO_2 obtained from mixing of two microemulsions are smaller than that from the combined method of homogeneous precipitation. However, the method of mixing two microemulsions used ammonium hydroxide instead of methyl oxalate as a precipitant material. To confirm the results another experiment following method 3 (mixing of two microemulsions) was run using methyl oxalate instead of ammonium hydroxide. The TEM image of CeO_2 obtained from this method is shown in Figure 88. The particles are spherical in shape and agglomerated the average particle size is 7.7 ± 0.3 nm compared to 7.6 ± 0.3 nm of CeO_2 using ammonium hydroxide as a precipitant material.

Considering the average particle size of CeO_2 using different methods but the same precipitant material (methyl oxalate), it was found that the average particle size obtained from mixing of two microemulsions was smaller than that from the combined method of homogeneous precipitation and microemulsion method. The method of preparation has more significant effect on the average size of CeO_2 than the precipitant material.

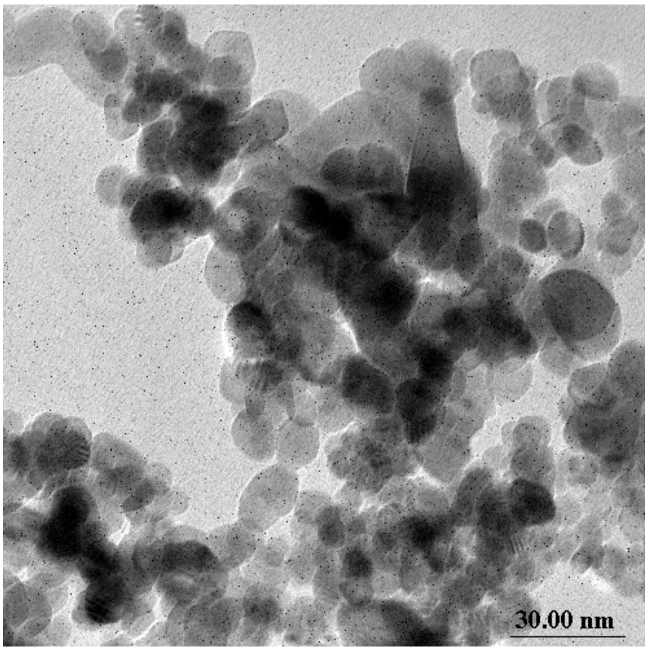


Figure 88 TEM Image of CeO_2 obtained from $Ce(NO_3)_3 \cdot 6H_2O$ as a cerium source, methyl oxalate as a precipitant material and PE4LE as a surfactant by mixing of two microemulsions (100,000x magnification).

2.5 Effect of the type of cerium sources

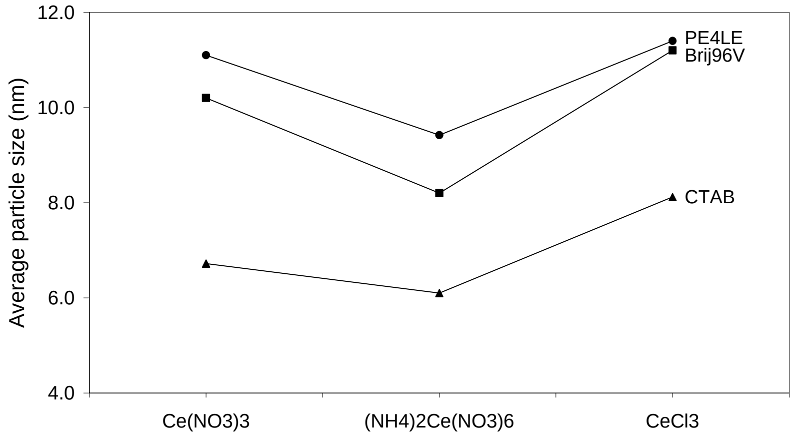
The experiment of this study used different cerium sources:

- Cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$)
- Ammonium cerium nitrate ($(NH_4)_2Ce(NO_3)_6$)
- Cerium chloride heptahydrate ($CeCl_3 \cdot 7H_2O$)

