# The Features of Self-Assembling Organic Bilayers Important to the Formation of Anisotropic Inorganic Materials in Microgravity Conditions

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## Objectives and Relevance to Microgravity Science

There is a growing need for inorganic anisotropic particles in a variety of materials science applications. Structural, optical, and electrical properties can be greatly augmented by the fabrication of composite materials with anisotropic microstructures or with anisotropic particles uniformly dispersed in an isotropic matrix. Examples include structural composites, magnetic and optical recording media, photographic film, certain metal and ceramic alloys, and display technologies including flat panel displays. While considerable progress has been made toward developing an understanding of the synthesis of powders composed of monodispersed, spherical particles, these efforts have not been transferred to the synthesis of anisotropic nanoparticles. Amphiphilic molecules can be used to prepare either "water-in-oil" or "oil-in-water" micelles, and these organic "template" structures have been used to control the size of growing inorganic particles. Larger concentrations of the segregated phase leads to the formation of rod-like micelles and, at even greater concentrations, bilayer structures. In our laboratories, we have demonstrated that these anisotropic micellular structures can be used as templates to prepare anisotropic particles in both metallic and inorganic salt systems.

The major objective of the program is to develop a fundamental understanding of the growth of anisotropic particles at organic templates, with emphasis on the chemical and structural aspects of layered organic assemblies that contribute to the formation of anisotropic inorganic particles. Target systems include both metal particles important to conductive pathways in microelectronics such as Ag/Pd alloys and Pt, and II-IV semiconductors such as CdSe and CdS. As part of our studies, we make extensive use of model membrane systems prepared by Langmuir-Blodgett methods in order to efficiently survey possible template systems and establish the important chemical and geometric features of the templates that influence particle growth. Lessons learned on the model systems are used to develop larger-scale preparations of the targeted inorganic materials at bilayer structures formed from "oil-in-water" segregated phase systems. It is these systems that will eventually lead to high yield, monodisperse preparations.

When going from the model systems toward larger scale solution preparations, the fundamental chemical and geometrical templating interactions will be in competition with effects caused by convection and in some cases sedimentation, and the limits of these procedures will be masked by gravity effects. Minimizing convectional induced fluid shear and sedimentation in the microgravity environment should allow extended structure organic templates to form rather than fragments or "rafts" that have resulted in our preliminary experiments at Earth's normal gravity. These

imperfections in the template structures makes it difficult to assess the role of the chemical and geometrical nature of the template in controlling particle size and dispersion. A further objective of this project is to develop template/particle systems that are suitable for potential microgravity investigations probing the mechanism of templated particle growth.

## Significant Results of the Investigation

*LB Film Model Systems*: Previous success using amphiphilic molecules assembled into specific lysotropic micellular structures as templates for the formation of anisotropic platinum particles has lead to LB model studies of silver and gold particles at organic templates. Four organic surfactants with different headgroups ($PO_3^{2-}$, $OSO^{3-}$, SH, $COO^-$) have been spread onto an aqueous silver nitrate solution. The resulting Langmuir films were then transferred onto different hydrophobic substrates to form multilayered LB films. Exposure of these films to formaldehyde vapor results in the formation of quasi-spherical silver particles which sizes range from 10 to 20 nm within one day. Further exposure to formaldehyde vapor involves the coalescence of these nanoparticles to give three dimensional aggregates which have been characterized by Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). Gold nanoparticles were generated by ultraviolet irradiation of LB films of octadecylamine (ODA), 4-hexadecylaniline (HDA) and benzyldimethylstearylammonium chloride monohydrate (BDSAC) deposited from aqueous $HAuCl_4$ subphases. In contrast, no gold crystals were observed in irradiated LB films prepared from monolayers of dipalmitoyl-DL-α-phosphatidyl-L-serine (DPPS) and dipalmitoyl-L-α-phosphatidylcholine (DPPC). There is a marked influence of the surfactants used to prepare the LB matrix on the shape of the gold particles. Particles formed in ODA and BDSAC LB films were grown with well defined crystal faces, while particles generated in HDA LB films were irregular in shape. The observation of gold particles in some of the films and not others indicates that strong attractive electrostatic interactions exist between the positively charged polar heads of ODA, HDA and BDSAC and the $AuCl_4^-$ anions present in the subphase.

*Reverse Micelle Templating*: Nanometer-sized composite particles (nano-composites) with core-shell structure have been prepared by arrested precipitation of metal or semiconductor clusters in reverse micelles, followed by hydrolysis and condensation of organometallic precursors in the microemulsion matrices. Temporally discrete nucleation and growth at elevated temperature (70 °C) give the resulting particles a narrow size distribution and defined crystallinity. Both the size of the core particles and the thickness of the coating layers can be varied by controlling processing parameters such as the ratio of water to surfactant and the ratio of water to organometallic precursors. By controlling the pH conditions and aging temperatures, a transparent gel composed of nanometer-sized inorganic clusters has been obtained. Quantum confinement effects on the cadmium sulfide nanosize clusters and nano-composites have been observed. For the silver metal clusters and nano-composites the shift of the absorption peak at the surface-plasmon resonance frequency due to classical limited mean-free path of the conduction electrons or quantum size effects has been observed. The enhanced third-order nonlinear susceptibility of the silver nano-composites results from the local field enhancement and size-effects, which has been experimentally demonstrated by optical phase conjugation technique.