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FORMATION OF MESOSTRUCTURED NANOPARTICLES THROUGH SELF-ASSEMBLY AND AEROSOL PROCESS

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ABSTRACT

Silica nanoparticles exhibiting hexagonal, cubic, and vesicular mesostructures have been prepared using aerosol assisted, self-assembled process. This process begins with homogenous aerosol droplets containing silica source, water, ethanol, and surfactant, in which surfactant concentration is far below the critical micelle concentration (*cmc*). Solvent evaporation enriches silica and surfactant inducing interfacial self-assembly confined to a spherical aerosol droplet and results in formation of completely solid, ordered spherical particles with stable hexagonal, cubic, or vesicular mesostructures.

INTRODUCTION

Nanostructured particles exhibiting well-defined pore sizes and pore connectivities (1-, 2-, or 3-dimensional) are of interest for catalysis, chromatography, controlled release, low dielectric constant fillers, and custom-designed pigments and optical hosts.[1,2] During the last several years considerable progress has been made on controlling the macroscopic forms of mesoporous silicas prepared by surfactant[3,4] and block copolymer[5] liquid crystalline templating procedures. Typically interfacial phenomena are used to control the macroscopic form (particles[1,6], fibers[7,8], or films[9,10]), while self-assembly of amphiphilic surfactants or polymers is used to control the mesostructure. To date, although a variety of spherical or nearly-spherical particles have been prepared,[1,6,7,11-13] their extent of order is limited as the range of attainable mesostructures. Schacht *et al.* [6]first demonstrated that mesoscopically ordered hollow spheres could be prepared via interfacial reactions conducted in oil/water emulsions with varying extents of imposed shear. Huo *et al.*[1] extended this general emulsion-based approach to prepare marble-like spheres with diameters of 0.1 to 2.0-mm. Tanev and Pinnavaia[12] condensed silica in the interlayer regions of multilamellar vesicles to form roughly spherical particles with stable lamellar mesostructures. Recently Bruinsma *et al.*[7] used spray drying to prepare hollow spherical particles or collapsed irregular particles. These various pathways to prepare nominally spherical mesostructured particles have so far resulted in irregular shapes and/or particles with non-uniform or ill-defined mesostructures.

We previously reported the formation of mesostructured silica (or nanocomposited) thin films through a rapid dip-coating process, which starts with a homogeneous solution containing silica, water, ethanol, and surfactant (initial surfactant concentration c_o << the critical micelle concentration *cmc*).[14,15] During drying, preferential alcohol evaporation enriches the thin films in surfactant, water, and silica, inducing micelle formation and successive co-assembly of silica-surfactant micellar species into liquid crystalline mesophases that nucleate from both air/liquid and substrate/liquid interfaces. We extended this approach to prepare silica nanospheres using

aerosol process, in which a 3-dimesional spherical air/liquid interface is used to guide the self-assembly process. Similarly, evaporation-induced interfacial self-assembly confined to a spherical aerosol droplet results in formation of completely solid, ordered spherical particles with stable hexagonal, cubic, or vesicular mesostructure. The process is simple and generalizable to a variety of material combinations.

EXPERIMENT

Precursor solutions were synthesized by the addition of cationic surfactant (CTAB $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$), non-ionic surfactant (Brij-56 - $CH_3(CH_2)_{15}$-$(OCH_2CH_2)_{10}$-OH, Brij-58 - $CH_3(CH_2)_{15}$-$(OCH_2CH_2)_{20}$-OH) or triblock copolymers (Pluronic-P123, $(EO)_{20}(PO)_{70}(EO)_{20}$) to an acidic silica sol (A2**).[16] Precursor solutions used to prepare organic/silica or metal/silica particles were synthesized by adding organic dyes (rhodamine B) or metal colloids to the silica sols, respectively. Gold colloids with particle sizes 1-3 nm, were prepared in inverse micelles according to the method of Brust *et al.*,[17] using 1-dodecanethiol as a stabilizing agent) directly to the precursor solutions. The acidic silica sol (A2**) was prepared by mixing TEOS [$Si(OCH_2CH_3)_4$], ethanol, water and dilute HCl (mole ratios: $1:3.8:1:5\text{x}10^{-5}$) and refluxing at 60°C for 90 minutes. The sol was diluted with ethanol (1:2) followed by addition of water, dilute HCl and surfactants. The final reactant mole ratios TEOS:EtOH:H_2O:HCl: surfacant were: 1:0-22:5-67:0.004:0.006-0.23.

