

Nanostructural Engineering of Complex Functional Particles

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Introduction

Particles offer a convenient and flexible pathway to deliver the potential benefits of nanotechnology in many applications ranging from protective coatings to drug delivery and screening. Achieving the full promise of such particles requires the ability to engineer their architecture and functionality at the nanoscale. This project is exploring such particle engineering through the use of evaporation-induced self-assembly (EISA) in droplets to introduce nanoscale porosity and architecture into silica and other oxide particles, coupled with several approaches for adding chemical and physical functionality to the particles. The incorporation of functionality via lipid bilayer coatings and molecular recognition should enable applications in drug screening and biological sensing, while functional modification to the pore interiors offers exciting prospects for stimuli-sensitive controlled release, as well as applications in catalysis, separations, and other areas.

Particle Synthesis by Evaporation-Induced Self Assembly

In evaporation-induced self assembly (EISA), a surfactant or amphiphile in an inorganic precursor solution (typically alkoxide) undergoes concentration-driven mesophase transformations as the solvent evaporates from the droplet. Simultaneously, reactions occur between the inorganic species that eventually solidify the particle and freeze the mesostructure. Removal of the organic provides mesoporous particles possessing the order introduced by the amphiphile. Thermodynamics, which drives the mesophase transformations, operates together with the kinetic influences of evaporation, inorganic reactions, and self-assembly to determine the architecture of the particles produced. We have demonstrated the ability to control the mesostructural order (hexagonal, cubic, lamellar) by virtue of the choice of amphiphile, solution composition, or use of additives.^[2-4] Pore sizes ranging from 2 to 7 nm have been produced in hexagonally ordered particles.

Furthermore, we have shown that this can be done for particle sizes ranging from submicron to tens of microns.^[2-4] Fig. 1 depicts the process and shows several examples of submicron mesoporous particles. Fig. 2 shows monodisperse hexagonally ordered particles produced using a vibrating orifice aerosol generator (VOAG), together with a particle fracture surface showing that the tubular pores terminate normal to the surface. Highly monodisperse particles are extremely attractive for quantitative diffusion studies and some particular applications.

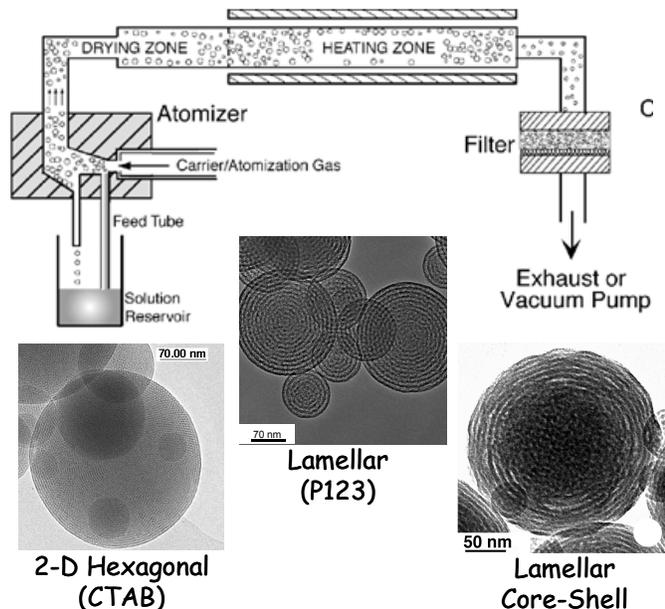


Fig. 1. Depiction of EISA in aerosols and several examples of submicron particle architectures.

Fundamental Understanding of EISA

Self assembly in droplet EISA is fundamentally different from conventional self assembly due to, among other things, the presence of the vapor-liquid (V-L) interface. We are investigating the influence of this interface on self assembly using a Monte Carlo (MC) model of lattice-gas systems. By creating small (~ 50 nm) drops to mimic the assembly of amphiphiles in a constrained environment, we observe a higher degree of order when assembly of spherical micelles occurs compared to assembly in the bulk. In order to use molecular modeling for larger systems (0.1 - 0.5 μm drops) a new coarse-grained lattice-gas model is currently under development. The approach can be viewed as applying a local mean field approximation. Initial MC tests show that the equation of state is well reproduced by the coarse-grained versions. More comprehensive assessments, including the calculation of interfacial properties such as the V-L tension, are underway.

Engineering of Functionality

Lipid Bilayer Coating and Pore Surface Functionalization:

The most sophisticated and novel applications of nanoengineered particles will involve synthetic or post-synthetic procedures to provide specific functionality. For example, we have developed a post-synthesis procedure using surface-initiated atom transfer radical polymerization (ATRP) of N-isopropyl acrylamide to produce PNIPAM-modified particles that demonstrate temperature-sensitive uptake and release of dye molecules.^[5] Functionality can be introduced to the particle outer surface by coating with derivatized phospholipid bilayers. We have developed a protocol for depositing such bilayer coatings on mesoporous particles, and have demonstrated that the properties are similar to those on nonporous beads.^[6] It was also shown that functionalization of the lipid bilayer can be achieved by incorporation of biotinylated lipids or a transmembrane protein.^[6]

Encapsulation and Controlled Release: Encapsulation of specific agents for subsequent controlled release represents a very attractive potential application of these particles. The functionality of the particles in this case is provided by virtue of the engineered transport properties of the particles, and by way of the method of encapsulation or containment. One example is provided by the encapsulation of CeCl_3 within a mesoporous silica shell using EISA (Fig. 3). After removal of the surfactant, the $\text{CeO}_2/\text{CeCl}_3$ core is surrounded by a mesoporous silica layer through which Ce^{+3} can be released to provide corrosion inhibition. Release measurements are discussed further below.

