Thin films and nanolaminates incorporating organic/inorganic interfaces

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Recent research on the solution-based fabrication of inorganic thin films and organic/inorganic nanolaminates has ranged from fundamental studies of biomineralization to the synthesis of novel materials and devices. Highlights include the elucidation of how biogenics and model organic nucleants affect the form of the biomineral; synthesis of mesoscale nanocomposite films by surfactant templating at interfaces; and fabrication of heterostructures with enhanced electronic and mechanical properties.

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Current Opinion in Solid State & Materials Science 1997, 2:358–364

Electronic identifier: 1359-0286-002-00358

Abbreviation
LB Langmuir–Blodgett

Introduction

The first known examples of organic/inorganic nanolaminate composites date back more than 500 million years to the emergence of mollusks [1]; the brickwork architecture of nacre or mother-of-pearl, consisting of alternating tablets of aragonite (a few hundreds of nanometers thick) and thin organic films (a few tens of nanometers thick), imparts to the mollusk shell an exceptional strength without the brittleness associated with pure inorganic phases. Although this model has continued to inspire materials scientists, research involving organic/inorganic interfaces, thin layers, and lamellar heterostructures has expanded far beyond their mechanical properties to include structural, electronic, and optical properties of mesoscale composites. We will review recent developments in the synthesis and processing of inorganic thin films at organic interfaces and between organic layers. In keeping with the spirit of biomaterials, we emphasize aqueous solution-based techniques at ambient or near-ambient temperature and pressure. Even this restricted focus covers a vast and rapidly growing literature; fortunately, many of the individual research areas are well reviewed, and we therefore emphasize the common themes behind the various synthesis strategies, leaving interested readers to follow the highlighted references to primary sources.

Related reviews of organic/inorganic interfaces and biomimetic thin films have recently been published [2•–6•]. Investigations of other interfaces and thin film geometries are also well served by recent reviews; examples include polymer films on inorganic substrates [7], patterned polymer and inorganic films on inorganic substrates [8], organic monolayers and organic/organic nanolaminate films [9•], and inorganic-on-inorganic thin films [10] and microlaminates [11].

The synthesis of inorganic-on-organic thin films and nanolaminates can be divided into two general approaches: nanoparticle based synthesis, where the inorganic phase is preformed, and molecular precursor based synthesis, where the inorganic phase forms *in situ*, either by precipitation or hydrolysis/condensation reactions.

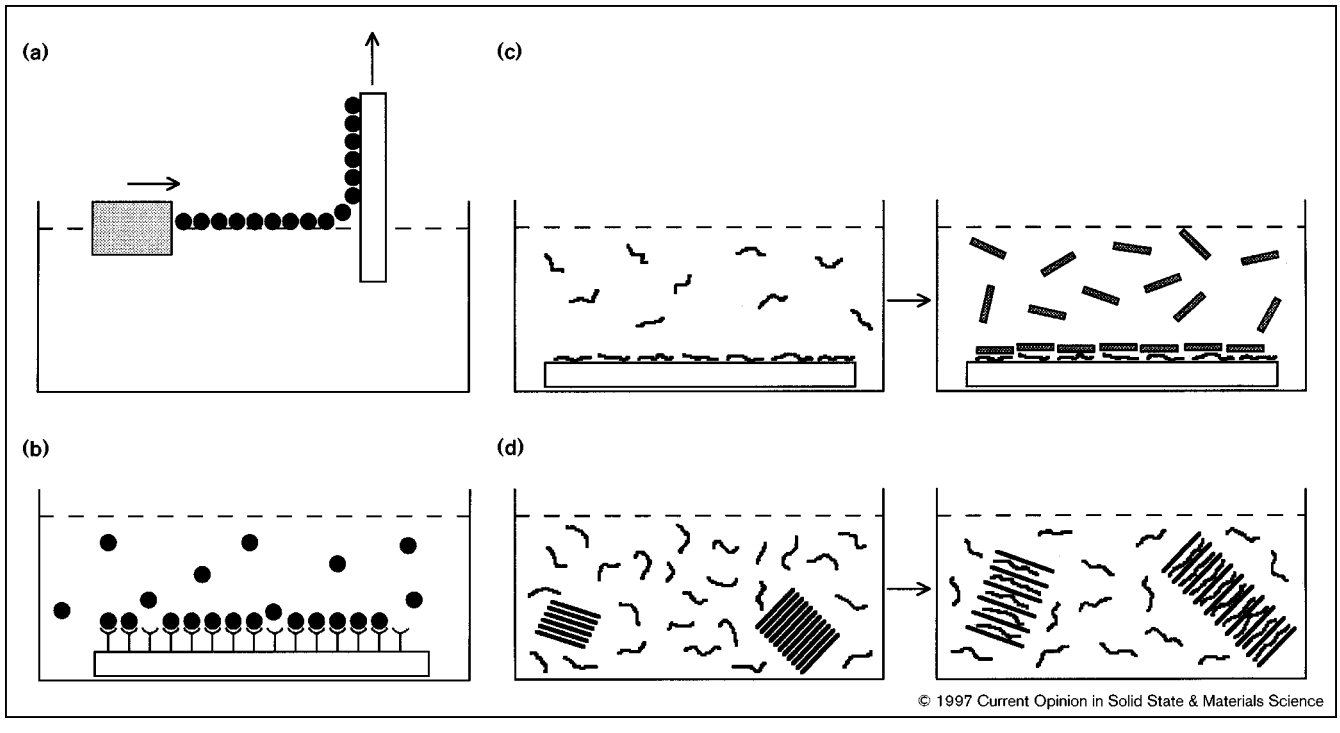
Synthesis from preformed inorganic phases

