

**Aerosol-assisted self-assembly of mesostructured spherical nanoparticles****Yunfeng Lu\*, Hongyou Fan\*, Aaron Stump\*, Timothy L. Ward\*, Thomas Rieker\*, and C. Jeffrey Brinker\*\*****RECEIVED  
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\*University of New Mexico/NSF Center for Micro-Engineered Materials, The Advanced Materials Laboratory, 1001 University Blvd. SE, Albuquerque, NM 87106.

\*\*Sandia National Laboratories, Direct Fabrication Department, 1831, Albuquerque, NM 87185.

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<sup>[1,2]</sup>. During the last several years considerable progress has been made on controlling the macroscopic forms of mesoporous silicas prepared by surfactant<sup>[3,4]</sup> and block copolymer<sup>[5]</sup> liquid crystalline templating procedures. Typically interfacial phenomena are used to control the macroscopic form (particles<sup>[1,6]</sup>, fibers<sup>[7,8]</sup>, or films<sup>[9,10]</sup>), 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,<sup>[1,6,7,11,12,13]</sup> their extent of order is limited as is the range of attainable mesostructures. We report a rapid, aerosol<sup>[14,15,16]</sup> process that results in solid, completely ordered spherical particles with stable hexagonal, cubic, or vesicular mesostructures. Our process relies on evaporation-induced interfacial self-assembly (EISA)<sup>[17]</sup> confined to a spherical aerosol droplet. The process is simple and generalizable to a variety of materials combinations. Additionally, it can be modified to

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**provide the first aerosol route to the formation of ordered mesostructured films.**

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.

Our process starts with a homogeneous solution of soluble silica plus surfactant prepared in an ethanol/water solvent with initial surfactant concentration  $c_0 \ll$  the critical micelle concentration  $cmc$ . Using the apparatus depicted in Figure 1, we generate an aerosol dispersion within a tubular reactor. In a continuous, ~6 second process, the aerosol particles are dried, heated, and collected. As recently demonstrated for thin film formation[17], during drying, preferential alcohol evaporation[18] enriches the particles in surfactant, water, and silica, inducing micelle formation and successive co-assembly of silica-surfactant micellar species into liquid crystalline mesophases. The resulting particles are commonly solid with highly ordered hexagonal, cubic, or vesicular mesostructures (see Figure 2). Through introduction of metal complexes or organic dyes/precursors into the starting solution, we can use the same process to prepare ordered nanocomposite particles (Figure 3).

Figure 2 shows representative TEM images of calcined silica particles prepared using CTAB, Brij-58, Brij-56, or P123 templates. Figure 3 shows TEM images of various metal-, organic-, and polymer-silica nanocomposite particles. CTAB produces particles

exhibiting a highly-ordered hexagonal mesophase over the concentration range  $c_o = 0.06$ - $0.16$ M (Figures 2A and 3A). Many of the particles have adopted a polyhedral shape that is hexagonal in cross-section, a macroscopic manifestation of the local packing geometry[19]. The non-ionic surfactants commonly resulted in vesicular mesostructures (Figures 2C, 3C), but cubic and hexagonal mesostructures were attainable also (Figures 2B and 3B). 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. Under processing conditions where the outer silica shells solidify before the drying shrinkage is complete, uniform dimpling of the shell surface results (Figure 3C), in order to preserve the solidified shell surface area. This may be contrasted with the shrinkage-induced formation of torroidal or raisin-like collapsed morphologies commonly observed for spray-dried powders[7].

Figure 4 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). 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).

The robustness of the 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 and even enzyme/silica composite particles while retaining the respective structure, function, and bio-activity of the guest species (A. Stump and R. Bhatia, unpublished). Furthermore, through addition of organic monomers and thermal initiators to the parent solution, we can co-organize and polymerize mesostructured silica-polymer

nanocomposite particles as recently demonstrated for coatings<sup>[21]</sup>. The mesostructures presented in Figure 3 illustrate the diversity of nanocomposite constructions and materials combinations attainable by our method.

Evaporation during aerosol processing creates a radial gradient in surfactant concentration within each droplet that steepens in time<sup>[22]</sup> and maintains a maximum concentration at the droplet surface. Starting with an initially homogeneous solution ( $c_0 < cmc$ ), 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<sup>[9,17,23]</sup>) causes ordered silica-surfactant LC domains to grow radially inward (see Figure 2D) rather than outward from a seed<sup>[24]</sup>. 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<sup>[7]</sup> and inhibit orderly self-assembly that must proceed with continual restructuring of the evolving silica-surfactant mesophase in order to accommodate drying shrinkage. Evidence for such a semi-solid state is the formation of continuous, uniform films on the collection surface when the furnace is maintained at low temperature (<150°C). As shown in Figure 5, film formation occurs via droplet coalescence. Important for applications such as membranes, the resulting films are highly ordered and can span holes hundreds of times greater in diameter than the film thickness.

