THE FEATURES OF SELF-ASSEMBLING ORGANIC BILAYERS IMPORTANT TO THE FORMATION OF ANISOTROPIC INORGANIC MATERIALS IN MICROGRAVITY CONDITIONS

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I. Project Hypothesis and Objective.

Materials with directional properties are opening new horizons in a variety of applications including chemistry, electronics, and optics. 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. The new applications and the need for model particles in scientific investigations are rapidly outdistancing the ability to synthesize anisotropic particles with specific chemistries and narrowly distributed physical characteristics (e.g. size distribution, shape, and aspect ratio).

While there has been considerable progress toward developing an understanding of the synthesis of powders composed of monodispersed, spherical particles, efforts to prepare anisotropic nanoparticles are lagging. 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 bilayer structures. In our laboratories, we have demonstrated that these anisotropic micellar structures can be used as templates to prepare anisotropic particles in both metallic and inorganic salt systems. This project aims to extend the methods that have been developed to other inorganic particle systems and to increase our level of understanding of how anisotropic particles are formed at lamellar templates.

As part of our studies, we make extensive use of model membrane systems prepared by Langmuir-Blodgett (LB) methods in order to efficiently survey possible template systems and establish the important chemical and geometric features of the templates that influence particle growth. Motivation for studying single-layer systems is two-fold. First, the chemical and structural properties of LB films are easily manipulated and characterized, allowing us to tailor the template system to the inorganic material being formed. Secondly, LB films on surfaces are less subject to the convectional shear, sedimentation, and agglomeration normally experienced by particles synthesized in the bulk solution. The surface confined bilayers can be used to establish how particle growth is limited by chemical and geometric considerations in the absence
of convection and sedimentation effects. Results from the surface confined studies are continuously utilized in the design and choice of solution micellar systems as they are tailored to the desired inorganic materials. The program uses what is learned on the model systems 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.

II. Justification for Microgravity Experiments.

The advantages of a microgravity environment for studying crystallization, nucleation and growth processes are well documented. In the present project, minimizing convectional induced fluid shear and sedimentation in the microgravity environment should allow extended organic templates to form rather than fragments or "rafts" that result at normal Earth's gravity. Convection limits the size of uniform template domains and also creates a non-uniform size dispersion. These imperfections in the template structures make it difficult to assess the role that the chemical and geometric identities of the template play in controlling particle size and dispersion. Reducing convection will also minimize the agglomeration of particles that are produced. Sedimentation is less of a problem than convection in the synthesis and processing of nanoscale particles or particles with nanometer scale in at least one dimension. Analysis demonstrates that the displacement due to gravity becomes less dominant as the particle size becomes smaller than about 0.25 \( \mu m \). In contrast, sedimentation will begin to mask template effects as particle sizes increase beyond several hundred nanometers.

III. Project Results.

_Metal Particles Formed in Free Standing Bilayer Templates._

Templating in free standing bilayers can be used to produce metal platelets as well as the semiconductors previously described. A variety of metallic platelets have been prepared in the water-octylamine system and the pentylamine/sodium dodecylsulfonate-toluene-water system including Ag, Ni, and Ag/Pd alloys of special interest to the electronics community. An image of an array of Ag platelets is shown in Figure 1. For each particle system, the surfactant system binary or ternary phase diagram has been determined in the presence of the relevant metal ions. Another complication is that after the platelets form, they must be protected by polymer dispersants to avoid aggregation of the metal particles. Poly(ethylene imine) was used to stabilize the metal particles shown in Figure 1.
Small, platelike particles of Pt$^0$ have previously been formed by the chemical reduction of Pt$^{2+}$ in a pentylamine/sodium dodecylsulfonate-toluene-water lyotropic bilayer system and platelet Ag particles were produced in an octylamine-water bilayer system. In each case, it was shown that both bilayer templating and the specific interactions of the amine groups were necessary to achieve the platelet particles. Using Langmuir-Blodgett model systems, the photochemical reduction of metal ions to form metal particles in layered templates has now also been demonstrated for Pt, Ag, and Au. The Pt$^0$ platelet size ranged from 3-5 microns in diameter, which is much larger than the particles seen in the related micelle preparations. Sedimentation and convection are not issues in the Langmuir-Blodgett model studies, suggesting that these factors may be responsible for limiting particle size in solution preparations.