Synthesis routes using preformed inorganic particles generally fall into four categories (Fig. 1): first, Langmuir-Blodgett (LB) deposition; second, covalent self-assembly; third, alternating sequential adsorption; and fourth, intercalation of organics into layered inorganic structures. These techniques have recently been individually reviewed [2•,5•,9•]. The inorganic particles can vary widely, with compositions ranging from metals to semiconductors to insulating oxides and silicates and shapes ranging from roughly spherical to plate-like. The organic phase is typically comprised of small amphiphiles or polymers. Substrates for thin films are typically flat and hydrophilic (e.g. oxidized silicon wafers, mica cleavage planes and metal films).

LB deposition has been used successfully with a variety of roughly symmetric nanoparticles; recent examples include semiconductors [12], ferroelectrics [13] and metals [14] transferred onto oxide substrates (also see the accompanying contribution by JH Fendler in this issue, pp 365–369). The particles are coated with a hydrophobic film, spread at an air/water interface, compressed by a Langmuir film balance, and transferred to a substrate by controlled dipping in the same way that amphiphilic films are transferred. Tuning the particle hydrophobicity is critical to this application, so that particles neither flocculate strongly (too hydrophobic) nor become solubilized (too hydrophilic) [14].

A different approach uses covalent self-assembly which circumvents the problem of flocculation and attaches particles directly and irreversibly to the substrate. Metal colloids have been covalently self-assembled onto a func-

Figure 1



Schematics of nanoparticle-based synthesis routes to the formation of inorganic-on-organic thin films and lamellar heterostructures. **(a)** Langmuir–Blodgett deposition of hydrophobically coated nanoparticles. A movable barrier (shaded) compresses the particles (black spheres) into a densely packed film at the air/water interface (shown by the dashed line); this film is transferred to a solid support by pulling the substrate through the interface. **(b)** Self-assembly of metallic nanoparticles on an organically functionalized surface containing binding sites for the particles. **(c)** Sequential adsorption of polyelectrolytes and oppositely charged nanoparticles. A charged surface is first coated with a single layer of oppositely charged polyions by immersing it in a solution of these polyanions (left) and rinsing. This polyanion layer is then coated with a single layer of oppositely charged nanoparticles by immersion into a nanoparticle suspension (right) and rinsing. This type of alternating adsorption can be repeated or varied as necessary to build up a nanocomposite film (the particles are shown here as planar but can be of any shape). **(d)** Infiltration of layered solids by polymers. A layered solid (shown schematically as closely spaced parallel stacks) exposed to an organic solution or polymer melt (left) transforms over a period of time into a solid with organics (right), provided that certain wetting requirements are satisfied.

tionalized organosilane film, which itself is covalently attached to a surface [15•,16]. Such metal colloid monolayers have been proposed as useful backing surfaces for surface enhanced Raman scattering (SERS) because they possess a uniform and well-defined mesoscale roughness which can be optimized independently of the substrate [16].