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<sup>[17]</sup>. Unlike films, which have flat liquid-vapor

interfaces and show a progressive change in mesostructure (disordered→hexagonal→cubic→lamellar) with increasing surfactant concentration[17], 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[25]. Although CTAB commonly forms lamellar mesophases in bulk and thin film samples[3,20,26], 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.

## Methods

Precursor solutions were synthesized by the addition of cationic surfactant (CTAB  $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$ ), non-ionic surfactant (Brij-56 -  $\text{CH}_3(\text{CH}_2)_{15}-(\text{OCH}_2\text{CH}_2)_{10}\text{-OH}$ , Brij-58 -  $\text{CH}_3(\text{CH}_2)_{15}-(\text{OCH}_2\text{CH}_2)_{20}\text{-OH}$ ) or triblock copolymers (Pluronic-P123,  $(\text{EO})_{20}(\text{PO})_{70}(\text{EO})_{20}$ ) to an acidic silica sol (A2\*\*). The acid concentration employed in the A2\*\* synthesis procedure was chosen to minimize the siloxane condensation rate[27], thereby promoting facile silica-surfactant self-assembly during aerosol processing. In a typical preparation TEOS [ $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ ], ethanol, water and dilute HCl (mole ratios: 1:3.8:1:5x10<sup>-5</sup>) were refluxed at 60°C for 90 minutes. The sol was diluted with ethanol (1:2) followed by addition of water and dilute HCl. Surfactants were added in requisite amounts to achieve initial surfactant concentrations  $c_0$  ranging from 0.004-0.23 M. The final reactant mole ratios TEOS:EtOH:H<sub>2</sub>O:HCl:surfactant were: 1:0-22:5-67:0.004:0.006-0.23. Sols used to prepare various nanocomposite particles were synthesized by addition of organosilanes, organic dyes, polymers, metal colloids, or commercial catalysts directly to the precursor solutions.

Spherical mesostructured particles were prepared using an aerosol reactor (Figure 1) operated at a volumetric flow rate of 2.6 standard litres/min. Under these conditions, the flow is laminar (Reynolds Number at 400°C = 75) and the entrained aerosol particles experience ~3 seconds of drying at nominally room temperature followed by ~3 seconds of heating at 400°C and finally collection on a filter maintained at 80°C. The collected particles were characterized by TEM, small angle x-ray scattering (SAXS), and N<sub>2</sub> sorption before and after calcination at 425°C in air or N<sub>2</sub> (heating rate = 1°C/min) to remove the surfactant templates.



## Figure Captions

**Figure 1** Schematic of aerosol reactor. Silica/surfactant aerosols were generated using a commercial TSI Model # 3076 atomizer operated with nitrogen as a carrier/atomization gas. This atomizer produces 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, TEM grid, or silicon substrate maintained at 80°C. For film experiments the furnace was not operated. For one experiment, HCl vapor was introduced into the reactor through a coaxial tube positioned at the center of the heating zone.

**Figure 2** Representative TEM micrographs of mesostructured silica particles. **A.** Faceted, calcined particles exhibiting hexagonal mesophase ( $d_{100} = 32.5 \text{ \AA}$ ). The sol was prepared using 5 wt% CTAB as the surfactant template and molar ratio, TEOS:EtOH:Water:HCl:CTAB=1:22:5:0.004:0.15. **B.** Calcined particles exhibiting cubic mesostructure. The sol was prepared using 4.2 wt% Brij-58 as the surfactant template and molar ratio TEOS:EtOH:Water:HCl:Brij-58=1:0:67:0.004:0.046. **C.** Calcined particles exhibiting vesicular mesophase ( $d_{100} = 92 \text{ \AA}$ ). The sol was prepared using 5% P123 as the triblock copolymer template and molar ratio, TEOS:EtOH:Water:HCl:P123 = 1:22:5:0.004:0.0096. **D.** uncalcined silica particles demonstrating 'growth' of ordered vesicular domains from the liquid-vapor interface. Particle interior exhibits disordered, worm-like mesostructure. The sol was prepared using 2.5% Brij-56 as the surfactant template and molar ratio, TEOS:EtOH:Water:HCl:Brij-56 = 1:13:67:0.004:0.04. All calcination treatments were performed at 425°C for 3 hours in air (heating rate = 1°C/min).

