

Nucleation of Calcite Crystals

Face-Selective Nucleation of Calcite on Self-Assembled Monolayers of Alkanethiols: Effect of the Parity of the Alkyl Chain**

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The use of self-assembled monolayers (SAMs) has provided an ideal platform to study the function of highly ordered organic surfaces for various applications, including nucleation of crystals.^[1–8] In particular, SAMs of alkanethiols with a range of functionalities supported on gold and silver have been demonstrated to effectively nucleate calcium carbonate crystals, with a high degree of orientational specificity for each surface.^[2,9–11] It has been shown that the face-selective nucleation of calcite cannot be explained in terms of the lattice match between the SAM and the crystal face it nucleates. It has been suggested that a match may exist between the direction of the SAM terminal groups and that of anions in the nucleated crystal.^[9] This situation would imply that the mechanism of the face-selective nucleation involves the translation of the orientation of the terminal groups on the SAM into the nucleating crystals. The validity of this hypothesis could not be explicitly tested in the previously reported systems, since the SAMs used differed in multiple parameters (for example, functional groups, metal support, chain length).

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Herein we verify the proposed mechanism by investigating the oriented growth of calcite on SAMs in which only one parameter—the orientation of the functional group—is varied. For this purpose, we utilized the so-called “odd-even effect” in the monolayers.^[8,12,13] Detailed structural studies of SAMs^[14,15] have shown that the orientation of long-chain alkanethiols ($\text{HS}(\text{CH}_2)_n\text{CH}_3$) adsorbed from solution onto metal surfaces is determined by the cant (α , Figure 1a) and

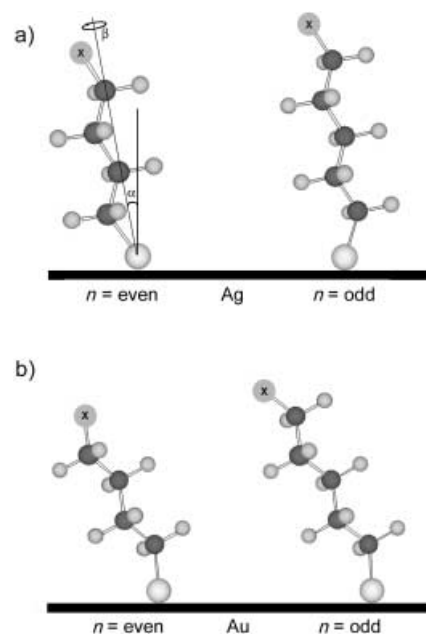


Figure 1. Schematic representation of even and odd chain length ω -terminated alkanethiols adsorbed on a) silver and b) gold. Note the differences in the orientation of the functional group X with respect to the interface as well as cant (α) and twist (β) angles.

twist (β) angles which the thiol molecules adopt in relation to the metal film during the formation of the monolayers. It has been demonstrated that when gold films are used to support SAMs, α and β have the same value and sign for all alkanethiol chains, while alkanethiol molecules assembled on silver show cant angles of opposite signs for alkyl chains of different parity. Therefore, the orientation of the terminal group X in SAMs on Ag is constant for both odd and even chains, and the terminal group X in SAMs on Au forms two different angles with the interface for odd and even chain lengths (Figure 1). SAMs with alkyl chains of different parity assembled on Au and Ag provide two ideal control systems to study the effect of terminal groups on the oriented growth of crystals. We anticipated that, if face-selective nucleation were controlled by the orientation of the functional groups in the templating surface, then all SAMs on Ag would induce the oriented crystal growth from the same crystal plane, while odd- and even-lengthed SAMs on Au should induce nucleation in two different crystallographic directions.

Several sulfanylalkanoic acids with different methylene chain lengths were assembled on gold and silver to template the nucleation of calcite. Sulfanyloctanoic acid ($\text{HS}-\text{C}_7-\text{COOH}$, denoted C_7), sulfanylundecanoic acid ($\text{HS}-\text{C}_{10}-$

COOH, denoted C_{10}), sulfanyldodecanoic acid (HS- C_{11} -COOH, denoted C_{11}), sulfanylpentadecanoic acid (HS- C_{14} -COOH, denoted C_{14}), sulfanylhendecanoic acid (HS- C_{15} -COOH, denoted C_{15}), and sulfanylheptadecanoic acid (HS- C_{16} -COOH, denoted C_{16}) were adsorbed from ethanol onto the surfaces of gold and silver that had been evaporated onto silicon (100) wafers.^[16] The crystallization of the calcite crystals with the SAMs was performed by following the previously published methods.^[9] Briefly, functionalized SAMs were submerged in a 20 mM calcium chloride solution in a desiccator containing ammonium carbonate on the side as the carbonate source. The crystallization process was performed at room temperature for two hours. The crystals were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and morphological computer-simulations analysis.

