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Aragonite coating solutions (ACS) based on artificial seawater

A. Cuneyt Tas*

Department of Materials Science and Engineering, University of Illinois, Urbana, IL 61801, USA

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ABSTRACT

Aragonite ($CaCO_3$, calcium carbonate) is an abundant biomaterial of marine life. It is the dominant inorganic phase of coral reefs, mollusc bivalve shells and the stalactites or stalagmites of geological sediments. Inorganic and initially precipitate-free aragonite coating solutions (ACS) of pH 7.4 were developed in this study to deposit monolayers of aragonite spherules or ooids on biomaterial (*e.g.*, UHMWPE, ultrahigh molecular weight polyethylene) surfaces soaked in ACS at 30 °C. The ACS solutions of this study have been developed for the surface engineering of synthetic biomaterials. The abiotic ACS solutions, enriched with calcium and bicarbonate ions at different concentrations, essentially mimicked the artificial seawater composition and started to deposit aragonite after a long (4 h) incubation period at the tropical sea surface temperature of 30 °C. While numerous techniques for the solution deposition of calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), of low thermodynamic solubility, on synthetic biomaterials have been demonstrated, procedures related to the solution-based surface deposition of high solubility aragonite remained uncommon. Monolayers of aragonite ooids deposited at 30 °C on UHMWPE substrates soaked in organic-free ACS solutions were found to possess nano-structures similar to the mortar-and-brick-type botryoids observed in biogenic marine shells. Samples were characterized using SEM, XRD, FTIR, ICP-AES and contact angle goniometry.

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1. Introduction

Aragonite ($CaCO_3$) is an abundant inorganic phase of marine biomineralization and geological dripstones (*e.g.*, stalactites and stalagmites) or various sedimentary formations [1–3]. The inorganic part of mollusc bivalve shells (clams, oysters, scallops and mussels), gastropods (snails), coral reefs and mother-of-pearl (nacre) is comprised of aragonite crystals stacked in a mortar-and-brick manner.

Aragonite (*Pnam* (Hermann–Mauguin No. 62), orthorhombic), calcite (R-3*c* (167), rhombohedral), and vaterite ($P6_3/mmc$ (194), hexagonal) are the anhydrous crystalline polymorphs of calcium carbonate. Hydrated and X-ray-amorphous calcium carbonate (ACC), on the other hand, can be formed as a precursor phase in some $CaCO_3$ syntheses [4,5]. Calcite is the most abundant and stable polymorph of calcium carbonate on earth, while vaterite (μ-$CaCO_3$), named after Heinrich Vater [6], is the least abundant among the three anhydrous polymorphs. Plummer and Busenberg [7] reported the solubility products (*i.e.*, $\log K_{SP}$ values) of calcite (−8.48 at 25 °C and −8.56 at 37 °C), aragonite (−8.33 at 25 °C and −8.40 at 37 °C) and vaterite (−7.91 at 25 °C and −8.05 at 37 °C) in water; therefore, aragonite has a slightly higher solubility than that of calcite.

While the synthetic $CaCO_3$ powders, usually of the calcite form, have found widespread use in cosmetics, food, toothpaste, plastics, paper-making, ink, paint, textile, pharmaceutical, and rubber industries, the crystallization of aragonite in seawater (instead of distilled water) for carbon sequestration remains as a developing area of research [8]. Despite significant research concentrating on the physical–chemical characterization of the mortar-and-brick-type aragonite of molluscan nacre, studies on the biomimetic synthesis of aragonite in artificial (or natural) seawater, in lieu of distilled/deionized water, and simultaneously at the sea surface temperature have either been limited or focused on calcite crystallization in seawater [9–20]. The objective of the current study is to contribute to this field of completely inorganic and biomimetic synthesis performed in artificial seawater (ASW). A significant number of non-biomimetic techniques have been suggested for synthesizing aragonite in distilled water, just to cite a few here, by Bragg [21], Backstrom [22], Wray and Daniels [23], Bills [24], Ota et al. [25], Wang et al. [26], Ahn et al. [27], Thachepan et al. [28], Park et al. [29], Beck and Andreassen [30], Sand et al. [31], and Jiang et al. [32].