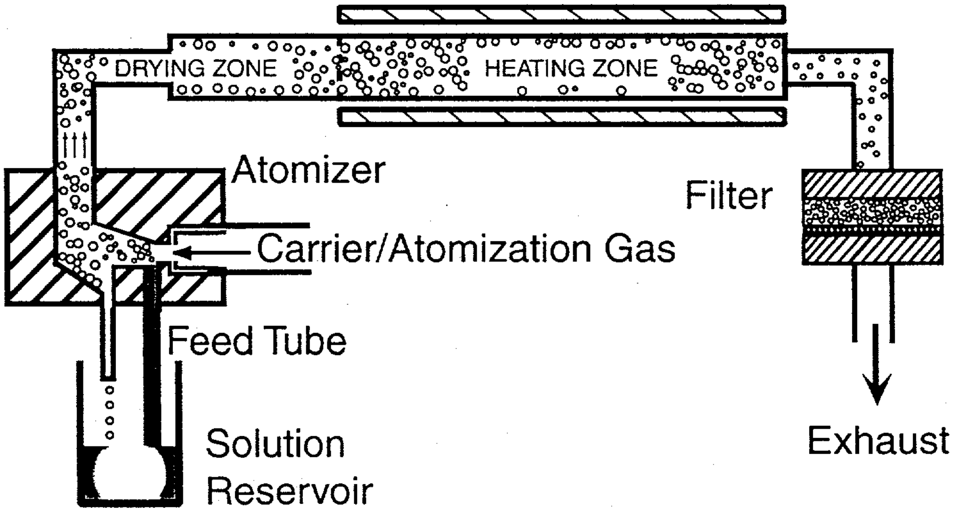

Figure 1 Schematic of the aerosol reactor

Spherical mesostructured particles were prepared using an aerosol reactor shown in Figure 1. A commercial TSI Model # 3076 atomizer operated with nitrogen as a carrier/atomization gas was used to produce aerosol droplets with a size distribution characterized by a geometric standard deviation of 2 (95% of the particles have diameters between 1/4 and four times the mean diameter). The pressure drop at the pinhole was 2.4 atmosphere, and the volumetric flow rate was 2.6 standard litres/min in the drying and heating zones maintained at room temperature and 400°C, respectively. These conditions establish very stable, reproducible laminar flow throughout the reactor (Reynolds Number at 400°C = 75), and the entrained aerosol particles experience ~3 seconds of drying followed by ~3 seconds of heating. Particles were collected on a Teflon filter maintained at 80°C, and were characterized by TEM (JEOL 2010, 200KV), small angle x-ray scattering (SAXS),[18] and N_2 sorption

(Micromeritis ASAP2010) before and after calcination at 425°C in air or N_2 (heating rate = 1°C/min) to remove the surfactant templates.

