Synthesis and Characterization of Yttrium-doped Core-Shell SiO$_2$ Nanoparticles by Reverse Micelle and Sol-gel Processing

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ABSTRACT

In this study, yttrium-doped SiO$_2$ nanoparticles are synthesized using a reverse micelle technique combined with metal alkoxide hydrolysis and condensation. Spherical Y-doped SiO$_2$ nanoparticles with a uniform size distribution are prepared using self-assembly molecules in conjunction with the hydrolysis and condensation of organometallic precursors. The water/surfactant molar ratio influenced the Y-doped SiO$_2$ particles distribution of the core-shell composite particles and the distribution of Y doped SiO$_2$ particles was broadened as the water to surfactant ratio increased. The particle size of Y increase linearly as the Y(NO$_3$)$_3$ solution concentration increased. The average size of the cluster was found to depend on the micelle size, the nature of the solvent, and the concentration of the reagent. The effects of synthesis parameters, such as the molar ratio of water to surfactant and the molar ratio of water to TEOS, are discussed.

Key words : Yttrium-doped SiO$_2$ particles, Nanoparticles, Reverse micelle, Sol-Gel Processing

1. Introduction

R ecently, the synthesis of nanometer-sized particles of metals, semiconductors and metal oxides has been investigated extensively because of their novel electrical, optical, magnetic, and chemical properties. Exciting potential applications of metal nanoparticles in catalysis,[1-6] DNA sequencing,[7-9] non-linear optical devices,[10] biological sensors,[11,12] information storage[13] and plasmonics[14] have been researched mainly due to the optical[15] and electronic properties of these materials.[16] Composites formed by silver ions or nano-clusters embedded in ceramics or glasses have recently attracted much attention as promising materials for applications in optoelectronics[17] and separation membranes.[18] Rare earth phosphors have been extensively applied in luminescence and display devices, such as fluorescence lamps, projection television tubes, field emission displays (FED), and plasma display panels (PDP).[19,20] The synthesis of nanoparticles and control of their properties are important in many critical areas of modern technology such as catalysis, ceramic processing, solar energy conversion, pharmaceutics, and photography. The effect of the size on the electronic and optical properties of these nanosize particles is an area of fundamental interest during the growth of the crystallite from the molecular level to the bulk material.[21] Many approaches have been explored regarding the preparation of spherical ultrafine particles, including

the use of colloids, polymers, glasses, and micelles for the successful control of aggregation.[21-24] Many new and unusual physical and chemical properties also arise as particles attain nanosize dimensions.[25,26] There is increasing recognition that aqueous synthesis offers growth control capabilities that can be conveniently exploited in preparing these desirable fine particles.[27] Compared to conventional solid-state reaction methods, solution-based synthesis results in higher levels of chemical homogeneity. Moreover, in a solution system, mixing of the starting materials at the molecular level is achieved in a solution-based system; this is especially important when multicomponent oxides are being prepared.

Yttria is a material of interest in ceramic technology for a variety of applications. It belongs to a relatively large group of sesquioxides with the C - type cubic structure, which is a defect analogue of the cubic fluorite structure (a$_{c-type}$ ~2x a$_{fluorite}$).[28,29] Yttria finds use as a chemically stable substrate, crucible material for melting reactive metals, and nozzle material for jet casting molten rare earth - iron magnetic alloys.[30] High surface area nanoporous yttria can be used as a catalyst carrier.[31]

In addition, surface coating or surface modification of a nanometer semiconductor and metal particles offers a new challenge to synthesis. Not only metal/silica nanocomposites, but also semiconductor/oxide and even semiconductor/insulator/metal multiple-layer can be prepared using this method.[32] The object of this study was to prepare Y doped SiO$_2$ nanoparticles through a combination of reverse micelle and sol-gel processing.

