

# Carbonate Crystal Growth Controlled by Interfacial Interactions of Artificial Cell Membranes

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Morphology of carbonate crystals grown on the surface of artificial cell membranes was controlled by changing the interfacial chemistry. For octadecyltriethoxysilane (OTE) films with terminal methyl groups interacting little with an aqueous calcium carbonate solution, calcite (104) crystals were formed. Polymerized pentacosadiynoic acid (PDA) films with terminal carboxylic acid groups induced deposition of calcite (012) crystals aligned along with each other within a polymer domain. On the other hand, stearyl alcohol (StOH) films with terminal hydroxyl groups induced deposition of aragonite crystals. When PDA was mixed with StOH, the 8:1 PDA:StOH (molar ratio) film produced dominating calcite (012) crystals without any crystal alignment, and the 4:1 mixture film produced minor calcite (012) crystals and major aragonite crystals. For the 2:1, 1:1, 1:2, and 1:4 mixture films, aragonite crystals were dominating. Hence, it is found that the chemical composition at the interface plays a very important role in controlling the morphology of deposited carbonate crystals.

*Key words:* carbonate crystals, interfaces, artificial cell membranes

## INTRODUCTION

Biological systems are capable of controlling inorganic crystal growth to a remarkable degree [1]. This oriented crystal growth has inspired numerous studies of template-directed crystallization at condensed surfactant thin films, which are often called artificial cell membranes due to their structural resemblance to natural cell membranes. Such attempts have been tried for the template systems like Langmuir monolayers and Langmuir-Blodgett films [2-4]. Owing to these works, calcite crystals with peculiar morphology were found to deposit preferentially at highly acidic interfaces where strong ionic interactions with solution containing calcium carbonate are present. Absence of such interaction results in natural calcite (104) crystals. However, the crystal morphology on the corresponding template films remained unchanged and could not be controlled.

In the present study, for the first time to the authors' knowledge, we try to control the morphology of the crystals by varying the composition of the template films, hence changing the interfacial chemistry and interaction with the solution. We chose template systems of polymerized pentacosadiynoic acid and stearyl alcohol because these two systems produce different crystal morphology due to different interfacial chemistry. The results show that the mixing of the two components influences strongly the crystal form and arrangement. Implications of this study will be very important both in understanding biomineralization processes and in developing related technologies like new nanocomposite materials and anti-calcium biomaterials or medical implants.

## MATERIALS AND METHODS

### Materials

Octadecyltrichloroethoxysilane (OTE, 99%) and 10, 12-pentacosadiynoic acid (PDA, 99%) were purchased from Huls America and Farchan Laboratories. Stearyl alcohol (StOH, 99%) and calcium carbonate ( $\text{CaCO}_3$ , 99%) were from Aldrich. Distilled water was purified with a Millipore water purifier and the initial resistivity was 18.2M $\Omega$ . Spreading solvents used for PDA and StOH were chloroform of reagent grade (Aldrich). The solutions of PDA and StOH were 1 mM and kept at a temperature of 4°C in the dark. The solutions were allowed to equilibrate at room temperature before use.

### Surface Isotherms

Surface isotherms of pure and mixture monolayers of PDA and StOH were obtained by using a standard Langmuir trough (KSV minitrough, Finland). The solutions were spread on the pure water (pH=5.5, 25°C) from microsyringes. About 20 min was waited until the solvent evaporated completely. The air/surfactant/water interface was compressed symmetrically by two teflon-coated barriers at a speed of 10 mm/min. The surface isotherms were acquired until the surface pressure reaches 30 mN/m.

### Film Formation

OTE film was formed on a cleaned glass plate by following the reported self assembly technique [5]. Measured advancing contact angle of water (pH=5.5) at 110° confirmed formation of a typical hydrophobic OTE film on the glass surface. StOH films at the air/water interface ( $\Pi$ =30 mN/m) were deposited on the OTE coated glass substrate, by using a horizontal

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