* Tel.: +1 217 344 6708; fax: +1 217 333 2736.
E-mail address: c_tas@hotmail.com
URL: http://www.cuneyttas.com.

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Artificial seawater (ASW) was formulated by Kester et al. [33] in 1967, as a revision to the 1940 recipe of Lyman and Fleming [34], and later evolved into an ASTM standard (D1141-98) [35]. The composition of ASW [33–35], together with the compositions of the novel solutions of this study, are presented in the following chapter. Briefly, ASW is an aqueous solution rich in Mg^{2+} and SO_4^{2-}; with a Mg^{2+}/Ca^{2+} molar ratio of 5.34 and a SO_4^{2-}/Ca^{2+} ratio of 2.82 [33–35]. ASW can also be obtained from a number of commercial vendors. On the other hand, the phosphate ion (PO_4^{3-}) concentration at the surface of seas and oceans is around 0.8 nM (nanomolar) and it can only increase to values ranging from 1.6 to 2.4 μM at depths of 1–3 km [36]. This deficiency of PO_4^{3-} ions makes it difficult to observe calcium phosphate crystallization in seas and oceans.

Electrochemically-polarized steel electrodes immersed in artificial [36–40] or natural [41] seawater were found to form crystalline calcareous deposits (scale) of aragonite, but not calcite, on their surfaces. The above electrochemical studies [36–41] inspired the current study and a number of aragonite coating solutions (ACS) are presented here which are completely inorganic, precipitate-free, and capable of forming aragonite, *in situ*, only upon heating to the typical tropical sea surface temperature of 30 °C [42,43], following 4 h of an incubation time at 30 °C.

SBF (simulated [44] or synthetic [45,46] body fluid) solutions, containing Ca^{2+}, Mg^{2+}, K^+, Na^+, HPO_4^{2-}, HCO_3^-, SO_4^{2-} and Cl^-, mimic the inorganic electrolyte composition of blood plasma, and were shown to deposit spherules of bone mineral-like carbonated apatitic calcium phosphate on immersed substrates when heated at the physiological temperature of 37 °C. On the other hand, Pan et al. [47] provided a careful clarification on why SBF solutions would not be suitable to predict the bioactivity of synthetic biomaterials immersed in those. The abiotic ACS solutions of this study mimic the liquid in which the inorganic phase (aragonite) of coral reefs or mollusc shells are forming.

ACS solutions described here may be useful to deposit high solubility aragonite, rather than low solubility Ca-hydroxyapatite ($\log K_{SP}$ being equal to −117.1) of SBFs, on the surfaces of porous or non-porous polymeric, metallic or ceramic implantable materials to modify their biocompatibility. The current demonstration of ACS solutions may also contribute to the broader carbon sequestration research to be performed in large quantities of seawater.

2. Materials and methods

2.1. Aragonite coating solutions (ACS)

High-purity (>99.9% pure) inorganic salts of Table 1 were added one by one, in the order given, to 500 mL of pre-boiled deionized water to prepare ACS solutions in sterile glass beakers. Precipitate-free ACS solutions had the autogenic pH (Orion Star 215 pH-meter, Thermo Scientific, USA) of 7.4 ± 0.06 at the time of preparation at room temperature (RT, 22 ± 1 °C). ASW (artificial seawater [35]) was also prepared as shown in Table 1. Static coating experiments were performed (for 48 h) at 30 °C in sealed high-density polyethylene (HDPE) bottles. A new HDPE bottle was used for each experiment and the experiments were repeated thrice.

Each crystallization bottle contained four pieces (10 mm × 10 mm × 1 mm) of ultrahigh molecular weight polyethylene (UHMWPE) coupons (DSM Medical, Netherlands) laid flat at the bottom. UHMWPE is the polymeric material used in various total knee and hip replacement implants. The coupons were washed with deionized water at the end of experiments, followed by dehydration in pure ethanol, and dried at RT for 36 h.

