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Synthesis of nanosize SiO_2 particles by a reverse micelle and sol-gel processing

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Abstract Nanosize SiO_2 composite particles have been synthesized within reverse micelle via metal alkoxide hydrolysis and condensation. The size of the particles can be controlled by manipulating the relative rates of the hydrolysis and condensation reactions of tetraethoxysilane (TEOS) within the microemulsion. The average size of synthesized particles was about in the size range 14~30 nm. The effects of synthesis parameters, such as the molar ratio of water to TEOS, the molar ratio of water to surfactant, and the amount of base catalyst, are discussed.

1. Introduction

The synthesis of nanosize powders is important to the microelectronics industry because of the pervasive drive to miniaturize components. The ability to synthesize nanosize particles and control their properties is important in many critical areas of modern technology such as catalysis, ceramic processing, solar energy conversion, pharmaceutics, and photography. The effect of 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 [1]. Many approaches have been explored for the preparation of spherical ultrafine particles, including the use of colloids, polymers, glasses, porous zeolite, and micelles to successfully control aggregation [2-4]. Many new and unusual physical and chemical properties also arise as particles attain nanosize dimensions [5-6]. There is increasing recognition that aqueous synthesis offers growth control capabilities that can be conveniently exploited to prepare these desirable fine particles [7]. Compared to conventional solid-state reaction methods, solution-based synthesis results in higher levels of chemical homogeneity. Also, in solution systems, mixing of the starting materials is achieved at the molecular level, and this is especially important when multi-component oxides are being prepared. As a solution-based materials synthesis technique, the micro-emulsion methods [8-9] offers the unique ability to effect particle synthesis and particle stabilization in one step. The solubilized water droplets serve as nanosize test tubes, thus limiting particle growth, while the associated surfactant films adsorb on the growing particles, thereby minimizing particle aggregation.

The object of this study was to prepare the nanosize SiO_2 particles by a reverse micelle and sol-gel technique and to determine the processing on the formation of the nanosize particles in performed in conjunction with hydrolysis of organo-metallic precursors such as tetraehoxy-silane (TEOS), followed by condensation in the water droplets.

2. Materials and Methods

The experimental procedure used to prepared SiO_2 nanosize composites is illustrated in Fig. 1. After nanosize water droplets were formed while stirring, TEOS was added into the stirred micro-emulsion. The amount of TEOS 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 nanosize particles. NH_4OH was injected into the micro-emulsion to accelerate the condensation reaction of metal alkoxide precursors. Reverse micelles were prepared from both ionic and nonionic surfactants. One of the anionic surfactants used to form reverse micelles was sodium bis (2-ethylhexyl) sulfosuccinate, usually called Aerosol OT or AOT (Fisher Sci. Co.) and the nonionic surfactants was poly (oxyethylene) nonylphenyl ether (Igepal CO-520, Aldrich Chemical

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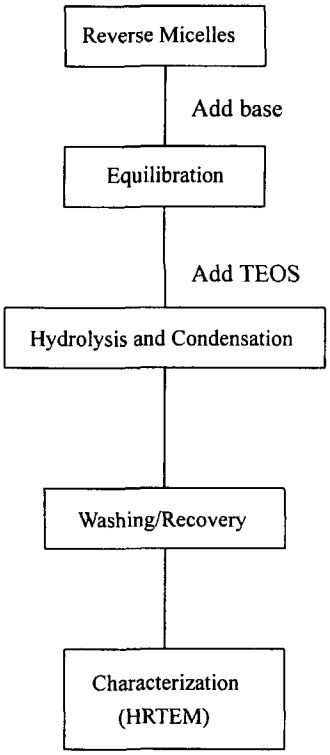

Fig. 1. Flow chart for the synthesis of nanosize SiO_2 particles.

Co.). Both surfactants were used without further purification. Other chemicals, such as tetraethoxysilane (TEOS, Aldrich Chemical Co.), cyclohexane, isooctane, and NH_4OH (29 %) (all from Fisher Scientific) were used as received. The structure, size and morphology of the resulting composites were examined by high resolution transmission electron microscope (HRTEM).