Indeed, both odd- (C_7 , C_{11} , and C_{15}) and even-lengthed (C_{10} , C_{14} , and C_{16}) carboxylic acid terminated alkylthiols supported on silver induced the nucleation of calcite from the same crystallographic plane. The nucleated plane was indexed as (012) on the basis of computer simulations on the orientation of crystals observed by SEM (Figure 2a,b). This assignment was further confirmed by XRD data that showed

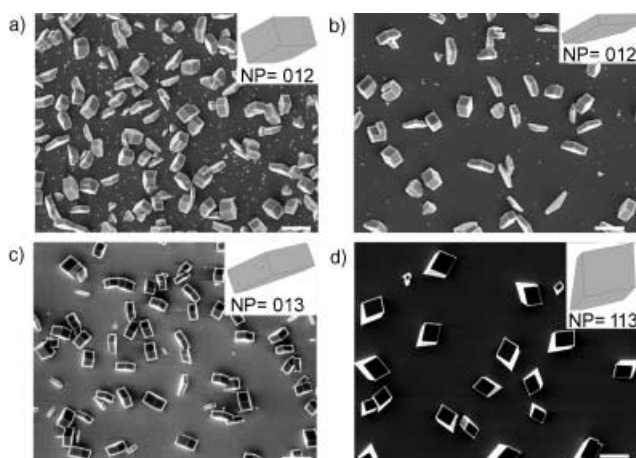


Figure 2. SEM micrographs of calcite crystals grown on carboxylate-functionalized self-assembled monolayers of a) C_{15} -Ag, b) C_{10} -Ag, c) C_{15} -Au, and d) C_{10} -Au. Scale bars: 20 μ m. The micrographs were recorded on a JEOL JSM-5600 LV system operating at 10 kV. Insets: Computer simulations of similarly oriented calcite rhombohedra with the nucleating planes (NP) indicated. The simulation were performed using SHAPE V6.0 software.

only strong (012) and (024) peaks in the diffraction pattern (Figure 3a,b). SAMs on gold, on the other hand, induced the highly oriented formation calcite in two distinct crystallographic directions. As deduced from the morphological analysis (Figure 2c), odd-length alkylthiols (C_7 , C_{11} , and C_{15}) templated the calcite growth from a range of (01*l*) faces ($l = 2-5$). The (012) and (024) peaks were observed in the corresponding XRD spectra (Figure 3c). Crystals observed on carboxylic acid terminated SAMs with an even chain length (C_{10} , C_{14} , and C_{16}) matched well with computer simulations of calcite crystals nucleated from the (11*l*)

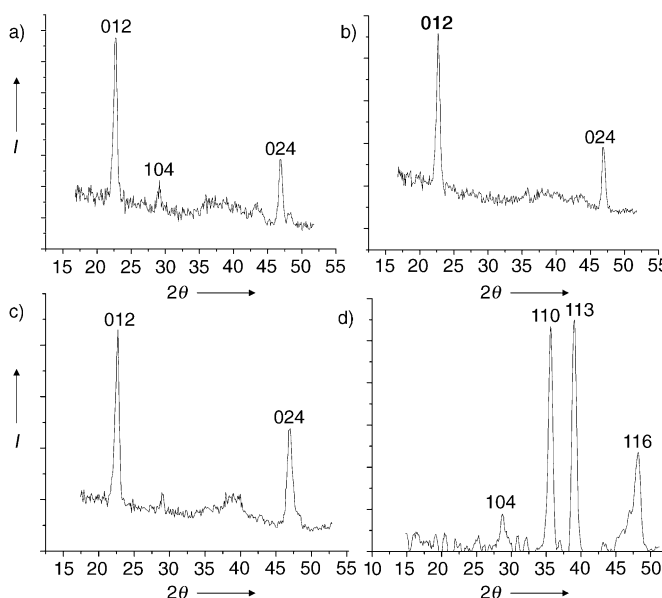


Figure 3. Representative XRD patterns of calcite crystals grown on a) C_7 , C_{11} , and C_{15} on Ag, b) C_{10} , C_{12} , and C_{16} on Ag, c) C_7 , C_{11} , and C_{15} on Au, and d) C_{10} , C_{12} , and C_{16} on Au. XRD measurements were made on a Bruker AXS instrument with a general area diffraction detection system (GADDS).

