**ARTICLE**

# Ceramic Thin-Film Formation on Functionalized Interfaces Through Biomimetic Processing

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**Processing routes have been developed for the production of thin ceramic films through precipitation from aqueous solutions. The techniques are based on crystal nucleation and growth onto functionalized interfaces. Surface functionalization routes have been developed by the mimicking of schemes used by organisms to produce complex ceramic composites such as teeth, bones, and shells. High-quality, dense polycrystalline films of oxides, hydroxides, and sulfides have now been prepared from "biomimetic" synthesis techniques. Ceramic films can be synthesized on plastics and other materials at temperatures below 100°C. As a low-temperature process in which water rather than organic solvents is used, this synthesis is environmentally benign. Nanocrystalline ceramics can be produced, sometimes with preferred crystallite orientation. The direct deposition of high-resolution patterned films has also been demonstrated. The process is well suited to the production of organic-inorganic composites.**

To keep pace with emerging technologies, materials engineers need to develop processing techniques that produce high-quality ceramics under conditions that are compatible with a wide range of other materials and components. The demand for ceramic coatings on plastics is high. Optical, magnetic, impermeable, hard, and active coatings for sensors and "smart" material composites all represent growing markets for ceramics deposited on or within plastics. Ceramic films are also in demand as active and passive components in microelectronic circuits as capacitors, memories, and insulating or passivating layers.

For many of the above applications, conventional ceramic processing, which involves high-temperature sintering, cannot be used. Even advanced "sol-gel" techniques (*1*), which involve heat-treating precursor (usually alkoxide) films, require processing temperatures in excess of 400°C. Unfortunately, temperatures in excess of 300°C are sufficient to pyrolyze most plastics, and many plastics cannot tolerate temperatures above 100°C because of softening or other phase transitions. While sol-gel glasses can be prepared at lower temperatures for applications such as protein encapsulation (*2*), the resulting materials are less than 70% dense, containing high porosity and internal surface area. For both sol-gel and conventional processing, shrinkage during densification can lead to the formation of large pores, crazing, and the buildup of undesired film-substrate stresses. The need for lower temperature near-net-shape processing is driving current research in low-temperature, vapor deposition techniques such as laser ablation and metal-organic chemical vapor deposition.

Emerging applications for ceramic films can require the microstructural or macrostructural control of film morphologies that are difficult to achieve with existing technologies. For advanced magnetic, optical, and ferroelectric films, the size, shape, and crystalline orientation of individual grains in polycrystalline films must be controlled to optimize film properties. Film patterning is often desired. Because most film deposition techniques produce continuous films, patterning is usually done after the film is deposited and requires the vigorous etching of materials that are resistant to chemical attack. The ability to deposit patterned films directly without etching would eliminate many expensive processing steps, eliminate the use of hazardous etchants, and increase yields.

The control of ceramic processing desired by engineers is routinely achieved in nature (*3*). Organisms deposit highly oriented, flaw-free ceramics from aqueous solutions under ambient conditions on substrates as delicate as living tissues (*4*). Minerals deposited within organisms (*5, 6*) include calcium oxalates, carbonates, and phosphates; iron oxides; and silica. Scientists have performed extensive studies to determine the mechanisms for biomineralization (*5–8*) and related processes in the fossilization of soft tissue (*9*). As a result of such mechanistic studies, it has been recognized that certain aspects of the natural processes used to make materials such as teeth, bones, shells, and kidney stones can be duplicated synthetically (*10, 11*).

Biomineralization is a complex process (*12*) that involves the controlled nucleation and growth of ceramics from aqueous solutions. Organisms create the proper organic matrix as a host for nucleation and growth, control solution concentrations and the supersaturation of precipitating phases, and control the kinetics and direction of growth using species such as soluble proteins. Rather than attempting to duplicate the entire biomineralization process, researchers are dividing the process into stages that can be understood and adapted to practical processing schemes (*13–15*). Processes mimicking biomineralization have now been used to prepare materials including iron oxides (*16, 17*), apatite (*18*), and CdS (*19*).

Although biominerals such as apatite clearly benefit the host organism, most demonstrations of biomineralization to date have not resulted in the formation of ceramics of technological interest. The focus of this article is to demonstrate how surface functionalization routes suggested by biomineralization can be used to create mineral coatings for industrial applications and to produce ceramic materials not found in organisms. With biomimetic processing, high-quality, oriented, and patterned ceramic films can be deposited on plastics and other materials at temperatures below 100°C (*15*). The results indicate that simple processing conditions can produce materials of both industrial and scientific interest. Here, key elements are described that control the chemistry of the aqueous deposition solution and functionalized surfaces to produce high-quality ceramic films. Industrial applications and future implications of the rapidly expanding field of biomimetic synthesis are also discussed.

## Nucleation and Growth in Aqueous Systems

Biomimetic synthesis involves the use of an aqueous solution of soluble precursors to deposit ceramic films on desired substrates or within a host matrix. Precursors are deposited (Fig. 1) when solution conditions are changed from a pH, concentration, and temperature regime in which precursors are soluble to a regime in which solutions are supersaturated, inducing crystal nucleation

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and growth. Nucleation and growth can occur either in solution (homogeneous) or on the surfaces of other solid phases (heterogeneous). Successful biomimetic synthesis occurs when heterogeneous nucleation is promoted and homogeneous nucleation is suppressed. Therefore, one key to successful biomimetic synthesis is an understanding of the factors that control crystal nucleation and growth in aqueous solutions.

According to classical theories for homogeneous crystallization (*20–22*), the free energy for formation of stable nuclei ($\Delta G$) depends on the degree of supersaturation ($S$), the temperature ($T$), the net solution-particle interfacial energy ($\sigma$), and the particle surface area ($A$):

$$\Delta G = -RT \ln S + \sigma A \qquad (1)$$

where $B$ is the ideal gas constant. Important parameters for particle formation, including the induction time for nucleation ($\tau$), the final number of nuclei ($N$), and the particle growth rate ($dr/dt$), are also controlled by the supersaturation, the interfacial energy, and the temperature:

$$\ln (1/\tau) = \ln B - (16\pi\sigma^3\nu^2)/3(kT)^3(\ln S)^2 \qquad (2)$$

$$\ln N = \ln P - Q\beta\sigma^3\nu^2/(kT)^3(\ln S)^2 \qquad (3)$$

$$dr/dt = K(S-1)^n \qquad (4)$$

where $K$, $B$, $P$, $Q$, $\beta$, and $n$ are constants, $k$ is Boltzmann's constant, and $\nu$ is the molecular volume of the precipitating phase.