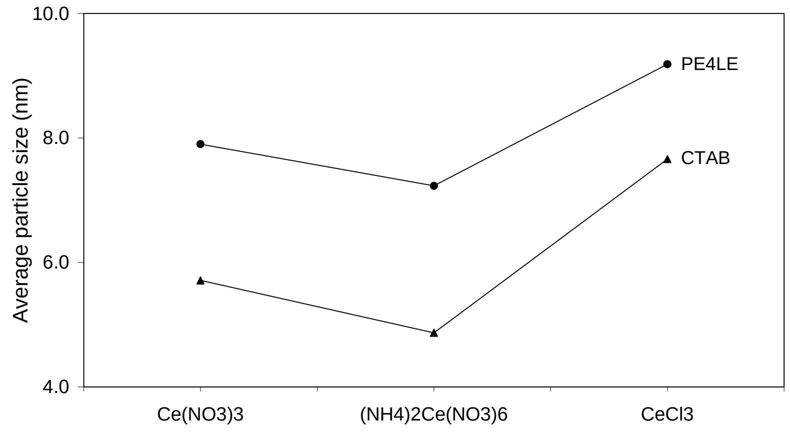
Consider the average size of CeO_2 particles with different cerium sources it was found that the average sizes obtained from $(NH_4)_2Ce(NO_3)_6$ are smallest and the average size of CeO_2 particles obtained from $Ce(NO_3)_3 \cdot 6H_2O$ are smaller than that from $CeCl_3 \cdot 7H_2O$. It can be explained that $(NH_4)_2Ce(NO_3)_6$ has lower surface tension than the others. An experiment was carried out by dropping the same concentration solution of $(NH_4)_2Ce(NO_3)_6$, $Ce(NO_3)_3 \cdot 6H_2O$ and $CeCl_3 \cdot 7H_2O$ on a glass surface, it was found that a droplet of $CeCl_3 \cdot 7H_2O$ showed less flat shape than the others which means $CeCl_3 \cdot 7H_2O$ has higher surface tension.

Cerium compound that has low surface tension, can disperse to small droplets in microemulsion easily, as a result, the small particles are produced. The comparison of different cerium sources is shown in Figure 88 to 90.

It can be seen that the average particle size of CeO_2 particles obtained from $(NH_4)_2Ce(NO_3)_6$ as cerium source are smallest and the average particle size of CeO_2 obtained from $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium source are smaller than that from $CeCl_3{\cdot}7H_2O$, the trend is the same with different surfactants and methods.



<u>Figure 89</u> Variation of the average size of CeO_2 particles with different cerium sources using microemulsion method.



<u>Figure 90</u> Variation of the average size of CeO_2 particles with different cerium sources using combined methods of homogeneous precipitation and microemulsion.

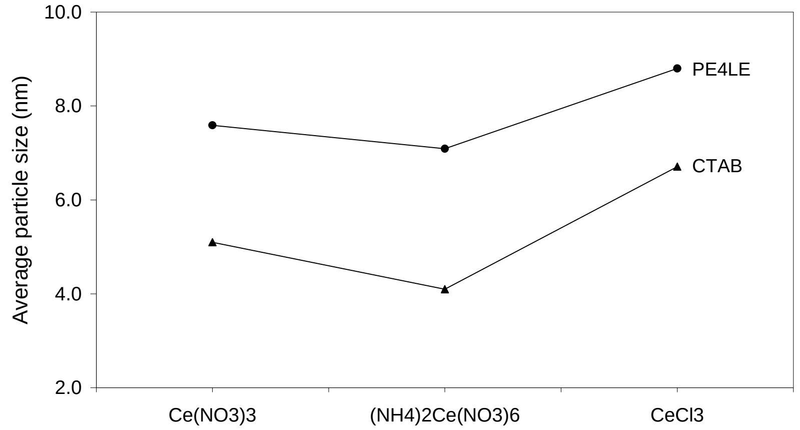


Figure 91 Variation of the average size of CeO_2 particles with different cerium sources by mixing of two microemulsions.

2.6 Effect of the sort of surfactants

The experiment of this study used different surfactants:

- Polyoxy ethylene-4-lauryl ether (PE4LE) the formula is $C_{12}H_{25}(OCH_2CH_2)_{23}OH$
- Polyoxy ethylene-10-oleyl ether (Brij96V) the formula is $C_{18}H_{35}(OCH_2CH_2)_{10}OH$
- Cetyl trimethyl ammonium bromine (CTAB) the formula is $C_{16}H_{33}(CH_3)_3NBr$

Consider the average sizes of CeO_2 with different surfactants, it was found that the average sizes obtained from PE4LE, Brij96V and CTAB are different in three cerium sources. The effect of sort of surfactant is more obvious than the type of cerium source. PE4LE and Brij96V are nonionic type but Brij96V has longer hydrocarbon (HC) chain length and has shorter polyoxyethylene (POE) chain length than PE4LE. If the hydrophobic hydrocarbon (HC) chain length is longer and the hydrophilic polyoxyethylene (POE) chain length is shorter the solubility of the surfactant in water decreases and its solubility in n-hexane increases, and surfactant tend to form aggregates which is called micelles. Since there are more micelles formed and the amount of water is the same, the sizes of the water droplets in micelles are smaller resulting in smaller sizes of the particles. The comparison of different cerium sources is shown in Figure 91 to 93.

CTAB is cationic type, when used only CTAB it did not form microemulsion, therefore butanol was used as a cosurfactant, butanol can reduce the CTAB concentration in microemlsion preparation. Their short hydrophobic chain and terminal hydroxyl group is known to enhance the interaction with CTAB monolayers at interface, which can influence the curvature of the interface and internal energy. The amphiphilic nature of butanol could also enable them to distribute between the aqueous and oil phase (organic solvent).