RESULT

Figure 2 shows representative TEM images of calcined silica particles (2A to 2D), silica/rhodamine B particle (2E), and silica/metal particle (2F). Usually, CTAB produces particles exhibiting a highly-ordered hexagonal mesophase over the concentration range c_o = 0.06-0.16M. As shown in Figure 2A, particles prepared using 5wt% CTAB show a highly ordered hexagonal mesophase (d_{100}= 32.5Å). Many of the particles have adopted a polyhedral shape that is hexagonal in cross-section, a macroscopic manifestation of the local packing geometry.[19] Figure 2B shows a cubic mesostructured particle prepared using 4.2wt% B58 surfactant, while Figure 2C shows vesicular mesostructured particles prepared using 5% P123 (d_{100} = 92 Å). Distinct from related bulk and thin film lamellar structures that collapse upon calcination,[20] the three-dimensional connectivity of the nested spherical shells comprising the vesicular mesophase mechanically stabilizes this structure against collapse during surfactant removal. Figure 2D shows that a particle prepared using 2.5 wt% B56 exhibits a disordered, worm-like interior and highly ordered vesicular exterior mesostructures, suggesting the 'growth' of ordered vesicular domains from the liquid-vapor interface. The robustness of the evaporation induced self-assembly (EISA) process combined with the short residence time of the particles in the furnace enable us to prepare a variety of mesostructured organic/silica, metal/silica. For an example, during aerosol processing, hydrophobic gold colloids partition into the hydrophobic micellar interiors and are subsequently incorporated in the hexagonal mesophase, as shown in Figure 2E. TEM and XRD indicate d_{100} = ~60 Å, (compared to 32.5 Å (see Figure 2A), consistent with incorporation of the gold colloids in the hexagonal silica mesophase. Figure 4B shows the hexagonal structured dye/silica particles prepared by adding 0.8 wt% rhodamine B to a silica/4.2 wt% Brij-56 sol. Inset shows an optical photomicrograph of the fluorescence emission imaged through a rhodamine B filter, confirming retention of the dye structure. Above results shown in Figure 2 have fully demonstrated the feasibility of preparing spherical mesostructured nanopartilces through self-assembly and aerosol process.

Figure 3 shows SAXS data for calcined mesostructured silica particles prepared with CTAB, Brij-56, and P123 surfactants along with the corresponding N_2 sorption isotherms ('as-prepared' particles had no internal surface area accessible to N_2 due to retention of the surfactant templates). Samples A, B and C were prepared as in figures 2A 2D, 2F, respectively. The major peak is indexed as the *[100]*-reflection of the hexagonal (CTAB) and vesicular mesophases. SAXS and N_2 sorption show the expected increase in *d*-spacing and pore size with increasing surfactant volume/molecular weight (CTAB<Brij-56<P123). Surface area of the particles prepared using 5% CTAB is as high as 1256 m^2/g, making it potential important for catalysis applications.

The mechanisms of formation of the mesostructured particles are similar to those in dip-coating process.[14,15] Evaporation during aerosol processing creates a radial gradient in surfactant concentration within each droplet that steepens in time and maintains a maximum concentration at the droplet surface. Starting with an initially homogeneous solution ($c_o < cmc$), the surfactant *cmc* is exceeded first at the surface of the droplet, and, as evaporation proceeds, *cmc* is progressively exceeded throughout the droplet. This surfactant enrichment induces silica-surfactant self-assembly into micelles and further organization into liquid crystalline mesophases. The radial concentration gradient and presence of the liquid-vapor interface (that serves as a nucleating surface) causes ordered silica-surfactant LC domains to grow radially inward rather than outward from a seed. Key to the formation of solid, completely ordered particles is maintenance of a liquid or liquid crystalline state throughout the course of the EISA process. Premature solidification would result in the formation of hollow particles and inhibit orderly self-assembly that must proceed with continual restructuring of the evolving silica-surfactant mesophase in order to accommodate drying shrinkage.[7] We note that the curvature of the particle surface profoundly influences mesostructure development. This is evident in the comparison of CTAB-templated particles (e.g., Figure 2A) and corresponding mesostructured films formed on flat substrates by EISA during dip-coating. Unlike films, which have flat liquid-vapor interfaces and show a progressive change in mesostructure (disordered to hexagonal to cubic to lamellar) with increasing surfactant concentration,[14] particles prepared with comparable CTAB concentrations exhibit only disordered or hexagonal mesophases. We conclude that, since the liquid-vapor interface serves as a nucleating surface for liquid crystal growth, the high curvature imposed by this interface alters the generally observed relationship between surfactant packing parameter and resulting mesostructure.[21] Although CTAB commonly forms lamellar mesophases in bulk and thin film samples,[3,20] apparently it cannot pack into a cone truncated by surfaces of high and opposite curvature needed to direct the vesicular mesostructure. Only surfactants containing EO blocks consistently gave vesicular mesophases.