3. Results and Discussion

Spherical SiO_2 nanometer size composite particles with a narrow size distribution were obtained in reverse micelles followed by in-situ hydrolysis and condensation in the micro-emulsion. The TEM micrographs presented in Fig. 2 show that the SiO_2 nanosize composites are essentially monodisperse and spherical in shape. Metal-organic derivatives within the micro-emulsion reaction matrix undergo a hydrolysis reaction and two possible condensation reactions, which can be represented as follows [10].

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

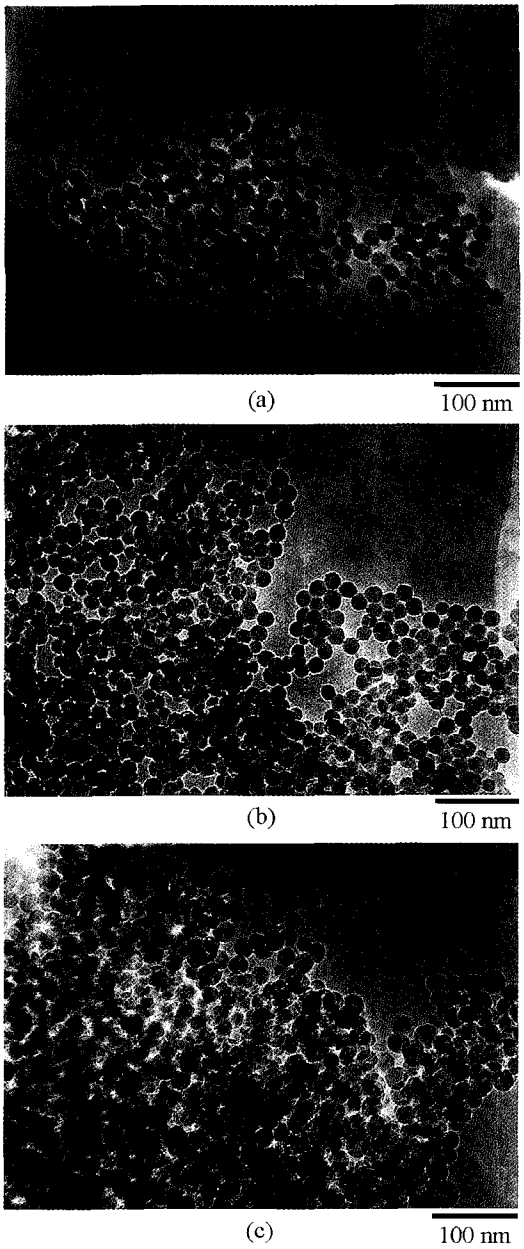

Fig. 2. TEM micrographs of nanosize SiO_2 particles synthesized at R = 8, x = 1 and (a) H = 10, (b) H = 20 and (c) H = 50.

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

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

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 partially hydrolyzed species. These hydrolyzed species remain bound to the micelles due to their enhanced amphiphilic character 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 contracts. Therefore, the size of the composite particles depends on the relative rates of the hydrolysis and condensation reactions. The change in R influenced the size distribution of the resulting particles. As R increased above 10, the distribution broadened, probably due to movement outside the region of the phase diagram where the micro-emulsion is stable.

Formation of the nano sized SiO_2 was achieved by in-situ hydrolysis and condensation of metal alkoxide precursors of tetraethoxysilane (TEOS) in reverse micelles. To control the size and morphology of the SiO_2, the ratio of water to metal alkoxide precursors H, and the amount of base added to enhance the hydrolysis and polycondensation (referred to as the ratio of TEOS to base X) have been paid special attention. The ratio H affects the rate of hydrolysis by increasing the rate of diffusion of TEOS alkoxide molecules into the reverse micelles. The size and size distribution of the resulting nanometer-sized composites were quantitatively characterized by electron microscopy. Figure 3