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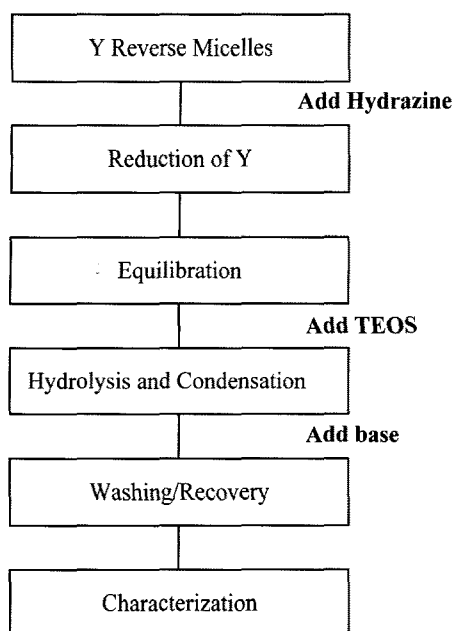 Tel : +82-55-213-3715   Fax : +82-55-262-6486

Fig. 1. Experimental procedure for the synthesis of Y-doped SiO$_2$ nanoparticles by reverse micelle and sol-gel processing.

2. Experimental Procedure

The experimental procedure used to prepare the Y-doped SiO$_2$ nanosize composites is illustrated in Fig. 1. Microemulsions of a total volume of 20 mL consisted of 4 g of Igepal, 10 mL of cyclohexane, 0.65~1.30 mL of 0.01 M, 0.02 M and 0.04 M Y(NO$_3$)$_3$ solution. The average of the synthesized particles was controlled by varying the R= [water]/[surfactant] ratio. The microemulsion was mixed rapidly, and after 40 min equilibration, one drop (~0.05 mL) of hydrazine hydrate (9 M N$_2$H$_4$X·H$_2$O, Aldrich Chemical Co.) was added as a reducing agent. After nanosize water droplets formed while stirring, TEOS was added into the stirred microemulsion. The amount of it was varied according to the different molar ratios of water to TEOS, H = [water]/[TEOS], which is the most important factor dictating the size of the nanoparticle. NH$_4$OH was injected into the microemulsion to accelerate the condensation reaction of metal alkoxide precursors. Reverse micelles were prepared from a nonionic surfactant, poly (oxyethylene) nonylphenol ether (Igepal CO-520, Aldrich Chemical Co.), which was used without further purification. The other chemicals, tetraethoxysilane (TEOS, Aldrich Chemical Co.), cyclohexane, and NH$_4$OH (28%) were used as received. The structure, size and morphology of the resulting composite nanoparticles were examined by transmission electron microscopy (TEM). For the TEM studies, samples were prepared by adding drops of freshly prepared cluster solution on a carbon film supported on a Cu grid.

3. Results and Discussion

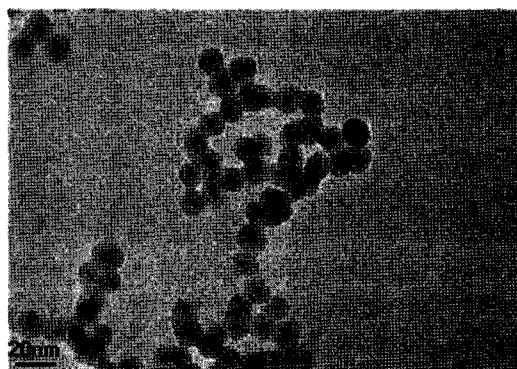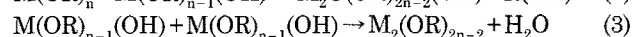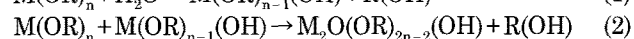Y-doped SiO$_2$ composite nanoparticles were obtained in

Fig. 2. TEM micrographs of Y-doped SiO$_2$ nanoparticles synthesized by a reverse micelle and sol-gel process (R=6, H=100, X=1).