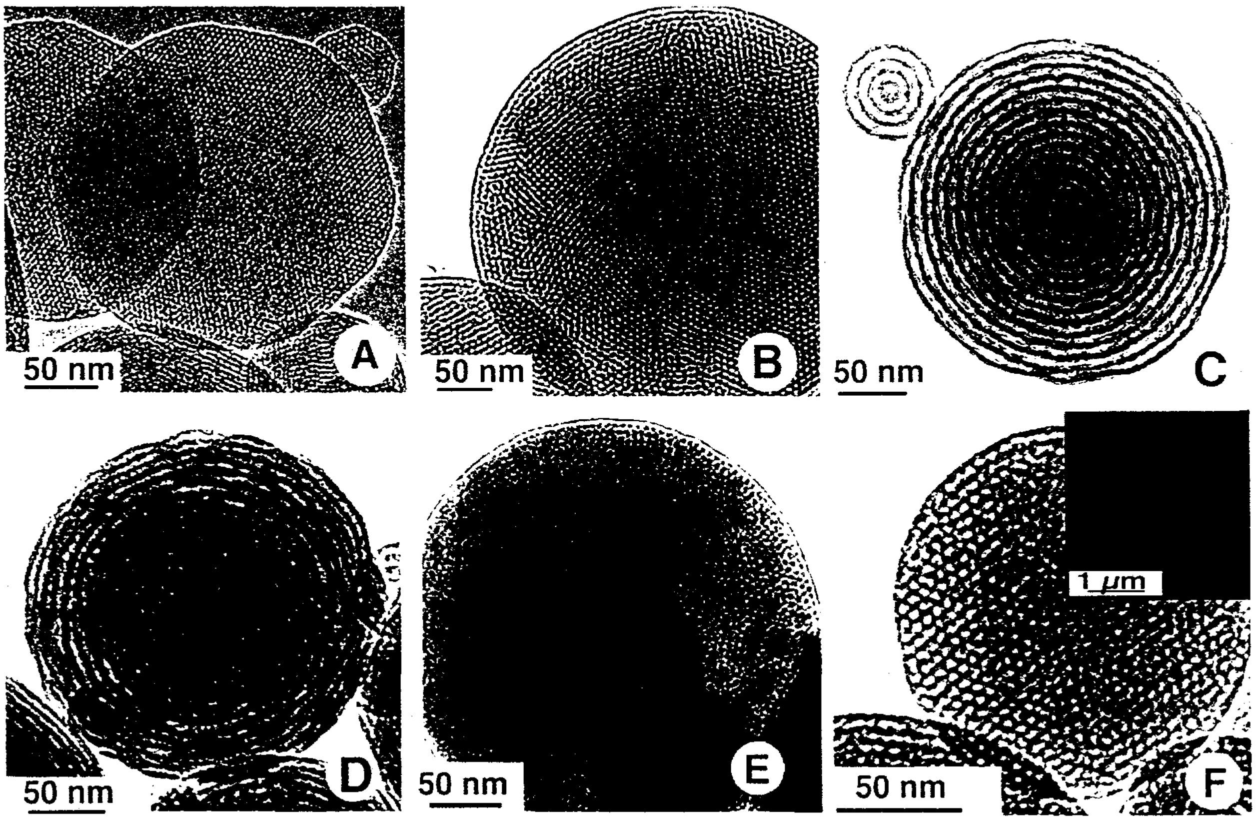

Figure 2 Representative TEM micrographs of mesostructured nanoparticles.