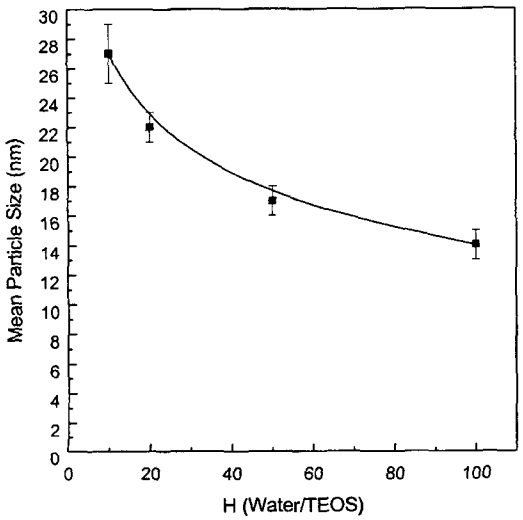

Fig. 3. The size of the nanosize SiO_2 particles with changing H ratio.

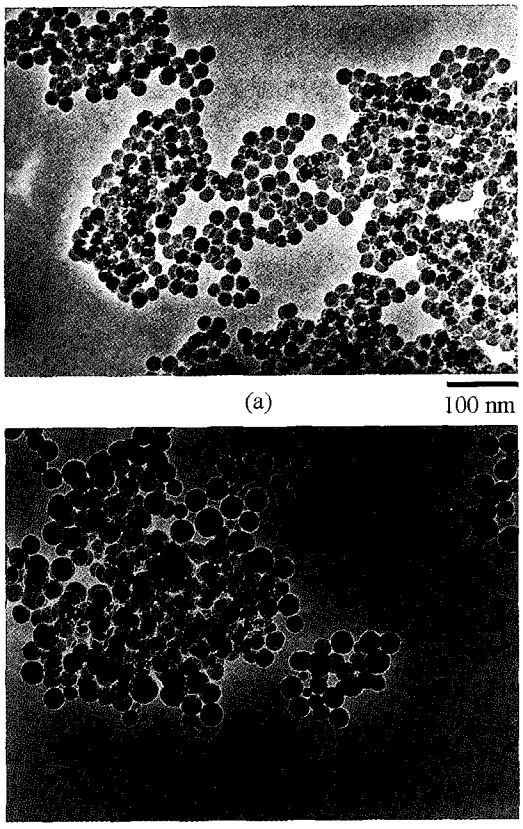

Fig. 4. TEM micrographs of nanosize SiO_2 particles synthesized as a function of surfactants at R = 6, H = 10, x = 1; (a) Igepal CO-520/Cyclohexane/Water, (b) AOT/Isooctane/Water.

shows that the size of the composite particles decrease linearly with H (water/TEOS). The median particle was determined by counting the number of particle size in a given area. The SiO_2 nano composites were determined to have a median diameter from 15 to 30 nm as H varied from 20 to 100 at R = 8, with a standard deviation of 2 nm.

Figure 4 shows that a uniform size distribution for the Igepal CO-520 system was obtained only for R less than 10, possibly due to the decreasing stability of the micellular phase. The ionic strength and the concentration have a great influence on the formation and stability of microemulsion systems [11]. Compared with ionic surfactants, nonionic surfactants are relatively insensitive to changes in electrolyte concentration [12]. The nonionic surfactant microemulsion system such as Igepal/cyclohexane/water was stable over several days, whereas the anionic microemulsion system such as

AOT/isooctane/water was only stable for several hours. It is probable that the intermicelle exchange process varies with solvent, resulting in slightly different size particles [13]. The reverse micelles become unstable and more polydisperse as surfactant is changed. This deviation could be due to the intermicellar collisions which result in a larger micellar size distribution with different surfactant.

4. Conclusions

Spherical nanosize SiO_2 particles with uniform size distribution have been prepared using self-assembly molecules, in conjunction with the hydrolysis and condensation of organometallic precursors. These nanometer size particles have excellent stability and reproducibility under optimum synthesis conditions. The average size of the cluster was found to depend on the micelle size, the nature of the solvent, and the concentration of reagent. TEM studies of particle formation indicate that the reaction process in the 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.

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