Similar expressions apply to heterogeneous nucleation and film formation at an interface, except that the surface free energy is described by three terms:

$$\Delta G = -RT \ln S + \sigma_{cl}A_{cl} + (\sigma_{cs} - \sigma_{sl})A_{cs} \qquad (5)$$

where $c$, $s$, and $l$ subscripts refer to interfaces involving the crystalline particle, the substrate, and the liquid phases, respectively. If interactions between the growing nucleus and a substrate surface represent a lower net interfacial energy than the particle-solution interfacial energy, heterogeneous nucleation is favored over homogeneous nucleation. In recent years, several investigators (*23–27*) have shown that by manipulating surface energies through chemical modifications and solution additives, the crystal phase, morphology, crystal growth habit, orientation, and even chirality of crystal grown in aqueous media can be modified and controlled.

The importance of supersaturation levels and surface energy effects can be seen upon consideration of the number of nuclei predicted to be produced in supersaturated solutions as a function of surface energy (Fig. 2). At supersaturation levels that are just sufficient to start homogeneous nucleation (curve 1, Fig. 2), a 10-fold increase in $S$ can increase the number of nuclei and the kinetics of nuclei formation by over 10 orders of magnitude. Substrate surfaces can lower the value of $\sigma$ by as much as 50% (curve 2, Fig. 2), increasing the number of nuclei (and formation rates) by over 10 orders of magnitude at the same degree of supersaturation. For the proper combinations of substrates and solutions, films form on surfaces at supersaturation levels that do not sustain homogeneous nucleation. Solid-solution interfacial energies tend to be small (*28*), on the order of a few kilocalories per mole (0 to 200 mJ/m$^2$), and are sensitive to subtle changes in surface chemistry such as solvation, ion adsorption, electrical double layer effects, surface complexation, and changes in van der Waals interactions. Crystal-substrate adhesion energies (*29*) (due to interfacial bond formation minus interfacial strain) can be dominant contributors to the net free energy for nucleation. The challenge of biomimetic synthesis is to understand and control interfacial chemistries in such a way as to enhance surface crystallization for desired crystal-substrate pairs.

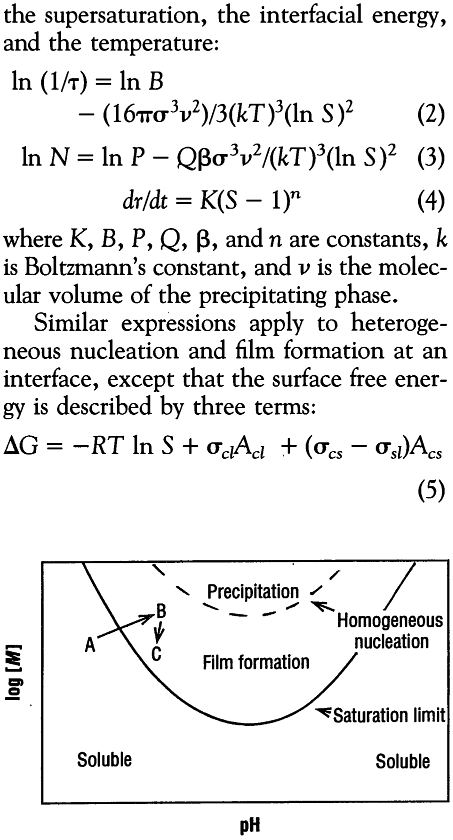

**Fig. 1.** Idealized solubility diagram for film-forming species dissolved in water. Solubility generally depends on species concentrations, [*M*], and pH. Film formation occurs when solution conditions change from (A) a regime in which precursors are soluble to (B) a condition of supersaturation. Proper supersaturation promotes film growth without precipitation. In a batch process, the consumption of reagents in film formation can change the degree of supersaturation (moving to C). Normally, the regime in which homogeneous nucleation and precipitation occur is to be avoided for optimum film growth.

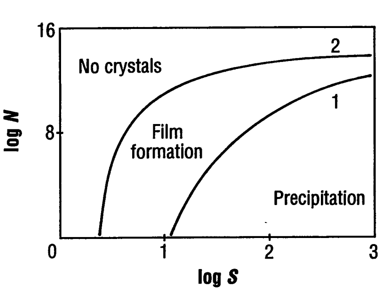

**Fig. 2.** Idealized diagram showing how the number of nuclei ($N$) is predicted to vary with supersaturation ($S$) and the net interfacial energy for nucleation ($\sigma$) according to classical nucleation theory. Curve 1 is representative of homogeneous nucleation behavior. Curve 2 is calculated by the assumption that all parameters are identical except $\sigma$, which is one-half of the homogeneous value. Curve 2 is indicative of net interfacial energies associated with heterogeneous nucleation.

## Surface Functionalization

Organisms are capable of controlling surface nucleation and growth on substrate materials that are themselves relatively inert. For example, in eggshell membranes, interactions between macromolecules and the collagen membrane matrix can induce or inhibit the crystallization of calcium carbonate or calcium phosphate during eggshell production (*30*). Most of the macromolecules known to promote surface nucleation contain functional groups that are anionic at the crystallization pH (*12*), including sulfate groups in polysaccharides (*31*), carboxylic acid groups on the aspartic acid–containing proteins in mollusks (*32*), and phosphate groups on proteins found in teeth and bones (*33*). The functional groups are thought to be capable of binding soluble ionic precursors to the substrate surface to stimulate the surface nucleation. While detailed mechanisms for the role of the anionic groups are still poorly understood, the natural phenomena can be mimicked by the introduction of similar groups onto substrate surfaces.