reverse micelles followed by in situ hydrolysis and condensation in the micro-emulsion. Fig. 2 shows that spherical Y-doped SiO$_2$ nanometer-sized composite particles with a narrow size distribution were obtained in reverse micelles followed by in-situ hydrolysis and condensation in the micro-emulsion. The core particles are formed by a homogeneous nucleation and growth process, and the shells are most likely formed through heterogeneous nucleation and growth. These two steps are different in terms of their mechanisms, controlling the formation of the composite nanoparticles is very sensitive to modest processing changes. The first step is a rapid, complete reduction of the metal to the zero valence state. The second step is growth via reagent exchanges between micelles.[33] The average size of the resulting particles was controlled by varying the water/surfactant molar ratio(R), water/TEOS molar ratio (H). NH$_4$OH was injected into the microemulsion to accelerate the condensation reaction of metal alkoxide precursors. The amount of NH$_4$OH was fixed according to the molar ratio of TEOS to NH$_4$OH, x=[TEOS]/[NH$_4$OH]=1.

Nucleation and growth of the Y particles is likely to be a diffusion-controlled process through interaction between micelles, but it may be influenced by many other factors such as phase behavior and solubility, the average occupancy of reacting species in the aqueous pool, and the dynamic behavior of the micro emulsion process.[33] Metal-organic derivatives within the micro-emulsion reaction matrix undergo a hydrolysis reaction and two possible condensation reactions, which can be represented as follows.[34]

$$M(OR)_n + H_2O \rightarrow M(OR)_{n-1}(OH) + R(OH) \quad (1)$$
$$M(OR)_n + M(OR)_{n-1}(OH) \rightarrow M_2O(OR)_{2n-2}(OH) + R(OH) \quad (2)$$
$$M(OR)_{n-1}(OH) + M(OR)_{n-1}(OH) \rightarrow M_2(OR)_{2n-2} + H_2O \quad (3)$$