Consider the average sizes of CeO_2 with cationic and nonionic surfactants it was found that when the cationic was used, a certain repellent action exists between the hydrophilic group of CTAB and cerium cations at grain surface, which makes the stabilizing effect of CTAB on grains weaker, and the average size of CeO_2 particles are smaller than using nonionic surfactant. This can be considered that the stabilizing effect of nonionic surfactant (PE4LE and Brij96V) on water droplets and particles mainly derives from its hydrogen bond with water. This action is weaker than that of ion bond, resulting in an increase of the average size of CeO_2 particles than that when CTAB was used.

The comparison of different surfactants are shown in Figures 66 to 68. It can be seen that the average particle size of CeO_2 particles obtained from CTAB as a surfactant are smallest and the average particle size of CeO_2 particles obtained from Brij96V as a surfactant are smaller than that from PE4LE, the trend is the same with different methods and cerium sources.

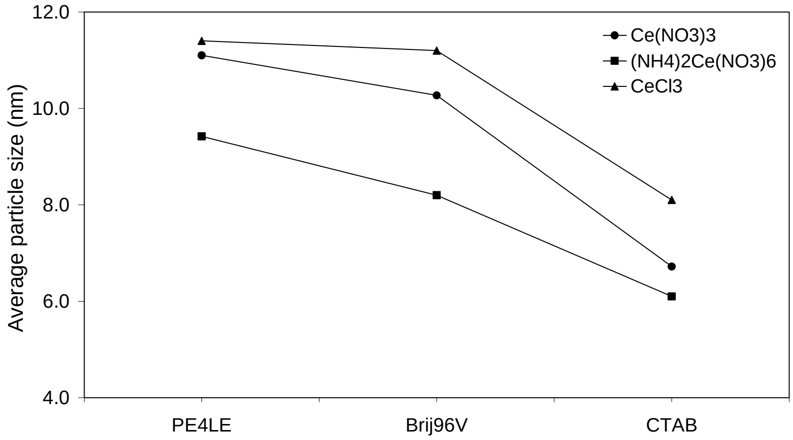


Figure 92 Variation of the average size of CeO_2 particles with different surfactants using microemulsion method.

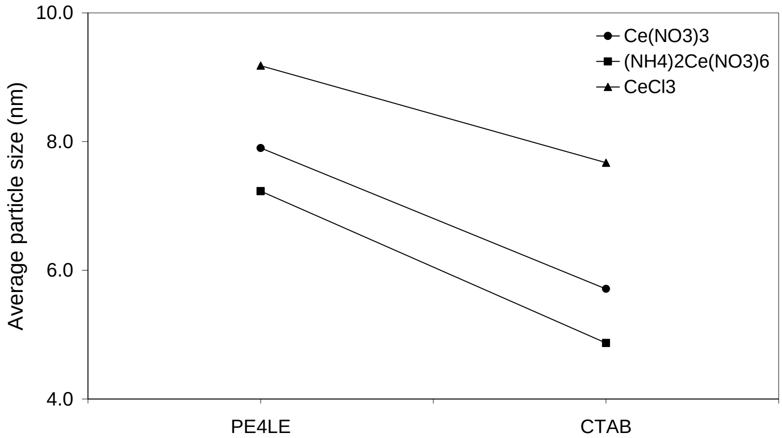


Figure 93 Variation of the average size of CeO_2 particles with different surfactants using combined methods of homogeneous precipitation and microemulsion.

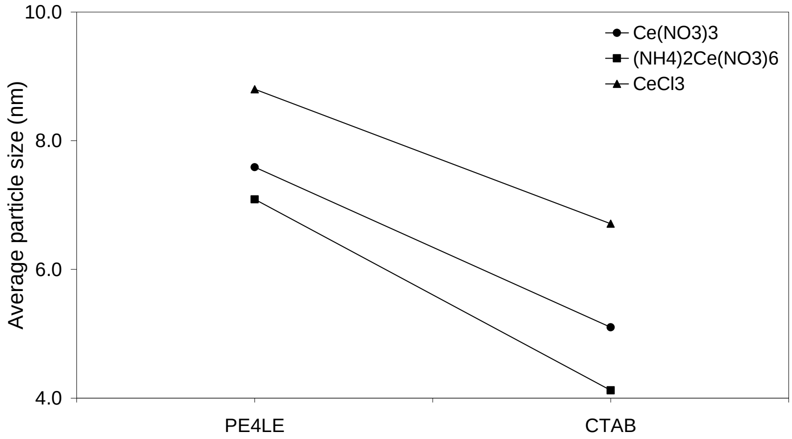


Figure 94 Variation of the average size of CeO_2 particles with different surfactants by mixing of two microemulsions.