Our research in biomimetic synthesis (*15, 34–40*) is based on the premise that the tailored macromolecules in living organisms represent a type of surface functionalization. We are studying mechanisms by which simple ionized surface functional groups mediate surface nucleation and growth. Below, several strategies are described for functionalizing surfaces, including (i) the chemical modification of plastics, (ii) the attachment of self-assembled monolayers, (iii) the electrochemical deposition of functionalized polymers, and (iv) the use of Langmuir-Blodgett (LB) films to study proteins and surfactants. With the above techniques, most materials of interest, including plastics, metals, and ceramics, can be activated for the surface deposition of solution-derived ceramic phases.

Many commercial plastics, including polystyrene, polycarbonate, and polyethylene, have lipophilic surfaces covered with hydrocarbons or aromatic ring systems. However, plastics can be chemically modified to produce ionic surfaces capable of interacting with soluble ceramic precursor species (*41, 42*). Sulfonate groups can be introduced into the surfaces of aromatic polymers such as polystyrene and polycarbonate through room temperature exposure to sulfuric acid solutions or vapor. By the variation of exposure times, surface sulfonate coverages can be systematically varied, transforming the native hydrophobic surfaces (with contact angles for wetting of 90°) to hydrophilic surfaces (with a contact angle near 0°) (*34*). For polyethylene, alternate chemical routes (*43*) can be used to introduce carboxylate, amino, hydroxyl, and phosphate groups into the surface. Functionalization routes exist for other polymers as well, with the functional group of choice being dictated by the specific chemistry of the polymer and by the ultimate requirements for nucleation and growth of desired ceramic films.

For the preparation of model surfaces on both metal and oxide substrates, our focus has been on functionalization using self-assembled monolayers (SAMs) (Fig. 3) (*15, 28, 44–47*). One species used to prepare the monolayers on oxides is $Cl_3Si(CH_2)_nX$. The chlorosilane end of the molecule is covalently anchored to the surface and cross-linked to adjacent silanes through hydrolysis and condensation reactions with surface hydroxyl groups. The hydrocarbon chain provides the driving force (van der Waals interactions) for self-assembly of the molecules into an ordered array. The active terminating group (X) provides a reactive handle that can be elaborated into anionic groups such as sulfate, phosphate, and carboxylic acids. The preparation of SAMs for biomineralization requires specialized organic and organometallic synthesis strategies applicable to two-dimensional substrate surfaces (*46*). Solid-state nuclear magnetic resonance (NMR) techniques (*47*) have been used to determine how key synthesis parameters, such as surface hydration, control silane polymerization. Under optimum conditions, the NMR results indicate that the predominant species in the SAM monolayers is an alkyl silane bearing one anchor to the oxide surface, one cross-linking bridge to adjacent silanes, and one dangling hydroxyl group.

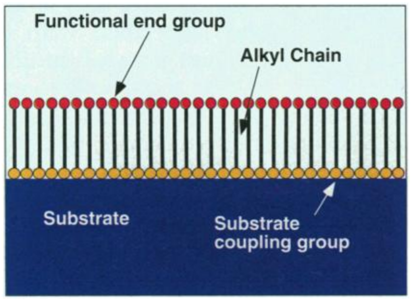

**Fig. 3.** Organic interface formation. The idealized depiction of a self-assembled monolayer shows points of attachment to the surface (either silane coupling agent or thiol group), the self-assembled alkyl chain [with 3 to 22 $-(CH_2)-$ groups], and the functional end groups used to induce crystal nucleation and growth (for example, $-COOH$, $-SO_3H$, $-PO_4H_2$, $-NH_2$, $-CH_3$).

The range of SAM terminal groups investigated to date in crystallization studies includes methyl, bromo, sulfonate, carboxylate, imidazole, azide, and thiazolidine. The concentration of any particular group can be varied systematically by the dilution of functionalized silanes within a methyl-terminated silane. The chain lengths of the "active" part of the SAM can be made to differ slightly from the "host" SAM so that active groups can be made to protrude from, or be imbedded within, the host to allow investigation of the importance of steric effects. A final attractive feature of SAMs is the ease with which they can be used to form patterned films.

A third route for functionalizing surfaces involves the deposition of thin polymeric films such as sulfonated or carboxylated polystyrene onto substrate surfaces through spin- or dip-coating techniques. On conducting substrates, electrochemical methods can be used to deposit pore-free functionalized polymers (*48*). For example, insulating sulfonated polyoxophenylene films can be deposited onto carbon or silicon by the electrochemical oxidation of solutions containing the monomers allylphenol and 4-hydroxybenzenesulfonic acid. Conducting polymers, including functionalized polypyrrole, polyphenylene, and polycarbazole, can also be deposited. Functional group concentrations can be controlled by variation of the starting monomer ratios. Depending on the functional groups used, the polymer films can function as permselective membranes, allowing the penetration of specific anions or cations from solution as precursors to ceramic film deposition. By the use of photolithographically patterned electrodes, the technique can also be used to produce patterned ceramic films.

A final and highly flexible functionalization route under investigation involves the use of surfactants, as exemplified by biological phospholipids. Mechanistic studies involving the nucleation of materials such as barium sulfate and calcium carbonate on LB films of long-chain phosphonate and carboxylate surfactants suggest that stereospecific interactions or even epitaxy between the functional group array and the crystal are critical to the nucleation and growth of desired phases, crystalline orientations, and crystal growth habits (*24, 49*). Similar LB films have been used as substrates to nucleate nanoparticles of materials such as CdS (*19*).

## Formation of Thin Ceramic Films on Functionalized Surfaces

By the appropriate control of solution and substrate chemistries, thin films of "biological" ceramics such as calcium carbonate (*42, 49*), calcium phosphate (apatite) (*18*), and calcium oxalate (CaOx) (*38, 39*) as well as "commercial" materials including FeOOH (*15, 34–36*), $Fe_2O_3$, $SnO_2$, CdS (*37*), and $Al(OH)_3$ can be formed. Below, results obtained for CaOx, $SnO_2$, and FeOOH are used to illustrate some of the techniques we are using to understand and control film formation.

