

Notes

Morphogenesis of Crystalline Carbonates Self-Assembled on Polyaminosiloxane

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Introduction

Biological systems use organic molecules (mostly proteins and polysaccharides) that function variously as nucleators, adhesives, aggregators, and cooperative modifiers in the processes of biomineralization, resulting in specific organic-inorganic hybrid materials (*e.g.*, seashells, bones, teeth, exoskeletons, etc.) with unique size, structure, morphology, mechanical strength, and optical properties regulated to optimally fit their functions.^{1,2} *In vitro* studies have suggested that anionic moieties such as carboxylates and phosphates play an important role in polymorph selection, crystal habit and growth rate, and attachment to cells.³

In addition, bottom-up approaches to the creation of nano- and micro-structured crystalline materials are providing alternatives for the processing of electronic, sensory, and optical devices. Chemical routes for mineralization processes have been developed to give specific polymorphs and morphologies of crystalline materials.⁴ Cabibil *et al.* reported self-organized nanoscale fibrous mineralization at the air interface of poly(γ -aminopropyl triethoxysilane) (PAPS) deposited on soda-lime glass substrates.⁵ The phenomenon was directly related to atmospheric CO₂ and Na⁺ ions leached out from the glass substrates. The growth of fibrous net-

works was dependent on the Na⁺ concentration segregated at the surface of PAPS matrices. Celio *et al.* reported the growth of aqueous HCO₂K-filled KHCO₃ microfibers from the interface between air and KOH-catalyzed PAPS matrices cast on boron-doped SiO₂/Si(100) wafers.⁶ Lee *et al.* reported the matrix-mediated mineralization at the air interface of NaOH-containing PAPS matrices.⁷ While mechanistic details might have remained debatable, here we present a new strategy utilizing anionic carbamate (-NHCO₂⁻) moiety to play a key role in the nucleation and growth of crystalline materials with hierarchical forms.

Experimental

The experiments were carried out at ambient laboratory temperature (24 ± 0.5 °C) and relative humidity (50~60%). The substrates (1×2 cm²) were cut from microelectronic grade Si(100) wafers covered with ~2 nm of native oxide and were cleaned by standard methods.⁵

A typical precursor solution (pH ~ 10.5) was prepared by mixing 1.5 g of γ -aminopropyl triethoxysilane (γ -APS, 99% purity, Aldrich Chemical Co.) with 28.5 g of high purity H₂O (Milli-Q; 18 M Ω). After the solution was stirred for 10 min, 2.25 mmol of MOH (M=K⁺ or Na⁺, EM Science) was added, increasing the pH to ~11.6.^{7,8} This MOH-catalyzed silica sol was vigorously stirred for ~7 days at ambient conditions to allow enough time for polycondensation, before preparing poly(γ -aminopropyl triethoxysilane) (PAPS) matrices. Because monomeric γ -aminopropyl silanetriol hydrolyzed from γ -aminopropyl triethoxysilane is stabilized as a result of intramolecular hydrogen bonding between an amine and a silanol groups, polycondensation occurs slowly and finally leads to fewer crystallites per unit area (lower areal number density of self-assembled carbonates).

Transparent PAPS matrices (ca. 40- μ m thick), denoted as M⁺/PAPS, were prepared by casting ~0.4 g of the basic silica sol on 1×2 cm² SiO₂/Si(100) wafers. The droplets wet the substrate and gelation occurred to form a clear, uniform, glassy PAPS matrix within 12 h. Schematic process for the specimen preparation is summarized in Figure 1, where sol-gel synthesis is a process, *e.g.*, the 3-D networks remain dynamic during gel aging; condensation reactions continue to occur as long as the remaining silanol and ethoxy groups move close enough to react.⁹

Two processes were performed for each Na⁺/PAPS and K⁺/PAPS matrices, respectively: (1) after gelation for 24 h, while controlling the relative humidity from 50 to 60%, the Na⁺/PAPS specimens were exposed to a warm and humid (~37 °C; relative humidity ~100%) ~40,000 ppm mixture of CO₂ and air for <10 s for nucleation, followed by extended exposure to the ambient condition. This process forms an

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Dedicated for the memory of Professor J. "Mike" White