The ionic strength (I) of a biomineralization solution, such as ACS-2, is calculated as shown in Eq. (1), using the formula of Debye and Hückel [48]. One simply enters into the below formula the concentrations of ions (in M, moles/L) and the valency of ions. The value of the ionic strength (expressed in molarity, M) then serves as a reliable numerical index to exchange between researchers using and/or developing different biomineralization media based on their specific research needs.

$$I = \tfrac{1}{2}[(18.72\times10^{-3})(2)^2 + (510.48\times10^{-3})(1)^2 + (0.7\times10^{-4})(1)^2 + (576.26\times10^{-3})(1)^2 + (32.81\times10^{-3})(1)^2 + (10.15\times10^{-3})(1)^2 + (54.6\times10^{-3})(2)^2 + (28.8\times10^{-3})(2)^2 + (8.5\times10^{-4})(1)^2 + (1.6\times10^{-4})(2)^2 + (5\times10^{-4})(3)^2] = 0.772\,M \quad (1)$$

where the ionic species are Ca^{2+}, Na^+, F^-, Cl^-, HCO_3^-, K^+, Mg^{2+}, SO_4^{2-}, Br^-, Sr^{2+}, BO_3^{3-}.

2.2. Sample characterization

The crystals deposited on the surfaces of UHMWPE coupons were imaged by scanning electron microscopy (SEM, Zeiss-Neon 40 EsB, 10 kV), after sputter coating with a 10 nm-thick layer of Au–Pd alloy prior to imaging. The phase composition of the deposited crystals (upon scraping those away from the surfaces of coupons) was investigated by Cu Kα X-ray diffraction using a Bruker D8 Advance diffractometer (XRD, 40 kV, 40 mA, 0.02° steps, 8 s at each step, single crystal quartz sample holders). The scraped crystals were ground in an agate mortar prior to XRD runs. Fourier-transform infrared spectroscopy (FTIR, Spectrum One, PerkinElmer) samples of the scraped crystals were prepared by mixing them with spectral-grade KBr powders at the ratio of 1 mg sample-to-300 mg KBr in an agate mortar using an agate pestle. Transparent FTIR pellets with a diameter of 10 mm were pressed in stainless steel dies at 1000 kg applied for 1 min. FTIR data were collected with 128 scans, at 2 cm^{-1} resolution, over the range of 4000–700 cm^{-1}. Quantitative magnesium analyses of the scraped crystals were performed by using inductively-coupled plasma atomic emission spectroscopy (ICP-AES, Model 61E, Thermo Electron). For the ICP-AES analyses, 70 mg portions of powder samples were dissolved in 5 mL of concentrated HNO_3 solution. The wettability of non-coated and aragonite-coated UHMWPE coupons were determined by using a computer-controlled contact angle goniometer (*Theta Lite*, Biolin Scientific, Espoo, Finland) *via* the static sessile drop method (3 μL drop volume) with deionized water at RT. The photographs captured by the goniometer's camera were analyzed by using the software ImageJ (National Institutes of Health) to measure the contact angle (θ). The reported contact angles were the average of six measurements on each sample.

3. Results and discussion

UHMWPE substrates were preferred in this study, instead of, *e.g.*, ordinary glass slides, to eliminate any issue(s) of the undesired leaching of inorganic ions from the substrate itself to interact with the crystallization and coating process. Artificial seawater (ASW) of Table 1, being a HCO_3^--deficient solution, did not form any crystals on the surfaces of UHMWPE coupons even after 20 days of immersion at 30 °C. The HCO_3^-/Ca^{2+} molar ratio of ASW is only 0.273, which is rather low for extensive $CaCO_3$ nucleation to occur. To increase the HCO_3^-/Ca^{2+} molar ratio in the ACS-1, ACS-2 and ACS-3 solutions to 1.75, the amounts (in g) of $NaHCO_3$ and $CaCl_2{\cdot}2H_2O$ was made equal to one another. The amounts of both $NaHCO_3$ and $CaCl_2{\cdot}2H_2O$ used in preparing the ACS-2 and ACS-3 solutions were respectively increased by 83 and 166% in comparison to those of the ACS-1 solution. ACS-1, ACS-2 and ACS-3 solutions of Table 1 were

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