As a first approximation, it may be assumed that the reverse micelle aggregates present in the solution are not affected by the addition of TEOS molecules or by subsequent reactions, and in particular that the aggregation numbers of the micelles remain unchanged. The TEOS alkoxide molecules would then interact rapidly with the water molecules inside the reverse micelles, forming par-
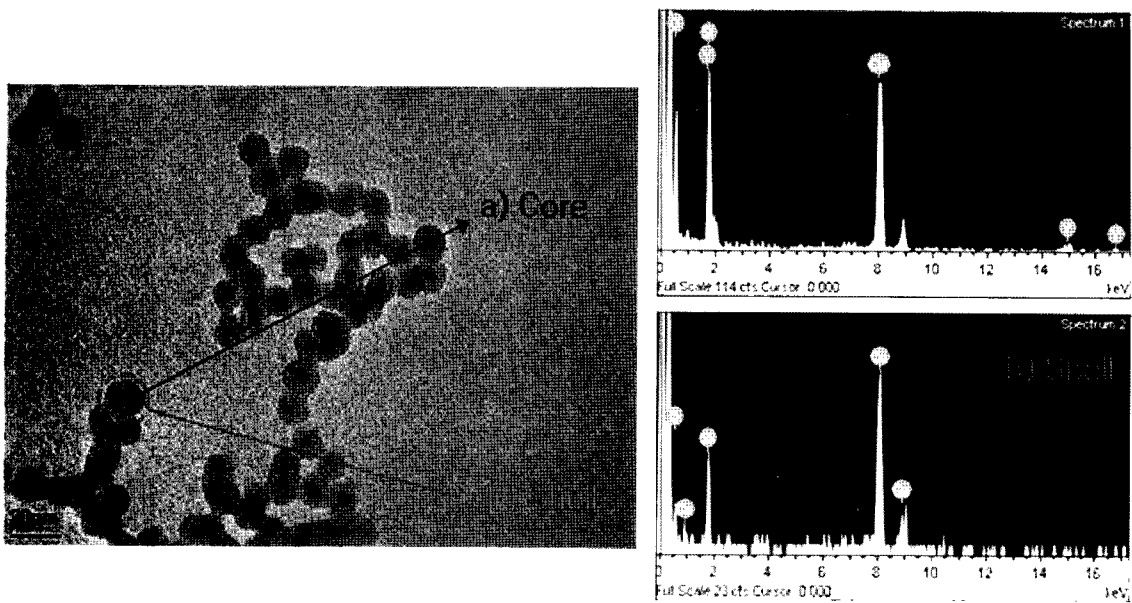
Fig. 3. TEM-energy dispersive spectroscopy (EDS) mapping of Y-doped SiO_2 nanoparticles: (a) Core, (b) Shell.
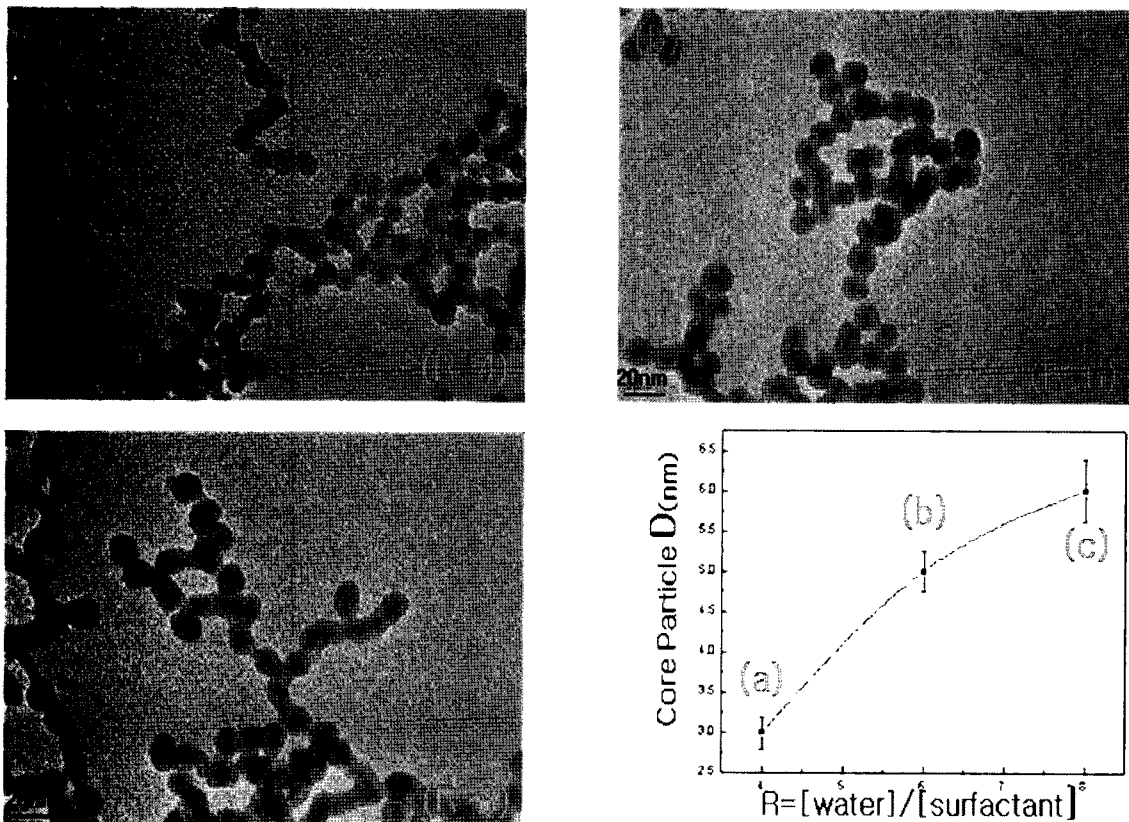

Fig. 4. The average size of the Y nanoparticles as a function of the concentration R values: (a) R=4, (b) R=6, and (C) R=8 (H=100, X=1, C=0.02 M).