Calcium oxalate films are useful for understanding nucleation and growth mechanisms. Studies of calcium oxalate nucleation are also of interest because CaOx is a primary constituent of kidney stones. Research on kidney stone formation (*50*) suggests that phosphates and acidic proteins promote the nucleation of CaOx in stones by the same mechanisms involved in the formation of biomimetic films. Calcium oxalate is an attractive model system because (i) its solubility is accurately known as a function of pH, ionic strength, and temperature; (ii) the solubility is more or less constant between pH 4 and pH 11 (Fig. 4); and (iii) the kinetics of homogeneous nucleation and growth are well documented for a wide range of solution conditions.

In normal batch reactors, nucleation and growth processes consume dissolved reagents and lower the degree of supersaturation. Changes in *S* can be prevented by the use of constant composition (CC) techniques (*50*). To achieve CC conditions in the CaOx system, a calcium electrode commands a burette system to add $Ca^{2+}$ and $Ox^{2-}$ to solution as ions are consumed in the formation of CaOx films. The CC experiment provides both nucleation times (the time before significant ion consumption is observed) and growth rates (from steady-state ion consumption rates) (Fig. 5A). The microscopic examination of substrates after CC depositions provides complementary information concerning the number and size of crystal nuclei produced at a fixed *S* for comparison with theory. We

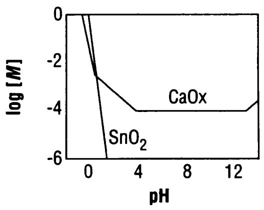

**Fig. 4.** Simplified solubility diagrams for CaOx and tin oxide showing the log of metal cation concentrations, [*M*], predicted to be present in equilibrium with the solid phases as a function of pH:

$$Ca^{2+} + H_2Ox \rightarrow CaOx + 2H^+$$

$$Ca^{2+} + HOx^- \rightarrow CaOx + H^+$$

$$SnCl_4 + 2H_2O \rightarrow SnO_2 + 4H^+ + 4Cl^-$$

The solubility of CaOx is relatively insensitive to pH between pH4 and pH12, in contrast to the solubility of tin oxide, which decreases by a factor of 10,000 between pH 0 and pH 1.

have used the CC experiment on functionalized SAMs (*38*) to demonstrate that imidazole promotes higher nucleation densities in CaOx formation than do thiazoladine, bromine, or methyl groups.

The CC experiments can be used to study the nucleation and growth of CaOx on high surface area suspensions of colloidal particles (*39*). For unaltered supersaturated solutions, induction times for CaOx formation can be long and are associated with nucleation on small foreign particles that are always present in solution (so-called "spontaneous" nucleation). In the presence of CaOx seeds, there is no barrier to further CaOx formation, and induction times are zero. In the presence of other colloidal surfaces, induction times are often observed that lie between the spontaneous and CaOx-seeded results. Such results indicate that foreign particle surfaces can lower the net interfacial energy, $\sigma$, required for the nucleation of CaOx. By determining induction times as a function of supersaturation (Fig. 5B) and using Eq. 2, we can quantify $\sigma$ for different solutions and substrates.

The CC results illustrate several key features of biomimetic processing. First, Fig. 5B illustrates how sensitive film formation is to $S$. A 50% decrease in $S$ (such as from 4 to 2) can increase induction times and decrease nucleation densities by more than 10,000 times relative to "spontaneous" nucleation. Second, a reduction in $\sigma$ due to the presence of a substrate can be sufficient to strongly favor heterogeneous over homogeneous nucleation. True homogeneous nucleation of CaOx is characterized by an interfacial energy (*51*) of 66 mJ/m$^2$, compared with the 32 mJ/m$^2$ associated with spontaneous nucleation.

Although no nucleation occurs for many plastics, other native surfaces, such as colloidal oxides (*39*) and apatite (*52*), effectively promote CaOx formation in the absence of surface functionalization. For example, $\sigma$ for CaOx nucleation on colloidal silica is 27 mJ/m$^2$. Results at pH 6.5 indicate that negatively charged colloidal silica (which complexes $Ca^{2+}$) is more effective than neutral $TiO_2$ or positively charged ($Ox^{2-}$-complexing) alumina in promoting CaOx nucleation. Results obtained on sulfonated polystyrene are similar to the results seen for silica, with $\sigma$ near 30 mJ/m$^2$ (*53*). Finally, Fig. 5B illustrates that surface selectivity depends on both $S$ and $\sigma$. At high $S$, nucleation occurs on most surfaces more or less independently of $\sigma$. As $S$ is lowered, surface selectivity becomes more pronounced, with the selectivity being greatest on surfaces having the lowest barrier to nucleation. Therefore, there is a trade-off between surface selectivity, enhanced at low supersaturation levels, and the kinetics of nucleation and growth, which are enhanced at high supersaturations. The more effective the substrate is at inducing nucleation, the less severe this processing trade-off becomes.

Processing issues are of real concern for materials such as tin oxide that have applications as hard, scratch-resistant, or optical coatings. In contrast to the model CaOx system, the solubility of tin oxide is not well characterized (*54*) and is extremely sensitive to solution pH (Fig. 4). For the tin oxide system, a pH change of one unit can change the equilibrium solubility by a factor of 10,000. The solubility and deposition of tin oxide is controlled by hydrolysis and condensation reactions involving poorly characterized hydrolysis products rather than the precipitation of an ionic salt. Because of the above difficulties, it is almost impossible to establish solution conditions under which heterogeneous nucleation can be stimulated in the complete absence of homogeneous nucleation. However, with light-scattering, Raman, and x-ray diffraction experiments, we have established conditions under which the heterogeneous nucleation of crystalline tin oxide can still be induced on substrates such as sulfonated polystyrene through direct deposition from solution at 40°C. We can produce uniform coatings of tin oxide on plastic parts having complex shapes (Fig. 6A). The coatings are conformal (Fig. 6B) and adherent. Transmission electron micro-