**Figure 3** TEM micrographs of a variety of nanocomposite particles. **A.** Silica/gold nanocomposite particle exhibiting an ordered hexagonal mesostructure. Colloidal gold (particle size 1-3 nm) was prepared in inverse micelles according to the method of Brust *et al.*[28], using 1-dodecanethiol as a stabilizing agent. The gold colloids were added to a silica/5wt% CTAB sol, prepared with molar ratio, TEOS:EtOH:Water:HCl:CTAB=1:0:67:0.004:0.15. During aerosol processing, hydrophobic gold colloids partition into the hydrophobic micellar interiors and are subsequently incorporated in the hexagonal mesophase. TEM and XRD indicate  $d_{100} = \sim 60 \text{ \AA}$ , (compared to 32.5  $\text{\AA}$  (see Figure 2(A)), consistent with incorporation of the gold colloids in the hexagonal silica mesophase. **B.** Fluorescent silica/rhodamine B nanocomposite particles exhibiting hexagonal mesophase. The sol was prepared by adding 0.8 wt% rhodamine B to a silica/4.2 wt% Brij-56 sol prepared with molar ratio, TEOS:EtOH:Water:HCl:Brij-56 = 1:13:67:0.004:0.068. Inset shows an optical photomicrograph of the fluorescence emission imaged through a rhodamine B filter, confirming retention of the dye structure. Samples were exhaustively washed prior to optical microscopy. **C.** Silica/polymer nanocomposite particle exhibiting puckered vesicular mesostructure (Inset: SEM image showing uniform periodic dimpling). The sol was prepared by adding poly(propylene glycol dimethylacrylate) (PPO, MW=660) and thermal initiator, 1,1'-Azobis (1-cyclohexanecarbonitrile) (ACHN) to a silica/5wt% P123 sol prepared with molar ratio, TEOS:Ethanol:Water:HCl:P123:PPO:ACHN = 1:22:5:0.004:0.0096:0.025:0.009. During aerosol processing the oligomer and initiator are incorporated into the hydrophobic portion of the template bilayers[21] resulting in thermally initiated polymerization of PPO. **D.** Silica/polymer nanocomposite particle exhibiting reticulated foam structure. The sol was prepared as in (3C) but with molar ratio TEOS:Ethanol:Water:HCl:P123:PPO:ACHN = 1:13:67:0.004:0.0096:0.025:0.009. The greater water concentration compared to (C) resulted in micelle formation (in the starting sol) and incorporation of PPO and ACHN into the micellar interiors. Subsequent micelle coalescence combined with thermally initiated polymerization during aerosol processing resulted in the reticulated nanostructure.

**Figure 4** Small angle x-ray scattering (SAXS) curves for silica particles exhibiting hexagonal (A) or vesicular (B and C) mesophases. Samples A and C were prepared as in figures 2A and 2C, respectively. Sample B was a calcined particle exhibiting a vesicular mesostructure ( $d_{100} = 65 \text{ \AA}$ ). The sol was prepared using 4.2% Brij-56 as the surfactant template and molar ratio, TEOS:EtOH:Water:HCl:Brij-56 = 1:13:67:0.004:0.068. Inset: Corresponding  $\text{N}_2$  adsorption-desorption isotherms, BET surface areas, and pore diameters. (Note the calculated pore diameter of Sample A is slightly less than 2.0-nm, the lower limit of mesoporosity according to the IUPAC definition. Thus the validity of the BET expression is questionable). SAXS experiments were performed at the University of New Mexico/Sandia National Laboratories SAXS facility<sup>[29]</sup>. ~0.5-mm thick samples were prepared by sprinkling powder on adhesive cellophane tape used as a 1.5-cm diameter window. SAXS data was collected (30 minutes/run) using the 5-m Pinhole instrument in short geometry ( $0.3 < q < 7 \text{ nm}^{-1}$ , where  $q$  is defined as  $(4\pi/\lambda)\sin(2\theta/2)$ , and  $2\theta$  is the scattering angle). SAXS data is uncorrected for background. Hydraulic pore diameters were calculated from the pore volume and BET surface area.

**Figure 5** TEM images of mesostructured films formed by an aerosol-assisted thin film deposition route, using a 5% P123 sol (identical to that in Figure 2C). **A.** Cross-sectional TEM image of hexagonal mesostructured film deposited on silicon substrate. **B.** Plan-view image of hexagonal mesostructured film deposited on holey carbon grid. **C.** TEM image of corresponding aerosol droplets during coalescence on a holey carbon grid. Film samples were prepared using the apparatus in Figure 1 but without operation of the furnace and replacement of the filter with a silicon substrate (A) or holey carbon grid (B). Partially coalesced droplets were prepared as in (B) but with introduction of HCl vapor to promote silica condensation and thereby 'freeze-in' the evolving mesostructure prior to complete coalescence. From (C) we conclude that film formation is possible by avoidance of particle solidification. However the semi-solid nature of the particles (along with their low surface tensions) enables film formation over holes much greater in diameter than the film thickness.

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Correspondence and requests for materials should be addressed to C.J.B (e-mail: cjbrink@sandia.gov)

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