Several nitrogen-containing headgroups were investigated to monitor the importance of specific interactions in the formation of Pt platelets. Plate-like Pt$^0$ particles were only observed with an amine headgroup, consistent with the results from micelle templating. The Au$^0$ and Ag$^0$ particle morphology was also influenced by the chemical nature of the headgroup. One of the templates studied was the phospholipid dipalmitoylphosphatidylserine (DPPS). Normally, phospholipids do not form stable Langmuir-Blodgett films. However, in the presence of Pt$^{2+}$, Pd$^{2+}$, and Au$^{3+}$ ions, stable LB films were observed. We showed that film stability originates from complex formation between the metal ion and the serine headgroup. This was the first time that a stable LB film of DPPS has been reported. Photoreduction resulted in formation of the corresponding metal particles, showing that the biomimetic phospholipid bilayers can also be used to template metal platelets.

Pd/SiO$_2$ nanosized particles have been synthesized using a reverse micelle technique combined with metal alkoxide hydrolysis and condensation. The size of the particles and the thickness of the coating can be controlled by manipulating the relative rates of the hydrolysis and condensation reaction of tetraethyl orthosilicate (TEOS) within the microemulsion. The average size of synthesized Pd/SiO$_2$ particles was in the size range 20–40 nm and Pd particles were 1–5 nm. The effects of synthesis parameters, such as the molar ratio of water to TEOS and the molar ratio of water to surfactant, have been developed. The core particles are formed by a homogeneous nucleation and growth process; the shells are most likely formed through heterogeneous nucleation and growth. The nucleation and growth of palladium particles is likely to be a diffusion-controlled process through interaction between micelles, but it can be influenced by many other factors such as phase behavior and solubility, average occupancy of the reacting species, the aqueous pool, and the dynamic behavior of the microemulsion.

The templating of inorganic particles at organic templates should be general, and to show this, we have extended the ideas to biorelevant systems. The inorganic mineral calcium oxalate monohydrate has been grown at Langmuir monolayers from supersaturated subphases. Selectivity is observed in the crystal faces attached to the monolayer, with the calcium-rich COM (10-1) face predominating. Also, crystal attachment is enhanced for negatively charged surfactant layers. The results imply that calcium binding to the monolayer plays a key role in particle nucleation. In addition, we observed that lower surface pressures on the monolayer lead to enhanced attachment. The result was opposite of what we expected, but suggests that fluidity of the template is important. These are important concepts related to templating of
Organic/inorganic interfaces that help clarify the mechanism of metal particle templating in micelle phases.

**Mechanism of Particle Growth at Lamellar Templates.**

The results on metal particles, along with our previous work on semiconductor systems, has now led us to a better, yet still incomplete, understanding of how the layered templates lead to anisotropic particles.\(^1\)\(^-\)\(^6\) The organic assembly regulates particle growth through a combination of three different processes, which vary in relative importance for any given template/particle system. The first process is that of confinement. The template defines a space in which the particle can grow. A second process is through specific interactions between the template and the particle. Here, the template acts similarly to an adsorbate or poison in homogeneous preparations and stabilizes certain crystallographic faces at the template interface. Finally, the template controls mass transport to the growing particle. The diffusion is easier parallel to the template walls, and particles will grow in the directions that material is supplied.

We have observed that there are at least two general mechanisms that lead to the templating of two different classes of platelike particles. Each mechanism takes advantage of the processes of confinement, specific interactions and mass transport. The first we will call crystal templating, where the products are anisotropic single crystal particles. These particles result from a slow nucleation event, giving relatively few nuclei, and subsequent growth of the individual crystals.\(^10\) The anisotropic shape results from a combination of crystallization physics (determined from the solid-state structure of the material), specific interactions between the template and growing crystal faces, and directional transport of the reactant to the crystal.\(^11\) Using micellar templates, we have observed single crystal metal platelets with dimensions up to several hundred nanometers and the size dispersion is broad. Using LB templates, particle sizes are somewhat larger, up to several microns, but there is also substantial polydispersity. The factors that control the size and polydispersity are not yet clear, yet we hypothesize that the size and uniformity of the template domains are important.