Perhaps the most versatile scheme for generating heterostructured thin films is sequential adsorption (reviewed in [9•]), this approach is based on the ionic self-assembly of charged (or polarizable) inorganic particles on oppositely charged polyelectrolyte layers. In a typical procedure, a flat anionic surface such as silica or mica is first covered by a molecular film of polycation by immersion in a dilute solution followed by rinsing; a layer of anionic particles is then similarly adsorbed from a dilute dispersion onto the polycationic film, and this alternating adsorption is repeated and varied as necessary to build up a nanolaminate film. The great advantage of this approach is that customized films can be built literally layer-by-layer; sequential adsorption is indeed a wet-chemistry analogue of molecular beam epitaxy that, in an inspired turn of phrase, has been termed 'molecular beaker epitaxy' [17]. Its success critically depends on each adsorption step being irreversible. Polyelectrolytes that adsorb electrostatically onto an oppositely charged layer adopt a flat conformation (rather than a random coil) to maximize their interaction, and this multiplicity of interaction sites ensures irreversible adsorption for polymers of moderate length (applications typically use polymers of >10 kD molecular weight). Alternating layers of polycations and polyanions have been shown to be flat and irreversibly adsorbed with little mixing between layers for tens of adsorption cycles [9•].

Sequential adsorption has been used to prepare heterostructured films using both roughly spherical and platelike particles [18,19•,20–23,24•]. A recent report provided evidence for the formation of stable, water-insoluble multilayers of alternating polycations and anionic platelets of montmorillonite [22]. This polycation/clay sequential adsorption appears to be a self-healing process, with large defects in the initial adsorption step becoming gradually smoothed out with further adsorption cycles [24•]. These

films have been shown to absorb moisture from the air, and have been used as humidity sensors with fast response times (a few seconds) [23]. Adsorption of metal and semiconductor nanoparticles in the inorganic layer results in films with tunable optical and electro-optical properties [18,20,21]. A recent observation [19•] of single-electron charging in a layer of gold nanospheres embedded in a complex heterostructure (effectively a nanocapacitor) demonstrates the feasibility of complex device fabrication using this relatively simple means of sequential absorption.

If, instead of tailor-made thin films, thicker stacks of simple ABAB... (where A and B are alternating layers of inorgnaic and organic material) type nanolaminates are desired for mechanical or electrical applications (see below), an elegant approach is to infiltrate organic molecules into the interlayer spaces of layered inorganics, creating a heterostructured stack in one step. The naturally occurring analogues for this approach are pillared clays. The success of this technique hinges on layered solids having exactly one weak-bonding direction which is susceptible to infiltration, but two strong-bonding directions so that the inorganic molecules do not become completely solvated by the organics. Polymers can be infiltrated either from the melt itself or from solution, or organic monomers can be infiltrated from solution and the polymerization performed *in situ*.

The most extensively studied nanocomposite systems in this class are polymer-infiltrated phyllosilicates [5•,25, 26,27•,28,29•,30–34,35•]. Direct intercalation from the polymer melt has recently been reviewed by Giannelis [5•]. Wetting considerations are of crucial significance in determining the polymer behavior; for instance, hydrophilic poly(ethylene oxide) (PEO) intercalates from the melt into the hydrophilic interlayers of montmorillonite, but hydrophobic polystyrene does not do so unless the interlayers are first hydrophobized by ion-exchanging with dialkyldimethylammonium [5•]. The dynamics of melt intercalation has also been investigated [25,26,27•], with the surprising result that the diffusion of polymer chains in the interlayer is comparable to that in the bulk melt. The group of Pinnavaia have used a different approach, swelling hydrophobically modified silicate layers by infiltration with epoxy, which then chemically hardens *in situ* [28,29•,30].

Enhancements in mechanical and chemical properties of polymer-phyllosilicate nanocomposites (as compared to pure polymer), have recently been reported, including an order of magnitude increase in tensile strength and modulus [29•] and an order of magnitude decrease in water permeability [5•]. The use of PEO-intercalated phyllosilicates as solid electrolytes has recently been reviewed [35•], and an enhanced ion conductivity has been reported for melt-intercalated (as compared to solution-intercalated) PEO-phyllosilicate [34]. A conductivity anisotropy has been measured for polyphosphazene-montmorillonite, which has been attributed to more tortuous ion diffusion paths perpendicular to the phyllosilicate planes [33].

Finally, organic intercalation has also been accomplished for layered compounds other than phyllosilicates. Recent examples include intercalation of α,ω-amino acids into zirconium phosphate interlayers followed by *in situ* polymerization to nylon-6 [36]; intercalation of pyrrole into MoS_2 interlayers followed by *in situ* polymerization to polypyrrole [37]; and electrochemical insertion of perfluorooctanesulfonate into graphite interlayers [38].