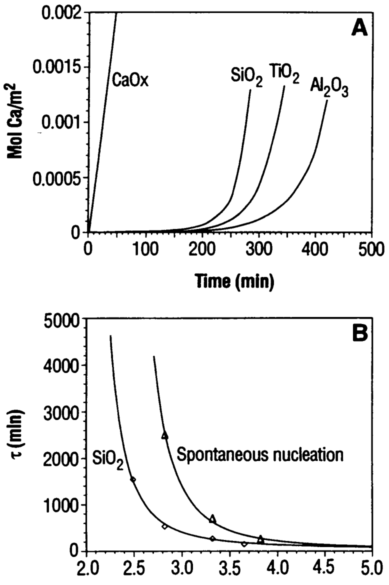

**Fig. 5.** (**A**) Moles of calcium ions added per square meter of colloidal suspensions versus time in constant composition experiments of CaOx formation at $S = 3.3$ and $T = 25°C$. CaOx forms immediately on CaOx seeds, whereas induction times of around 240, 290, and 370 min are observed for CaOx formation in the presence of silica, titania, and alumina, respectively. (**B**) Induction times for CaOx formation versus supersaturation ($S$) for both unseeded solutions (spontaneous) and solutions containing colloidal silica. Solid lines represent theoretical curves calculated with Eq. 2 and surface energies listed in the text.

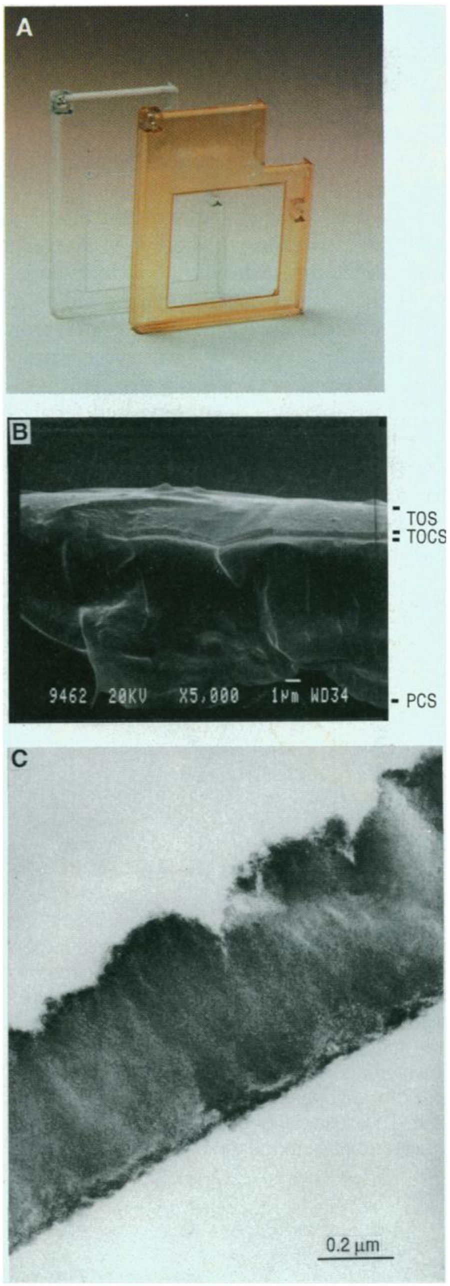

**Fig. 6.** (**A**) Sulfonated polystyrene part before (left) and after (right) coating with FeOOH showing the complexity of shapes that can be coated with biomimetic processes. (**B**) Scanning electron micrograph of the fracture surface of a 0.4-μm-thick tin oxide film (between lines) deposited on the same type of polystyrene sample. The coating is adherent and conformal. Abbreviations: TOS, tin oxide surface; TOCS, tin oxide cross section; PCS, polystyrene cross section. (**C**) Transmission electron micrograph of the dense tin oxide coating in (B) showing that the film consists of densely packed 4-nm-diameter crystallites of cassiterite.

graphs (TEMs) (Fig. 6C) reveal that the coatings are dense, having a microstructure consisting of 4-nm grains of cassiterite. Such dense, nanocrystalline materials are extremely difficult to produce through conventional ceramic processing. While comparable crystallite sizes can be obtained by sol-gel processing, the reported materials have consisted of discrete particles rather than films, with particle sizes ranging from 25 to 200 nm (*55*). Such ultrafine particles would exhibit extensive growth during sintering to make a dense film.

The iron oxide system exhibits different levels of processing complexity. At least nine different hydroxide, oxyhydroxide, and oxide phases can be precipitated from aqueous media depending on the pH, iron concentration, redox chemistry, counterion and complexation chemistry, and temperature (*56*). We have deposited ferrihydrite [$Fe(OH)_3$], goethite (FeOOH), hematite ($Fe_2O_3$), and magnetite ($Fe_3O_4$) films on sulfonated polystyrene. For magnetic storage media, ideal films consist of highly oriented, acicular grains of maghemite [$Fe_2O_3$ having the structure of magnetite ($Fe_3O_4$)]. Our current synthesis method for such films involves the deposition of highly acicular phases such as FeOOH (for morphology control) followed by a conversion into the desired magnetite phase. Goethite films are formed by the heating of acidic Fe(III) salt solutions to stimulate nucleation (see Eqs. 2 and 3). Nucleation can also be stimulated by a uniform pH increase. The pH adjustments are not made by the addition of titrants, which generate temporary pH gradients sufficient to promote homogeneous nucleation. Instead, homogeneous pH adjustments are made by the in situ decomposition of reagents such as urea.

The role of surface functionalization on surface nucleation and growth is dramatic for the case of goethite deposited on polystyrene (*15*). The three regimes of nucleation behaviors exhibited by Fe(III) solutions in the presence of polystyrene substrates are shown in Fig. 7. In region A, no nucleation is observed in solution or on any substrates (corresponding to the "soluble" regime in Fig. 1 and the "no crystals" regime in Fig. 2). In region B, FeOOH films form on only those polystyrene samples that have been sulfonated (corresponding to the "film formation" regimes in Figs. 1 and 2). In region C, nucleation is observed everywhere: in solution as well as on sulfonated and unsulfonated polystyrene (corresponding to the precipitation regimes in Figs. 1 and 2).