The second mechanism we will call aggregate templating. Here, the products are assemblies of smaller single crystal particles that aggregate in the shape of a platelet. The constituent particles need not have the same shape of the final product, and are most often spherical. The mechanism involves rapid nucleation followed by diffusion of the nuclei to form the platelets. The ultimate particle shape is limited by the vectoral diffusion of nuclei, which in turn is controlled by the shape of the template. At first glance, the influence of specific interactions on particle shape would appear to be less important in this mechanism, however, the chemical make-up of the template can affect the rapid nucleation event which in turn influences the polydispersity of the product. Particles formed through aggregate templating have a smaller dispersity than the single crystal particles. Preparations yielding particle sizes ranging from a few nanometers up to hundreds of nanometers have been developed for CdS in micelle templates.\(^1\)

**Anisotropic Particle Suspensions.**

A potential application of anisotropic particles are a mesogens in colloidal suspensions.\(^12\),\(^13\) These complex suspensions of anisotropic inorganic particles are sometimes called "mineral
liquid crystals," because of the phase behavior and optical properties that parallel molecule and polymer-based liquid crystals. The electronic and chemical structures of inorganic extended solids could lead to hybrid materials that combine liquid crystalline behavior with traditional solid-state properties, such as conductivity or magnetism, which can be tuned through chemical synthesis.

We have experimented with anisotropic suspensions based on the family of layered metal hydroxides, Cu$_2$(OH)$_{4n}$X$_n$, where X is an anionic ligand. When X is an alkylcarboxylate, then organic suspensions exhibit lyotropic behavior. The layered copper hydroxycarboxylates form as very small flat needles, a micron or less in length. The surface of the particles is hydrophobic as a result of the alternating organic/inorganic layered structure. The particles can be taken up in organic solvents, such as toluene, to yield anisotropic suspensions. The mixed organic/inorganic nature of the family of metal hydroxycarboxylates provides an opportunity to demonstrate the idea of combining properties into a single-phase material, as some examples are magnetic. We show, below, that the complex suspensions can be cast into transparent, anisotropic magnetic films.

Polycrystalline powders of the copper(II) hydroxycarboxylates can be dispersed in organic solvents such as toluene, xylene, or benzene. The resulting mixtures show different phase behavior that depends on the concentration range and temperature. The general trend for the copper(II) hydroxystearate particles dispersed in toluene at ambient temperature, is shown in Figure 1. At low concentration, below about 1.5%, the particles do not disperse throughout the solvent, but rather there is segregation of the suspended particle phase and the clear, pure solvent. If viewed through cross polarizers, the suspended particle phase is birefringent, while the pure solvent phase is isotropic. As the concentration of polycrystalline solid is increased, a gelatinous phase results that is also birefringent (Fig. 2).

An optical micrograph of the gel phase, observed through untreated glass plates and obtained through crossed polarizers, is shown in Figure 3. The optical birefringence shows a marble texture characteristic of liquid crystalline phases. Upon heating either the biphasic or gel phases, an isotropic solution is obtained above a clear point. For the copper(II) hydroxystearate the clear point is 70 °C ± 1 for all compositions. The birefringent domains are recovered upon cooling through the clear point. Also consistent with the characteristic fluidity associated with
liquid crystalline behavior, the birefringent domains change shape and size in response to external stimuli such as shear or uneven pressure.

Oriented Films
The suspensions can be cast onto a surface that, after solvent evaporation, leaves an oriented thin film. For example, casting the copper(II) or nickel(II) hydroxystearate suspensions onto Mylar, followed by lifting off of the surface, results in self-standing, flexible, transparent films (Figure 4a). Since the solvent has been removed, the thin films are comprised of only the starting powder, but are now transparent because the individual crystallites are aligned, leading to decreased scattering. A scanning electron microscope image (Figure 4b) shows that the texture of the film is very homogeneous, and the particles show a preferential orientation with the long axis parallel to the surface of the film.

FIGURE 4. (a) A free-standing film of copper(II) hydroxystearate set on top of the word "film." The film was cast from a nematic gel in toluene. (b) an SEM image of the edge of a copper(II) hydroxystearate film showing texture that results from the alignment of the particles parallel to the surface, the scale bar corresponds to 20 μm.

FIGURE 3. Crossed polarized micrograph of a copper hydroxystearate gel (5% weight). A marble texture with black domain boundaries can be seen. The picture area has dimensions 97 x 58 μm².
IV. Publications Resulting From this Award.

Journal Articles.


Proceedings Articles.


V. Students Supported by this Award.

Renal Backov
Sarah Lane
Eduardo Perez
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D. Yener

Students have recently found employment at:

Unilever
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References Cited.