tially hydrolyzed species. These hydrolyzed species remain bound to the micelles due to their enhanced amphiphilic characters brought about by the formation of silanol groups. It is likely that hydrolysis occurs within each reverse micelle, whereas condensation (particle growth) may occur also by intermicellar contacts. Therefore, the size of the composite particles depends on the relative rates of the

hydrolysis and condensation reactions. Fig. 3. shows the spectrum of Y-doped SiO_2 composite nanoparticles according to a TEM - EDS analysis. The core particles show Y pattern peaks and the shells show SiO_2 pattern peaks. Fig. 4. shows the core size of the Y-doped SiO_2 nanoparticles synthesized at H=100, X=1, C=0.02 M with different concentration R values of (a) R=4, (b) R=6, and (C) R=8. It was found as the
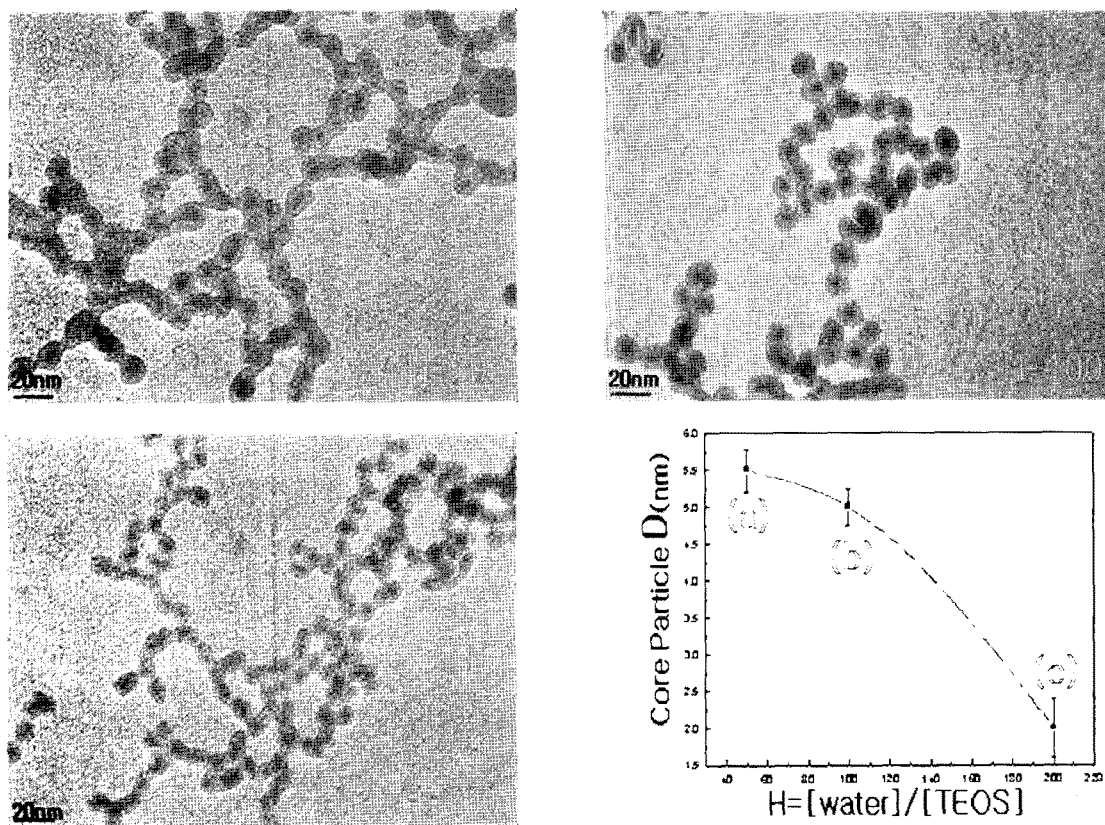
Fig. 5. The average size of the Y nanoparticles as a function of the concentration H values: (a) H=50, (b) H=100, and (C) H=200 (R=6, X=1, C=0.02).
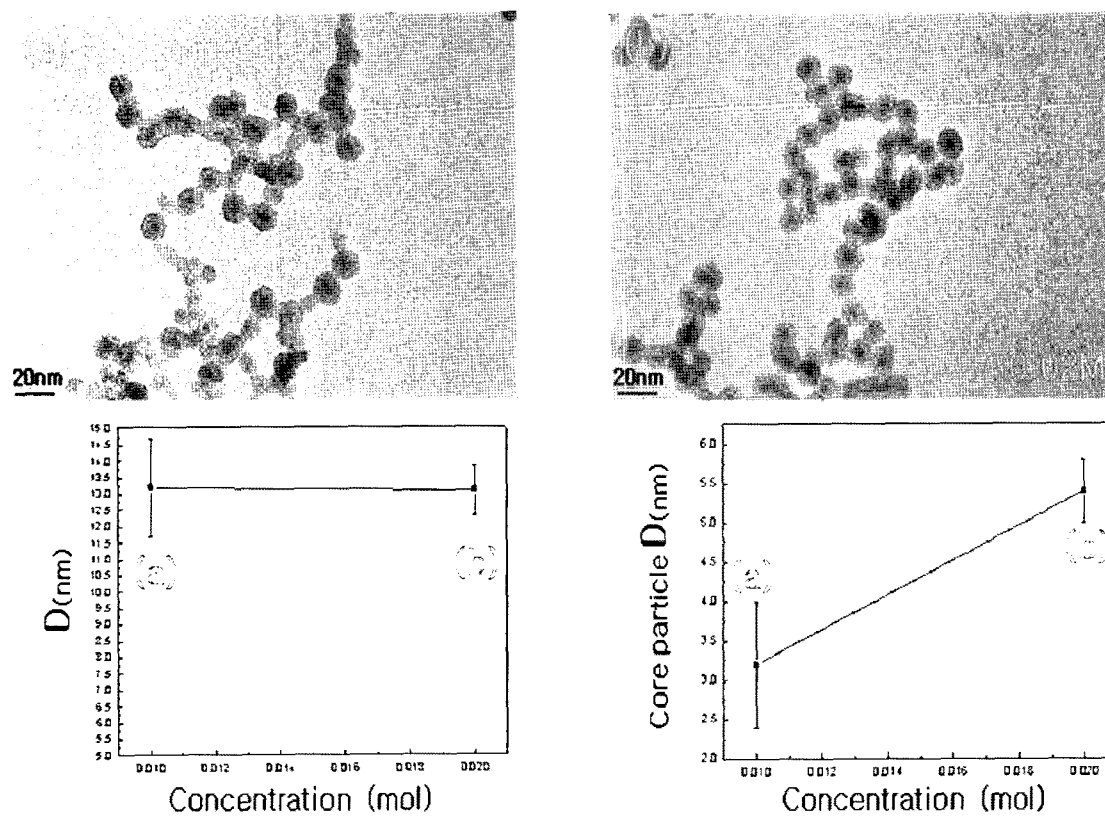

