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Shape, Size and Morphology Control of Inorganic Crystals With Self-Assembled Monolayers

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ABSTRACT

Self-assembled monolayers (SAMs) provide simple, yet sophisticated surfaces to mimic the effect of proteins associated with the process of biomineralization. A careful selection of organic molecules with an appropriate surface chemistry (i.e. $\text{HS}-(\text{CH}_2)_n-\text{X}^-$ supported on a metal surface) allows the nucleation and growth of oriented calcite crystals and provides opportunities to study the formation of inorganic crystals assisted by organic molecules. We have successfully crystallized calcite crystals on different SAMs in the presence of additives such as proteins and/or ions in solution, and found correlations between the orientations of crystals to their final shapes, sizes and morphologies. We report here our experimental results demonstrating how underlying organic molecules along with inorganic additives can control and mold the final shape, size and morphology of calcium carbonate crystals.

INTRODUCTION

Sophisticated structures created by nature have always fascinated and inspired scientists. Namely, biominerals including calcium carbonates, silica, and iron oxides can be observed in biology with multitude of morphologies, which can vary dramatically depending on their function.[1, 2] Many attempts have been made to control various parameters of crystals, including their orientation, size, shape and morphology to elucidate the formation and morphogenesis of biominerals.[3-10] We have reported previously the effectiveness of magnesium ions in controlling the size, shape and morphology of oriented calcite crystals when used in conjunction with carboxylic acid functionalized self-assembled monolayers on silver surface.[11] Here, we extend the studies to include SAMs terminated in different functional groups supported on gold surfaces to analyze the generality of the effect of Mg ions on the morphology and size of oriented calcite crystals nucleated from various crystallographic planes.

EXPERIMENTAL

Substrates were prepared by e-beam evaporation of Au (500 nm) on Si(100) wafer primed with Ti (2nm). The substrates were quickly removed and immediately immersed in 5mM solutions of alkanethiols in ethanol at RT. The following thiols were used: HS-

$(\text{CH}_2)_{11}\text{-OH}$, $\text{HS-(CH}_2)_{10}\text{-COOH}$, $\text{HS-(CH}_2)_{15}\text{-COOH}$, and $\text{HS-(CH}_2)_{11}\text{-SO}_3^- \text{Na}^+$. The adsorption of alkanethiols to the metal thin films were allowed to take place for 24 hours, after which the substrates were exhaustively rinsed with EtOH, followed by H_2O wash. Crystallization of calcite crystals on SAMs took place in a reaction vessel containing 20 mM CaCl_2 . Various amounts of MgCl_2 were also added to the reaction vessel. The crystallization was initiated with an addition of ammonium carbonate to a separate reaction vessel placed along side the reaction vessel containing SAMs. The crystallization was allowed to take place for 2 hrs at RT in a closed desiccator. Each substrate was rinsed with H_2O and dried. Scanning electron microscope (SEM), X-ray diffraction measurements (XRD), statistical analysis and computer simulations were utilized to study the crystals.

RESULTS AND DISCUSSIONS

As seen in Figure 1, crystals nucleated from SAM surfaces showed oriented calcite crystals, which have nucleated from different nucleating planes depending on the alkanethiols used to functionalize the surfaces. According to the XRD measurements, morphological analysis and computer simulations, crystals grown on: (i) $\text{HS-(CH}_2)_{10}\text{-COOH}$ on Au uniformly nucleated from the (113) plane of calcite (Figure 1a); (ii) $\text{SH-(CH}_2)_{15}\text{-COOH}$ on Au nucleated from the (013) planes (Figure 1b), and (iii) $\text{HS-(CH}_2)_{11}\text{-OH}$ on Au surface uniformly nucleated from the (104) plane of calcite (Figure 1d). (It is important to mention that although the majority of the crystals observed fall under the nucleating planes mentioned above, few crystals do not conform to the given nucleating planes, possibly due to the nucleation occurring at defect sites). Crystals nucleated from $\text{HS-(CH}_2)_{11}\text{-SO}_3^-$ on Au showed two distinctly different families of orientation – the (106) and (1.0.12) nucleating surfaces (Figure 1c). The appearance of two different nucleating planes for Au-SO_3^- may be due to the presence of two different

Figure 1. Calcite crystals nucleated from a) $\text{Au-C}_{10}\text{-COOH}$, b) $\text{Au-C}_{15}\text{-COOH}$, c) Au-SO_3^- , and d) Au-OH .

interfacial geometries of the SO_3^- group that can be fixated upon the interaction with Ca ions. Overall, the preferred crystallographic orientations of these crystals follow the orientations of the functional groups in alkanethiols as suggested earlier.[12] The crystals were not uniform in size and shape.