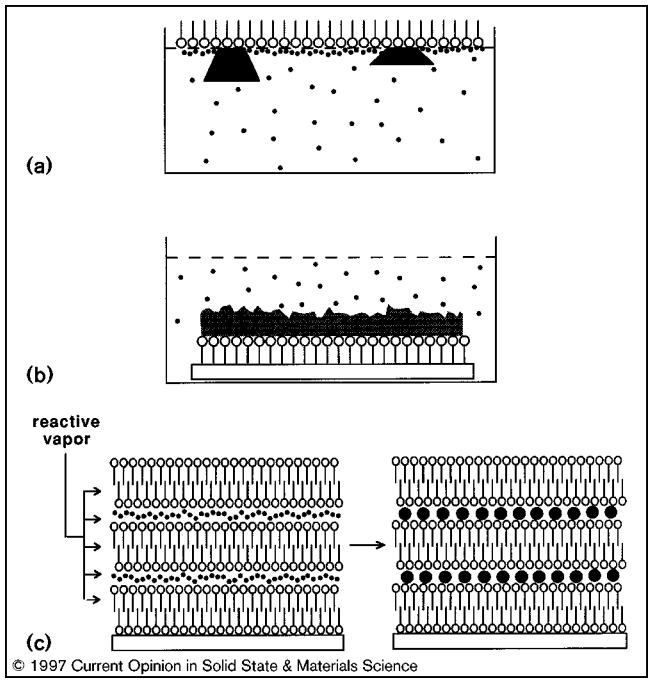
Synthesis from molecular precursors

The inorganic phase of a nanocomposite can alternatively be assembled *in situ* from molecular precursors rather than from nanoparticles. The natural prototype of this approach is biomineralization (for recent reviews and research see [39–43]), where the organic layer often plays an active role as a structural or chemical template which directs the heterogeneous nucleation or condensation of the inorganic phase. In an analogous biomimetic approach, synthetic organic layers have been employed to nucleate inorganic thin films and complex organic/inorganic nanolaminates at interfaces (see Fig. 2).

Langmuir monolayers at the air/water interface have been used as simple and versatile nucleants for inorganics, because the nucleating functionalities and their interfacial organization can be controlled by the appropriate choice of amphiphile and surface pressure. This approach was pioneered by Heywood and Mann [44] to investigate the nucleation of biominerals and was later extended to the nucleation of semiconductor and metal nanoparticles [2•]. A recent report on the formation of thin films of gold nanoparticles [45] illustrates a fairly typical procedure. The aqueous subphase contains the molecular precursor ($HAuCl_4$) in solubilized form. The headgroup of the amphiphile (here either a thiol or a cation) interacts strongly with the precursor, creating a high concentration at the air/water interface. Slow reduction to elemental gold is accomplished either by exposure to CO vapor or to ultraviolet light. Similar procedures combining solubilized precursors, high interfacial concentrations due to strongly interacting headgroups, and reactive molecules introduced through the vapor phase have been used to nucleate a variety of semiconductor particles [2•]. In general the headgroup type and surface pressure are found to play an important role in the film morphology [45,46•], and this effect is a subject of active research. An interesting variation of this approach is heterogeneous nucleation *from the melt*, that is the interfacial prefreezing, to crystallize ice at air/water monolayers of alkanols [47].

Inorganic thin films have also been grown at chemically functionalized solid/liquid interfaces (reviewed in [3•]), including cross-polymerized LB films [48], covalently self-assembled monolayers [4•,49–52], and reactive poly-