Figure 8 shows untreated and sulfonated areas of a patterned polystyrene sample (see below) after immersion in a $10^{-3}$ M $Fe(NO_3)_3$, $10^{-2}$ M $HNO_3$ solution for 24 hours at 70°C (within region B in Fig. 7). Under the above deposition conditions, homogeneous nucleation and growth are suppressed and very few crystals are deposited on the untreated polystyrene. In contrast, the sulfonated polystyrene sample is covered with a >90% dense, continuous film of FeOOH. Results on partially sulfonated samples indicate that the nucleation density and net growth rate of FeOOH on polystyrene are directly related to the sulfonate site density, suggesting that the sulfonate groups initiate nucleation and growth at the surface. Infrared and x-ray photoelectron spectroscopy evidence suggests that goethite nucleation is preceded by the complexation of hydrated Fe(III) monomers by sulfonate groups.

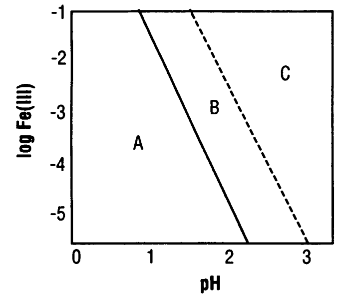

**Fig. 7.** The pH and Fe(III) concentrations corresponding to distinct nucleation regimes in solutions held at 70°C. Region A, no nucleation in solution or polystyrene substrates. Region B, film formation observed only on sulfonated polystyrene. Region C, film formation observed on both sulfonated and unsulfonated polystyrene. The colloidal particles observed in region C are due to homogeneous nucleation.

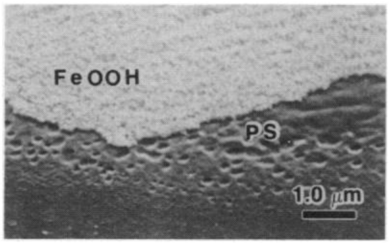

**Fig. 8.** Scanning electron micrograph of the boundary between sulfonated and unsulfonated regions of a polystyrene (PS) surface exposed to iron nitrate solutions. Nucleation and growth processes have generated a continuous FeOOH film on the sulfonated region (bright area), while nucleation in the unsulfonated region is negligible.

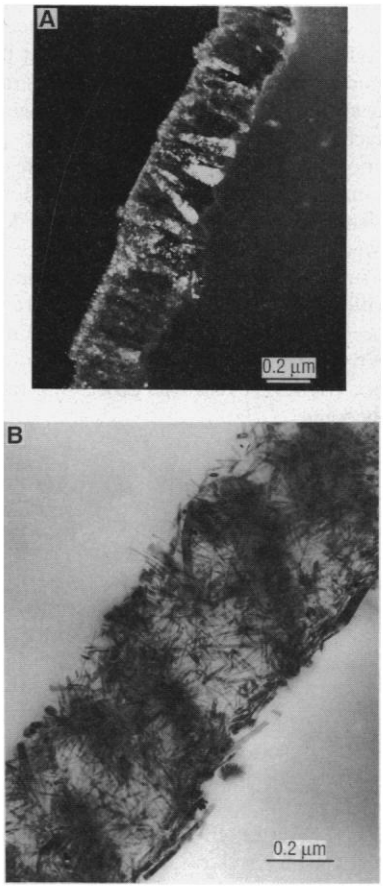

**Fig. 9.** (**A**) Dark-field TEM of an oriented FeOOH film on a sulfonated SAM surface. Bright regions show crystalline grains oriented with the *c* axis perpendicular to the substrate surface. (**B**) Transmission electron micrograph of a crystalline FeOOH film generated by the curing of a ferrihydrite film in 2 M KOH at 100°C for 24 hours, showing random nucleation and growth.

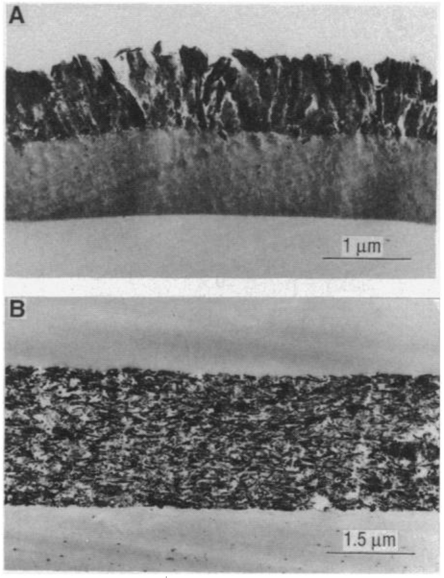

**Fig. 10.** (**A**) Transmission electron micrograph cross section showing the perpendicular orientation of magnetic crystallites deposited on sulfonated polystyrene with the use of a biomimetic approach. (**B**) Transmission electron micrograph cross section of a commercial VCR tape showing longitudinal orientation relative to the substrate. The higher crystallite densities and perpendicular orientation in the biomimetic film are desired for maximizing magnetization.

Biological systems routinely produce highly oriented microstructures. In the case of FeOOH, we have been able to achieve similar oriented microstructures on sulfonated SAMs under the proper deposition conditions (*34*) (Fig. 9A). The best microstructures contain highly oriented needles, with the *c* axis oriented perpendicular to the substrate surface. The film morphology is preserved upon thermal conversion to magnetite (Fig. 10). As the TEM results in Fig. 10 indicate, the biomimetic films have enhanced crystallite densities and orientations relative to the particles present in commercial video recording tape.