Nucleation of calcite crystals on SAMs with small amount of Mg ions added to the crystallization solutions (mol Mg/molCa, $n = 0.5$) yielded crystals, which in addition to the preferred crystallographic orientations, showed homogeneity in crystal sizes and shapes (Figure 2). The number of non-oriented crystals nucleated from the defect sites was dramatically reduced. As seen in Figure 3, the size distributions of calcite crystals nucleated on SAMs is profoundly different with the addition of Mg ions to the crystallizing solutions. Crystals grown in the absence of Mg ions showed random crystal size distribution ranging from 2 μm to 30 μm , while the addition of Mg ions yielded

Figure 2. Calcite crystals nucleated upon the addition of Mg ions from the a) Au-C₁₀-COOH, b) Au-C₁₅-COOH, c) Au-SO₃⁻, and d) Au-OH, with Mg/Ca ratio = 0.5.

significant narrowing of the crystal size distribution for Au-C₁₀-COOH, Au-C₁₅-COOH, and Au-SO₃⁻ surfaces, with average crystal sizes of 13 μm , 15 μm , and 12 μm respectively, as measured from the SEM micrographs.

Another noticeable feature is the change in the morphology of calcite crystals upon the addition of Mg ions (compare Figures 1a,b to Figures 2a,b). The presence of Mg ions during crystallization of calcite has produced a uniform development of new crystal faces, which were previously not observed.

Figure 3. Size distribution of calcite crystals nucleated from Au-C15-COOH; a) $n=1.5$, b) $n=1.0$, c) $n=0.5$, and d) $n=0$.

On the Au-SO_3^- surface (Figure 2c), only crystals nucleated from the (106) plane were formed upon the addition of Mg, suggesting the effectiveness of Mg ions at the nucleating stage in fixating the SO_3^- groups in the geometry that favors the nucleation from the (106) plane only. Interestingly, when small amounts of Mg ions were present during crystallization on the Au-OH surface, the inhibition of crystallization and the formation of amorphous calcium carbonate (ACC) spherulites was observed (Figure 2d). This is an interesting finding, since ACC spherulites are highly soluble and difficult to stabilize. The remarkable homogenization of crystal sizes and shapes is due to the selective incorporation of Mg ions into calcite crystals. The observed effects were even more pronounced when higher concentrations of Mg were used

Gradual increase of Mg ions ($n > 1.0$) in the crystallization solution with Au-C₁₀-COOH, Au-C₁₅-COOH and Au-SO₃⁻ surfaces showed nucleation of oriented calcite crystals favoring asymmetric growth along the c-axis. The development of acicular crystals observed on all three surfaces is due to the preferential binding of Mg ions to the {hk0} planes, thus slowing the growth in the a,b plane of calcite crystals.[13, 14] Detailed analysis of asymmetric growth of calcite in the presence of Mg ions and SAMs will be reported elsewhere.

CONCLUSION

Crystallization of calcium carbonates induced by the presence of SAMs favored the nucleation of oriented calcite crystals. The nucleating planes of calcite crystals are controlled by the alkanethiols adsorbed on the substrates. The addition of Mg ions to the crystallization solution of calcium carbonates in the presence of SAMs yielded remarkable homogenization of crystals sizes, shapes and nucleating planes for Au-C₁₀-COOH, Au-C₁₅-COOH and Au-SO₃⁻. The combination of Mg ions and Au-OH surface induced the formation of ACC. We believe, therefore, that the use of highly ordered

organic surface along with the addition of foreign ions as growth modifiers provides outstanding multi-parameter control over the crystallization process.

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