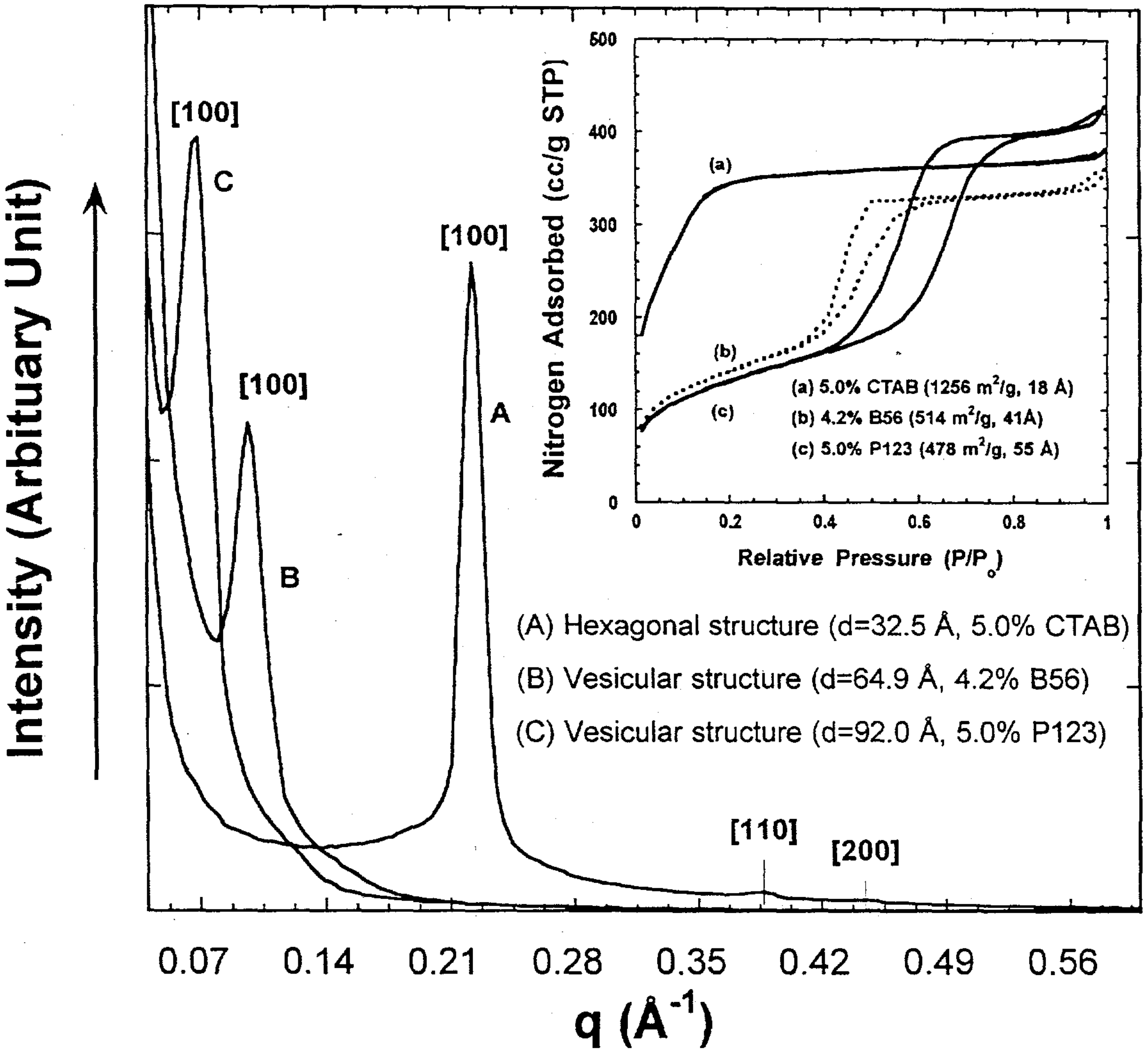

Figure 3 Small angle x-ray scattering (SAXS) curves for silica particles exhibiting hexagonal (A) or vesicular (B and C) mesophases. Inset: Corresponding N_2 adsorption-desorption isotherms, BET surface areas, and pore diameters. Hydraulic pore diameters were calculated from the pore volume and BET surface area.

CONCLUSION

We have developed a methodology to prepare mesostructured nanopartilces through aerosol assisted self-assembly. This method provides a simple and efficient approach to prepare nanoparticles with controlled morphology and mesostructures, which are important for catalysis, chromatography, controlled release, and customer designed filler applications.

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