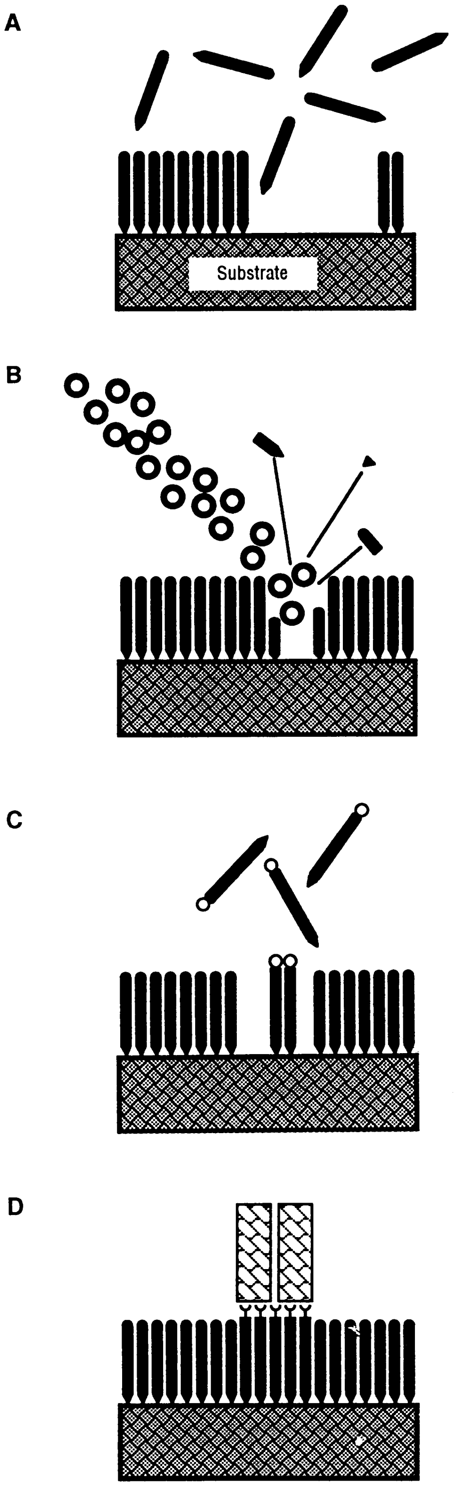

**Fig. 11.** Schematic diagram showing the steps involved in biomimetic lithography. (**A**) Deposit inert organic layer on the substrate, (**B**) etch selected regions with ion or electric beam, (**C**) deposit active organic layer in etched regions, and (**D**) mineral growth from aqueous solution occurs only on patterned region.

On sulfonated polystyrene, films can be produced having a "haystack" microstructure (Fig. 9B) indicative of random nucleation and growth in an amorphous gel. Analytical TEM results show that the random microstructures occur when polymer sulfonation is not confined to the surface but when it forms a thick alteration layer. In water, the sulfonated surface layer swells, and initial nucleation and growth occur within the swollen polymer matrix. The deposition in surface layers is similar to that reported for iron oxide depositions in polymer hosts in other laboratories (*16*, *57*). The polystyrene results illustrate one method for producing a "graded" interface to enhance film adhesion. The results also illustrate the promise of biomimetic methods for the fabrication of unique inorganic-organic composites.

## Film Patterning

The results obtained for the deposition of iron oxide and other ceramics on functionalized surfaces show that surface film formation depends on the presence or absence of specific functional groups. The high degree of surface selectivity afforded by functionalization has been exploited in the production of patterned FeOOH films (*40*) (Fig. 11). The lateral resolution of surface patterns that can be produced is limited by the resolution afforded by state-of-the-art patterning techniques such as photolithography. The highest definition patterns we have produced to date involve patterned SAMs. First, a methyl-terminated SAM is deposited. Electron or ion beams are then used to destroy regions of the SAM selectively, producing patterns of contrast between "bare" and SAM-coated substrate material. The samples are then exposed to solutions containing functionalized trichlorosilanes to backfill the patterned regions. The resulting SAM, now patterned with the desired functional groups, is then immersed in the crystallization solution. Crystals of desired phases grow only on regions that have been functionalized. Lateral growth appears to be negligible. For such systems, well-defined patterns of FeOOH films have been produced with a lateral resolution of less than 10 μm by direct deposition from solution, minimizing the need for etching or other post-crystallization patterning steps.

## Pros and Cons of Biomimetic Processing

Processing advantages of biomimetic coating techniques include (i) low temperature, low cost, environmentally benign processing; (ii) the formation of dense crystalline

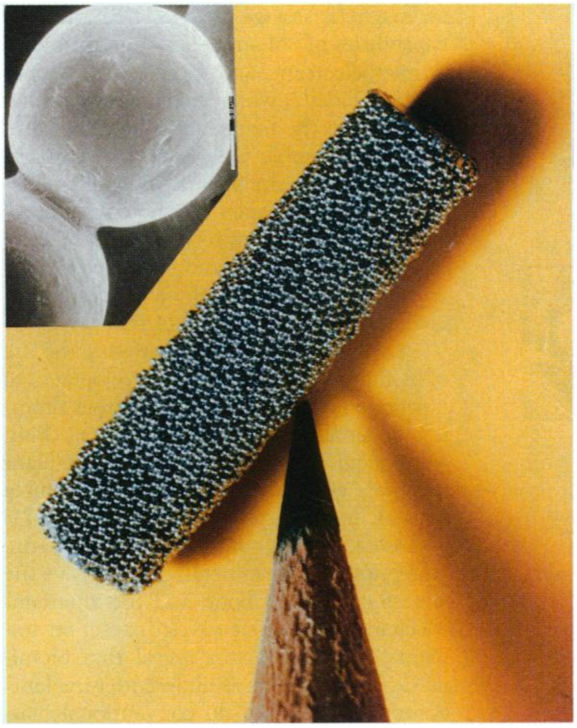

**Fig. 12.** Porous titanium implant showing complex morphology requiring a surface coating of hydroxyapatite for bonding to bone. Inset shows higher magnification of octacalcium phosphate–coated spheres within the implant.

films without the requirement of subsequent thermal treatments; (iii) the ability to coat complex shapes and porous materials uniformly; (iv) compatibility with a wide range of substrates, including plastics and other temperature-sensitive materials; (v) microstructural control, including crystal orientation and the ability to produce nanophase materials; and (vi) the direct deposition of patterned films with micrometer-scale pattern resolution. Many of the above processing advantages are beyond the current capabilities of conventional thin-film processing techniques such as sol-gel and vapor deposition.