crystallographic planes ($l = \text{ca. } 3$; Figure 2d). The corresponding XRD spectra showed the (110), (113), and (116) calcite peaks (Figure 3d). It is important to note that SAMs supported on silver controlled the nucleating plane of calcite within about $2-4^\circ$, while the orientational specificity of calcite crystals formed on SAMs supported on gold appeared to be generally lower (within about $10-15^\circ$) and to greatly depend on the substrate preparation. This observation indicates that the carboxylate groups of adsorbed thiols may have more azimuthal freedom on the gold surfaces.^[17]

Our results unequivocally confirmed the proposed mechanism of the translation of the stereochemical and orientational information at the organic/inorganic interface.^[9,13,18,19] To gain a better understanding of the recognition at the nucleation stage we performed further analysis of the structure of the SAM/calcite interfaces. Previous studies^[20-22] of the carboxylic acid terminated Langmuir monolayers and SAMs in the presence of Ca^{2+} and Cd^{2+} ions have shown a considerable ordering of the surface that results in the fixation of the carboxylic groups in a specific orientation. In particular, it has been shown that the overlayer of Ca^{2+} ions on a SAM of HS- C_{15} -COO⁻ fixes the terminal groups in a preferred orientation, in which one C–O bond is parallel to the substrate.^[23] We simulated the structure of the CO₂⁻ terminated SAMs in the solution of Ca^{2+} ions by combining the above structural information with the reported cant and twist parameters of the SAMs on different substrates.^[14] On silver ($|\alpha| = 10-14^\circ$, $\beta = 42-45^\circ$), the planes of the carboxylate groups for both odd and even chain lengths form an angle of about 30° with the surface normal. This orientation closely matches that of the carbonate ions in calcite crystals oriented in the [012] direction (Figure 4a). On gold ($\alpha = 26-28^\circ$, $\beta = 50-55^\circ$), the planes of the carboxylate groups in odd chain

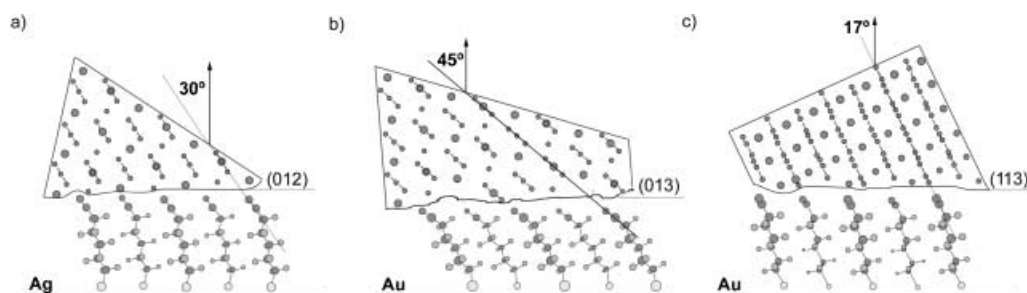


Figure 4. Schematic representations depicting the alignment of carboxylic groups on SAMs with the carbonate groups in calcite for a) odd (and even) chain length SAMs on Ag, NP = (012); b) odd chain length SAMs on Au, NP = (013); c) even chain length SAMs on Au, NP = (113). The C–O bonds in the surface carboxylate groups are parallel to the C–O bonds in the carbonates in the nucleated calcite crystals.

lengths form an angle of 40–45° with the surface normal, which is nearly parallel to the carbonate ions in calcite crystals oriented in the [01 \bar{l}] direction ($l=2-4$; Figure 4b). For even chain lengths on Au, the plane of the carboxylate group in a symmetrical, bidentate arrangement forms an angle of about 17–22° with the surface normal, which would closely match the orientation of the carbonate ions in calcite crystals nucleated from the (11 \bar{l}) plane ($l \approx 3$; Figure 4c).

We propose, therefore, that when carboxylate-functionalized SAMs are introduced into the Ca²⁺ solution a counterion overlayer is formed by bonding of the Ca²⁺ ions to the carboxylate groups on the SAMs, which also fixes the position of the carboxylate functionalities on the SAMs.^[23] The formation of the counterion layer starts the nucleation process by attracting free carbonate ions in solution. The ordered carboxylates may serve as surrogate oxyanions for the nucleating crystals, thus inducing the oriented bonding of the subsequent carbonates at the same angle to the carboxylate functional groups on the surface of the SAMs. This would ultimately result in a fixed, highly controlled, oriented growth of the crystals.

These observations raise a fascinating possibility that the oriented growth of crystalline materials can be regulated not only by controlling the functionality and the lattice of the templating surface, but also by varying the orientation of the terminal groups. The translation of the structural information at the organic/inorganic interface is a plausible mechanism that can explain the enormous variety of crystallographic orientations of biologically formed minerals: even slight changes in the conformation of a biological macromolecular template would result in the fine-tuning of the orientation of the nucleated crystals.

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