Figure 2



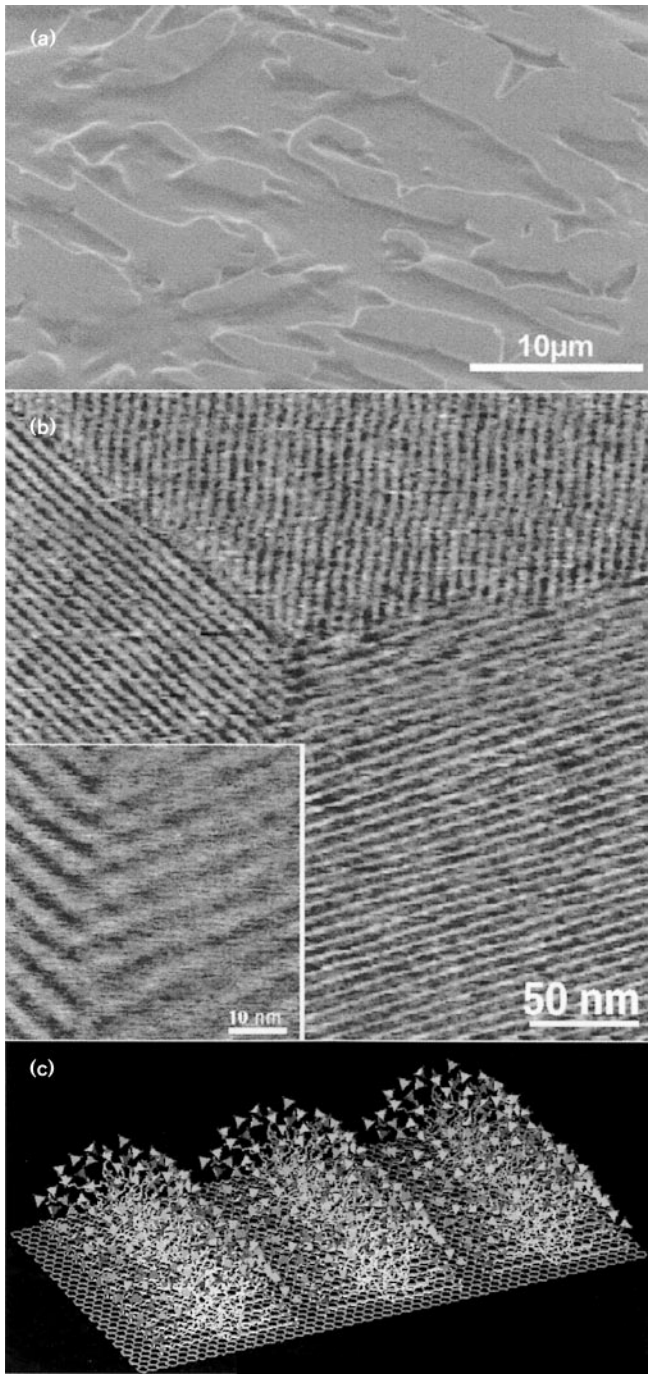
Schematics of molecular-precursor-based synthesis routes to the formation of inorganic-on-organic thin films and heterostructures. **(a)** Heterogeneous nucleation and crystal growth at a Langmuir monolayer. Attractive interactions between precursor molecules (small dots) in the subphase and the monolayer headgroups (circles) create a high interfacial concentration of precursors and give rise to interfacial nucleation of crystals (dark polygons), often after exposure to ultraviolet light or a reducing gas. **(b)** Heterogeneous nucleation and crystal growth at an organically functionalized surface. Attractive interactions between precursor molecules and the functional groups create a high concentration of precursors near the monolayer, giving rise to particles and/or films (the latter is shown). **(c)** Infiltration of a cast film of amphiphiles with molecular precursors (small dots) followed by condensation to nanoparticles (large dots) by exposure to a reducing gas. (For the final synthesis route, templating with interfacial surfactant aggregates, see Fig. 3.)

mer and biopolymer surfaces [3•,53•,54•]. Fundamental investigations of calcium carbonate biomineralization onto biomacromolecular matrices have shown that the crystal phase can be switched between calcite and aragonite by the presence of the respective soluble shell proteins, either in solution [54•] or preadsorbed onto the matrix [53•]. Applications-oriented work has focused on the near-ambient solution growth of ceramic thin films, especially of oxides and hydroxides, on functionalized self-assembled monolayers (reviewed in [4•]). Aqueous growth of titania thin films on sulfonated monolayers at 80°C resulted in an anatase phase [49], whereas ethanolic growth on hydroxylated monolayers resulted in a rutile phase [50]; patterned films of titania have also been grown using a photopatterned sulfonated substrate [51]. Near-ambient solution growth of iron oxyhydroxide films on sulfonated surfaces exhibited dense, continuous films, similar to vapor-grown films when the solution was held at just below critical supersaturation, thereby encouraging heterogeneous while suppressing homogeneous nucleation [52]. Differences in crystallographic orientation of goethite films grown on sulfonated polymers versus sulfonate-functionalized monolayers have been taken as evidence of strong surface control in the case of the self-assembled monolayers [4•].