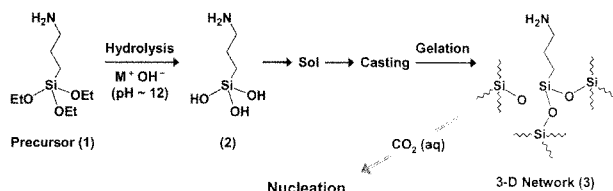


Figure 1. Schematic sol-gel process for preparing glassy organosilica matrices composed of poly(γ -aminopropyl triethoxysilane) (PAPS) with MOH ($\text{M}=\text{Na}^+$ or K^+), denoted M^+ /PAPS: when dissolved in aqueous MOH solution, γ -aminopropyl triethoxysilane (1) is quickly hydrolyzed to form a silanetriol (2) and the byproduct ethanol, $\text{CH}_3\text{CH}_2\text{OH}$. The reactive silanetriol (2) species undergo condensation reactions (with the removal of H_2O) to form an oligomeric sol and finally lead to a gel with 3-D networks (3).

opaque white layer on top of Na^+ /PAPS from which mineralization occurs; (2) without any intentional exposure to relatively high $[\text{CO}_2]$, the latter K^+ /PAPS matrix was simply exposed to the air (CO_2 : ~0.03% v/v at 15 °C) of ambient conditions with relative humidity in the range of 50~60%.

Results and Discussion

Figures 2(A) and 2(B) present typical images of self-assembled carbonate derivatives respectively, observed by scanning electron microscopy (SEM). The images exhibit features of typical of inorganic crystals.

In Figure 2(A), nucleation was initiated by bathing Na^+ /PAPS matrices under a warm and humid mixture of CO_2 and air ($[\text{CO}_2]$ is on the order of 10^2 of that of ambient air) for <10 s. The root-mean-square roughness (~560 nm) was measured by the contact mode of atomic force microscopy (AFM). The SEM image exhibits the floral structure typical of the mineralization process. The crystal mineralized at the air- Na^+ /PAPS interface is composed of C, O, and Na, as identified by energy dispersive X-ray spectrometry (EDS) equipped in SEM. The carbon and oxygen are attributed to the $\text{CO}_2(\text{aq})$ dissolved within the polymeric matrices

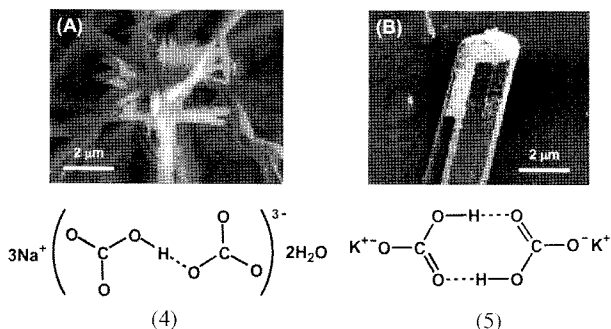


Figure 2. (A) A floral shape of crystalline $\text{Na}_3(\text{CO}_3\text{HCO}_3) \cdot 2\text{H}_2\text{O}$ self-assembled at the air interface of Na^+ /PAPS matrix and (B) A KHCO_3 microtube self-assembled at the air interface of K^+ /PAPS matrix.

enhanced by the basic pH (~11.6).^{7,8} In complementary experiments, the growth rate and areal number density of mineralization increased when $[\text{NaOH}]$ was doubled, but very few was found when NaOH was replaced by an equal concentration of NaHCO_3 or Na_2CO_3 . These observations suggest the importance of pH on the absorption of CO_2 from ambient air into hydrated Na^+ /PAPS matrices. A powder X-ray diffraction (XRD) measurement identifies the mineralized material as $\text{Na}_3(\text{CO}_3\text{HCO}_3) \cdot 2\text{H}_2\text{O}$, named hydrated sodium bicarbonate carbonate dihydrate 4 that contains a symmetric $(\text{CO}_3\text{HCO}_3)^{3-}$ anionic structure.

Without bathing in warm and humid CO_2 above, nucleation to the microtubes on K^+ /PAPS matrices was initiated under the atmospheric relative humidity in the range of 50~60%. This indicates the amount of CO_2 in air (~0.03% v/v at 15 °C) is sufficient and the control of humidity is critical. Because $\text{CO}_2(\text{g})$ is highly soluble in H_2O (0.5 mg/L at ambient conditions and 25 °C), the extent of $[\text{CO}_2]_{\text{aq}}$ dissolved from air can be affected by the extent to which polymeric matrices are hydrated. The microtubes are always high-aspect-ratio structure. Figure 2(B) exhibits a typical scanning electron microscopic image that demonstrates tubular structure. The microtube was mechanically broken using a microsize tungsten tip before measuring SEM, to make sure of the structure different from a rod-type. X-ray powder diffraction (XRD) confirms the presence of crystalline dimeric anion of KHCO_3 5 in the microtubes. Adequate carbon and oxygen for the bicarbonate species 5 was derived from the dissolution of $\text{CO}_2(\text{aq})$ from air, and the concentration in PAPS was influenced by the concentration of KOH doped in the matrices.