While the duplication of biomineralization methods holds great promise for the low temperature fabrication of ceramic films, there are several critical challenges for the existing technology. First, solution and substrate conditions must be carefully controlled for optimum film formation. The control of supersaturation can be a problem, especially for systems showing extreme pH sensitivity. The consumption of reagents during film formation can change supersaturation levels and must be compensated in scale-up operations. Aqueous nucleation and growth routes can generate metastable or amorphous phases including hydroxides or oxyhydroxides, rather than desired oxide phases. Some phases of interest, such as quartz and alumina, are attainable now only under hydrothermal conditions that are too aggressive for use with plastics or other sensitive substrates. For some applications, deposition rates (as slow as 1 μm/day) are too sluggish. The limited solubilities of precursors now used to prepare films such as tin oxide dictate the use of highly acidic or basic solutions that can corrode or degrade certain substrates. Difficulties associated with the control of species solubilities are magnified for multicomponent systems [such as PbO-$ZrO_2$-$TiO_2$ (PZT) and $LiNbO_3$], in which the simultaneous precipitation of different species is desired.

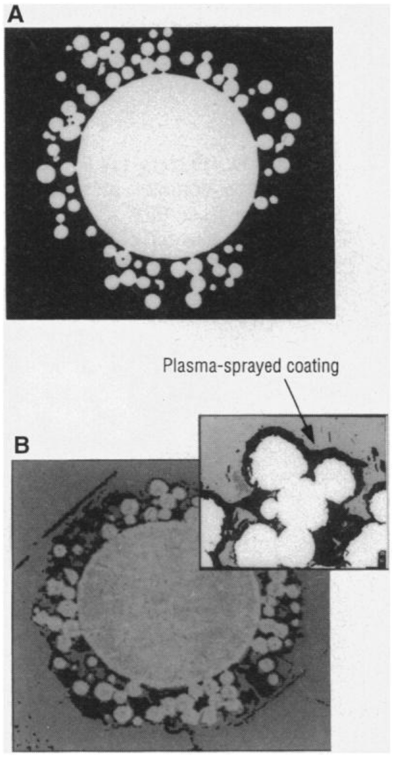

**Fig. 13.** (**A**) Porous titanium implant with biomimetic octacalcium phosphate coating. (**B**) Porous titanium implant with conventional plasma-spray coating.

Although substrates can be prepared with an ever expanding range of surface functional groups, research has not yet progressed to the point where we can predict which functional groups will be most effective in nucleating a specific crystalline phase with a specific crystalline orientation. The tailoring of substrates to promote the growth of oriented films is a particular challenge. Many of the above problems are being addressed through modifications in both solution and surface complexation.

## Industrial Applications

Potential applications for biomimetic coatings span a broad range of industries. Pacific Northwest Laboratory (PNL) is working with the automotive industry to apply hard, abrasion-resistant coatings to plastic gears and other components subject to wear. The possibility of applying hard optical coatings to plastics to replace glass in windows and reduce vehicle weight is also of interest. The deposition of oriented films of iron oxide phases such as maghemite is being explored for magnetic storage media. The patterning capabilities of "biomimetics" are of interest in microelectronic and optoelectronic applications. Finally, while the work to date has centered on the fabrication of ceramic thin films, the possible use of biomimetic techniques to synthesize organic-inorganic nanocomposites could open up whole new industries in the fabrication of "smart" composite materials (58) combining enhanced mechanical properties, physical properties, chemical properties, or all of these.

A specific application illustrating the use of biomimetic coatings is the development of biocompatible coatings for the porous titanium materials used in bone implants. PNL has coated SAM-treated titanium implant materials with conformal films of insoluble octacalcium phosphate (OCP) (Fig. 12). The OCP coatings are precursors to apatite (the primary bone mineral) and improve the adhesion between bone and the titanium. Mechanical push-out strength tests on implants tested in rabbits reveal that biomimetic OCP coatings result in better implant-bone adhesion than do conventional plasma-spray coatings. The biomimetic OCP coatings are relatively phase-pure, in contrast to the plasma spray coatings that contain highly soluble phases such as amorphous calcium phosphate and calcium oxide. In addition, the biomimetic coatings are much more uniform and do not clog pores within the implant designed to facilitate interlocking bone growth, in contrast to the plasma-spray coatings (Fig. 13).

## Impact on Related Fields

Work in the biomimetic synthesis of ceramic films is already impacting areas outside ceramic thin-film fabrication. The program will help biomedical researchers understand problems such as kidney stone formation and mechanisms for biomineralization. While the work is aimed at forming films, the surface functionalization research will also help us develop strategies for inhibiting surface deposition from aqueous media. Scale formation is a tremendous problem in many fluid-transfer systems, costing U.S. industry billions of dollars per year. The use of surface functionalization could be an effective strategy for preventing or inhibiting the formation of surface deposits that clog pipes and orifices in many industrial systems (59). The impact of the field on materials processing, biomedicine and biochemistry, and chemical engineering explains why there is a renewed interest in studies of surface nucleation and growth involving aqueous and biological systems.

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Reports, Research Articles, and Articles that include original research data, theories, or syntheses and are fundamental contributions to basic knowledge or technical achievements of far-reaching consequence are eligible for consideration for the prize. The paper must be a first-time publication of the author's own work. Reference to pertinent earlier work by the author may be included to give perspective.

Throughout the competition period, readers are invited to nominate papers appearing in the Reports, Research Articles, or Articles sections. Nominations must be typed, and the following information provided: the title of the paper, issue in which it was published, author's name, and a brief statement of justification for nomination. Nominations should be submitted to the AAAS–Newcomb Cleveland Prize, AAAS, Room 924, 1333 H Street, NW, Washington, DC 20005, and **must be received on or before 30 June 1994**. Final selection will rest with a panel of distinguished scientists appointed by the editor of *Science*.

The award will be presented at the 1995 AAAS annual meeting. In cases of multiple authorship, the prize will be divided equally between or among the authors.