So far we have discussed single-phase thin films, incorporating only one organic/inorganic interface. Very recent research has shown the feasibility of nanolaminate film formation incorporating several organic/inorganic interfaces by using supramolecular surfactant assemblies as templates for inorganic nucleation. Such an approach can begin with cast surfactant films which are then infiltrated with inorganics [55•,56,57], or the surfactants and inorganics can co-assemble on an interface in one processing step [6•,58•–60•]. In the first approach [55•], an aqueous dispersion of dialkyl amphiphiles is cast onto a solid substrate, creating a multibilayer surfactant film; this is then dipped into a solution containing inorganic (Cd^{+2}) ions, which intercalate into the interheadgroup spaces; finally, exposure to a reactive gas (H_2S) yields nanometer-sized inorganic (CdS) clusters without disrupting the multibilayer structure, resulting in a nanocomposite 'organic/inorganic superlattice' [55•], without the need for sequential adsorption steps. Although the only examples of this approach so far are lamellar thin films, it should also prove possible to infiltrate thin films of other surfactant phases (e.g. hexagonal, cubic), as has already been shown for the bulk solution phases [61].

The second approach uses interfacial self-assembly of surfactants and polymerizable inorganic precursors to heterogeneously nucleate a complex nanocomposite film from solution (see Fig. 3). The solution analogue of this approach using cationic surfactant micelles and polymerizable silicate precursors was invented in 1992 [62], and extensions to a variety of surfactants and inorganics have been vigorously pursued since that time (for recent results and reviews see [63–66]). Following the recent discovery that distinct, ordered surfactant aggregates (analogous to bulk micelles) also exist at solid/liquid interfaces [67•], the nucleation of a surfactant/silicate mesophase thin film consisting of hexagonally packed cylinders parallel to the substrate (mica) was reported [58•]. This mesophase was consistent with the interfacial self-assembly observed for the surfactant alone [67•], and further investigation of surfactant/silicate mesophases at other interfaces, such as silica and graphite [6•] showed that in each case the interfacial structure of the nanocomposite was consistent with the interfacial self-assembly of the pure surfactant [67•]. This strongly suggests that surfactant/surface interactions and the resulting aggregate structure are responsible for nucleating the nanocomposite thin film. The case of graphite is particularly instructive, since its inert, hydrophobic surface cannot bind silicates but can hydrophobically bind surfactant tailgroups [6•]. Other recent work has shown that unattached surfactant/silicate

Figure 3



Templating of surfactant-silicate mesoscopic thin films on graphite using interfacial surfactant aggregates [6•]. **(a)** Scanning electron microscope image of a mesoscopic silica film grown at the graphite-solution interface for 24 hours. **(b)** Atomic force microscope image of surfactant-silicate tubules on top of a growing film. Note that these tubules are straight and parallel and occur in only three orientations (related to the graphite symmetry axes [67•]). A close-up of a boundary between two orientations (inset) shows intercalating tubules. **(c)** Schematic of the first surfactant layer on graphite showing parallel half-cylindrical aggregates [67•] surrounded by silicate ions (tetrahedra). This initial aggregate layer serves as a foundation for the mesoscopic silica film. For more information see [6•].

thin films can also be formed at air/water [59•] and oil/water [60•] interfaces.

Conclusions

Most of the above approaches to nanocomposite films are 'biomimetic' in the sense that organic/inorganic interfaces are employed in synthesis and processing conditions that are aqueous, environmentally benign, and ambient. However, it seems appropriate to end this short review with recent work that takes this idea to a daring extreme — synthesizing nanocomposite films by inserting a flat substrate into an appropriate living organism. This is the 'flat pearl' technique, originated by researchers at University of California at Santa Barbara [68,69••], wherein substrates with varying surface chemistries are inserted into the shell-secreting region of a live abalone and removed after one to thirty days. The nanocomposite biomineral film grown *in vivo* on the substrate possesses a morphology similar to the natural shell biomineral. Flat, hydrophilic substrates are first coated by the organism with a nucleating organic sheet, followed by nucleation of a thin calcite layer, followed by an abrupt transition to nacreous aragonite, evidently initiated by soluble proteins [69••]. Rough or hydrophobic substrates result in abnormal calcite nucleation, which is arrested by the secretion of a second organic sheet, after which normal mineralization proceeds as above. The extraordinary chemical sensitivity of this process is further demonstrated by the fact that re-insertion of an already mineralized flat pearl does *not* reset the growth mode (i.e. by secreting a new organic sheet) but merely continues the growth of aragonite on top of the existing nacreous surface [69••].

Acknowledgement

We gratefully acknowledge financial assistance from the US Army Research Office grant DAAH04-95-1-0102.

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