Fig. 6. The average size of the Y nanoparticles as a function of the concentration values: (a) 0.01 M and (b) 0.02 M (R=6, H=100, X=1).

R value increases, the core size of the particle increases. Fig. 5. shows the core size of the Y-doped SiO_2 nanoparticles synthesized at R=6, X=1, and C=0.02 M with different concentration H values of (a) H=50, (b) H=100, and (C) H=200. It was found as the H value increases, the shell thickness of the particle and the particle size decrease. Fig. 6. shows the core size of the Y-doped SiO_2 nanoparticles synthesized at R=6, H=100, X=1 with different concentration values of (a) 0.01 M and (b) 0.02 M. It was found as the concentration value increases, the core size of the particle increases.

4. Conclusion

Spherical Y-doped SiO_2 nanoparticles with a uniform size distribution were prepared using self-assembly molecules, in conjunction with the hydrolysis and condensation of organometallic precursors. The water/surfactants molar ratio influenced the Y particle distribution of the core-shell composite particles, and the distribution of the Y particles was broadened as R increased. The particle size of Y increased linearly as the $Y(NO_3)_3$ solution concentration increased. The average size of the cluster was found to depend on the micelle size, the nature of the solvent, and the concentration of the reagent. TEM studies of the particle formation process indicated that the reaction process in a complex system containing reverse micelles and TEOS is governed by a diffusion-controlled process. By controlling the ratio of water to surfactant and the ratio of water to TEOS, the particle size can be adjusted.

Acknowledgment

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