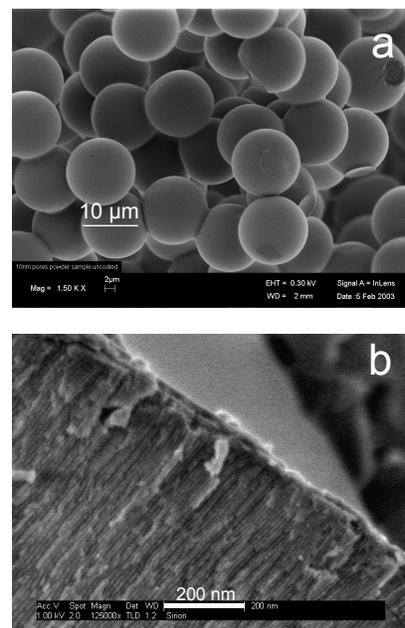


Fig. 2. Monodisperse hexagonal mesoporous silica particles (a) displaying normal pore orientation at the particle surface (b).

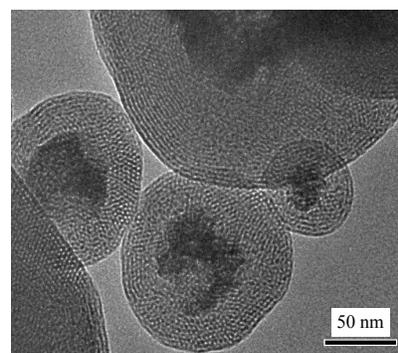


Fig. 3. TEM of composite particles containing a core of $\text{CeO}_2/\text{CeCl}_3$ and shell of ordered mesoporous silica.

Catalyst Applications: Mesoporous oxide particles are enticing candidates for heterogeneous catalysis applications due to the precise control of pores size, and very high pore volume and surface area. One important issue associated with catalytic applications of these materials is the thermal stability of the mesoporous silica structure. We have found that the simple addition of cationic dopants Al^{+3} and Zr^{+4} at low levels lead to dramatically enhanced surface area stability in moist environments above 700 °C, as well as in boiling water. In addition, several approaches have been explored for the incorporation of noble metals into the pore structure of these particles. We have observed that confinement of metal to the pore interiors is often difficult. However, we recently found that impregnation of hexachloroplatinic acid, followed by reduction in the presence of water vapor, leads to the formation of platinum nanowires within the pores of the hexagonally ordered mesoporous silica (Fig. 4). This provides a powerful imaging technique, showing the swirling nature of the tubular pore bundles. Continued impregnation and reduction may lead to very high catalyst loadings with improved thermal stability compared to conventional catalyst supports.

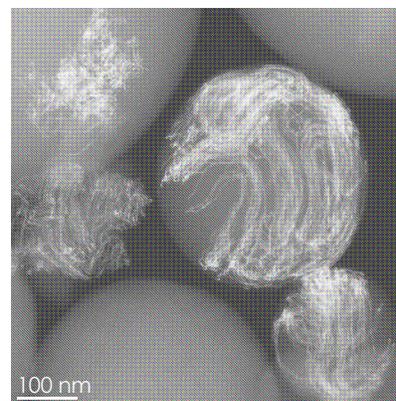


Fig. 4. Annular dark field TEM showing Pt nanowires filling pores of hexagonally ordered mesoporous silica particles.

Particle Transport Properties: Transport (diffusion) rates within particles are important for a wide variety of applications where the ultimate goal is to utilize the particle to deliver or take up a specific agent. Diffusion rates in these particles can be tailored via the type of mesostructure, the pore size, the particle architecture, and modification of the pores or particle surface. Several of these strategies are being investigated. For the silica-encapsulated Ce particles shown in Fig. 3, diffusion of Ce^{+3} out of the particles occurred over approximately one hour in an acidic aqueous environment, and modeling indicated an effective diffusion coefficient of approximately $10^{-15} \text{ m}^2/\text{s}$ through the CTAB-templated mesoporous silica. Other release studies using fluorescent dyes have been conducted on larger monodisperse CTAB-templated particles with PNIPAM-modified pores. These particles showed a slower, temperature-dependent release rate of fluorescein dye, with an effective diffusion coefficient that varied from $5 \times 10^{-16} \text{ m}^2/\text{s}$ at 50 °C to $9 \times 10^{-17} \text{ m}^2/\text{s}$ at 25 °C.^[5] These results reflect the effects of pore modification, and demonstrate the functionality of the PNIPAM-modified pores. Confocal fluorescence spectroscopy has also been used to observe and quantify diffusion in these particles.^[6] We continue to explore methods to provide better control of the release rate and period.

References

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