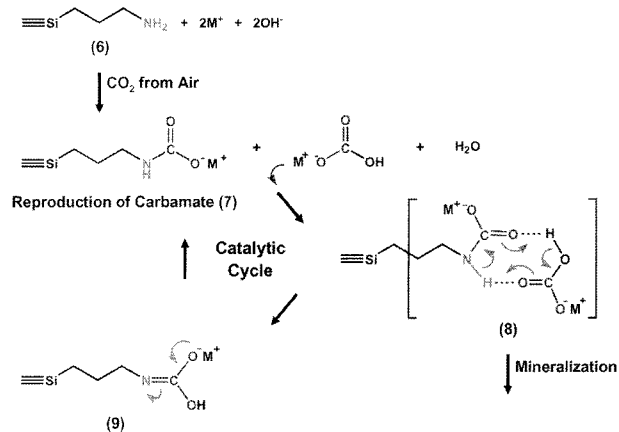


Figure 3. Catalytic cycle of a mineralization mechanism for growing floral and tubular shapes of carbonate derivatives self-assembled at the air- M^+ /PAPS interface under relative humidity of 50~60%: hydration, CO_2 absorption, and the formation of carbamate 7 from primary amine functionality 6 of PAPS followed by coupling with $\text{HCO}_3^- \text{M}^+$ to form a complex intermediate 8, leading to crystalline carbonate derivatives (4 and 5 in Figure 2) and reproducing carbamate 7 through the isocyanate derivative 9.

In accounting for the influence of pH on the mineralization process, the localized surface chemistry depending on the pH is considered at the exposed interface between M^+ /PAPS ($M = Na^+$ or K^+).¹⁰ The pH of the M^+ /PAPS silica sol solution is ~11.6 after mixing MOH with aqueous γ -APS solution (pH = 10.5). The pH of the gel matrices hydrated under 50~60% relative humidity likely exceeds 11.6. At pH 11.6, the dissolved CO_2 in an aqueous solution to CO_3^{2-} (~97%) is the dominant inorganic species deep within the hydrated M^+ /PAPS matrices.¹¹ A local pH decrease, however, occurs at the exposed air- M^+ /PAPS interface as a result of an acid-base reaction between CO_2 from air and the primary amine functionality with the consequent formation of carbamate ($-NHCO_2^-$).^{5,6} The formation of the carbamate moiety is identified from X-ray photoelectron spectroscopic (XPS) evidence, where deconvolution of the nitrogen 1s (400.3 eV) line provides the position and component of the carbamate nitrogen ($-NHCO_2^-$) at 401.3 eV.

Based on the results, a mineralization mechanism (Figure 3) is proposed for the growth of crystalline carbonate derivatives, floral $Na_3(CO_3HCO_3) \cdot 2H_2O$ and tubular $KHCO_3$ (**4** and **5** in Figure 2) crystallites. This involves anionic carbamate ($-NHCO_2^-$; **7**) derived from the reaction between $CO_2(aq)$ and the primary amine species **6** of PAPS. The carbamate **7** forms a complex hydrogen-bonded intermediate **8** with $HCO_3^-M^+$ previously formed at the exposed interface of MOH-catalyzed PAPS matrices with air.¹⁰ The intermediate **8** subsequently undergoes catalytic rearrangement simultaneously to mineralize the crystalline carbonates (**4** and **5**) and to reproduce carbamate **7** through the isocyanate derivative **9**. Although **8** is not directly observed, it is consistent with the mineralization to form the observed crystalline structures in XRD.

Conclusions

The nucleation and growth of crystalline carbonate materials (**4**, **5**) are matrix-mediated from the matrices (ca. 40- μm thick) of mesoporous poly(γ -aminopropyl triethoxysilane) (PAPS), where CO_2 (0.03% v/v) from air is utilized as a carbon source in the mineralization process under relative humidity of 50~60%. A catalytic cycle via the reproduction of carbamate ($-NHCO_2^-$) intermediate **8** is proposed for the mineralization mechanism for growing the *floral* and *tubular* shapes of crystalline carbonate assemblies (**4**, **5**) at each

air interface of the matrices of MOH-catalyzed PAPS, M^+ /PAPS ($M = Na^+$ and K^+). This mechanism would give rise to novel crystallization strategies for producing hierarchically structured materials.

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