Artificial Nacre by Alternating Preparation of Layer-by-Layer Polymer Films and $CaCO_3$ Strata

Hao Wei, Ning Ma, Feng Shi, Zhiqiang Wang, and Xi Zhang*

Key Lab of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, P.R. China

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In this paper, we described the fabrication of hybrid nanocomposite by bottom-up alternating preparation of organic and inorganic layers, toward the mimicking biomineralization process of natural nacre. The organic layers are layer-by-layer (LBL) polymer thin films of diazo-resins (DAR) and poly(acrylic acid) (PAA), with reactive DAR for cross-linking the thin films and PAA for providing a surface for facilitating the biomineralization. The inorganic layers are $CaCO_3$ strata, which were prepared via the CO_2 diffusion method. Scanning electron microscopy observations show that the nanocomposite fabricated in this way has the alternate organic−inorganic multilayered structure, similar to the natural nacre's brick-and-mortar structure. The thicknesses of $CaCO_3$ strata can be controlled by selecting the diffusion time of CO_2. Moreover, the thickness and content of organic matrixes may be adjusted by controlling the layer number of LBL polymer thin films. TGA analysis reveals that the content of organic composite is about 6.9%, which is close to the content of organic matrix in the natural nacre. This study represents an efficient and controllable way for fabrication of artificial nacre.

Introduction

Nature is a perfect designer fabricating various complex and elegant materials with far better properities than the man-made materials by using some simple mechanisms.[1] The bottom-up fabrication method should be a general mechanism to form the biomineral materials, which are widespread in biological systems and have attracted an increasing interest because of their unique structures and mechanical properties.[2−4] Among them, the nacre of abalone shell is the best example of a bottom-up fabricated material, which is composed of about 95% inorganic aragonite and 5% organic matrix, exhibiting perfect physical properties being twice as hard and 1000 times as tough as its constituent phases.[3] The distinctive mechanical quality stems from its highly regular brick-and-mortar arrangement of aragonite ($CaCO_3$) and organic matrix.[4,5] The mortar consists of the soluble and insoluble biomacromolecules; the insoluble biomacromolecules act as the framework and the soluble biomacromolecules, unusually rich in aspartic acid,[6] locate on the insoluble framework[7] and offer the necessary negatively charged surface for the epitaxial nucleation of aragonite crystals.

Inspired by the delicate structure of natural nacre, various man-made mortars including Langmuir−Blodgett films,[8] self-assembled multilayered films,[9] and spin-coating films of bio-[10] or synthetic macromolecules,[11] and different methods such as alternate soaking,[9c] supramolecular self-assembly,[12] and sequential deposition,[13] were employed to mimic the process of biomineralization. Of these, only the last two offer the possibility to introduce periodic microstructures. Nonetheless, there remains a great challenge for effective mimicry of the biomineralization process, leading to fabricating artificial nacre with regular $CaCO_3$ and organic multilayered structure similar to the natural nacre.

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* Corresponding author. E-mail: xi@mail.tsinghua.edu.cn.

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Layer-by-layer assembly is a versatile and elegant technique for fabricating various thin functional films by alternately immersing a charged substrate into two solutions of the oppositely charged polyelectrolytes.[14] Until now, many LbL films with various compositions and properties have been developed by changing the building blocks[15−22] or exploiting different driving forces[23−26] for the film buildup. Among these functional multilayered assemblies, much attention was been paid to the fabrication of inorganic−organic hybrid film with various nanoparticles and polyelectrolytes.[27] The structure of natural nacre is one of the inorganic−organic hybrid materials with alternative strata of $CaCO_3$ and organism; recently, the LBL films were used to explore the mechanism of the controlled crystallization of inorganic crystal such as $CaCO_3$[9] and FeOOH[28] on organic matrix, toward mimicking the formation process of natural nacre. However, the conventional method is not feasible in the fabrication of $CaCO_3$/polyelectrolytes hybrid multilayered films. The main reason is that different from normal inorganic nanoparticles, the $CaCO_3$ nanoparticles are very unstable and rapidly aggregate to big particles and then transform from ACC to vaterite, aragonite, or calcite. So we cannot obtain the uniform and dense $CaCO_3$ layer on the polyelectrolyte multilayer films by alternately immersing the substrate into polyelectrolytes and $CaCO_3$ solution.

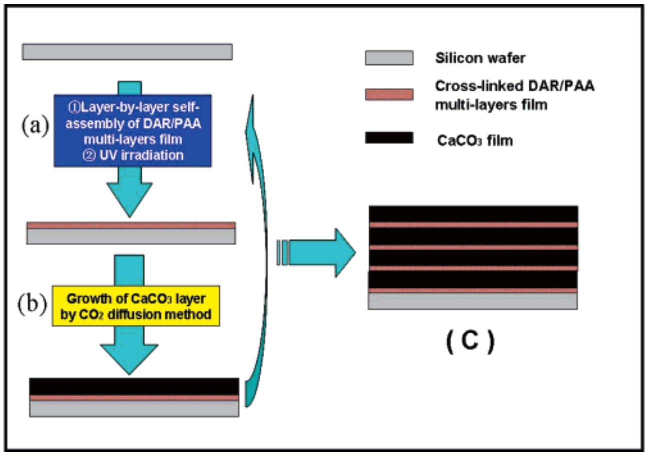

Figure 1. Schematic illustration for the fabrication of artifical nacre: (a) LbL self-assembly of DAR/PAA multilayered film via the alternating deposition method; (b) preparation of $CaCO_3$ nanolaminated structure on the DAR/PAA multilayered films by CO_2 gas diffusion method; (c) preparation of the mutlilayer organic/inorganic hybrid composite by alternately repeating steps (a) and (b).

In this paper, we report an attempt to combine the LbL assembly technique and the method of $CaCO_3$ crystal growth via CO_2 diffusion and fabricate the artificial nacre with regular multilayered structure similar to natural nacre by alternately bottom-up fabricating the organic and inorganic layers. On one hand, the fabrication of the man-made mortar is based on layer-by-layer assembly, which allows buildup of thin films with controlled thickness and composition, and their surface property can be easily controlled by selectively attaching the various building blocks with different functional groups. On the other hand, $CaCO_3$ strata are prepared by the so-called CO_2 diffusion method,[29] which has proved to be an effective approach to control the growth of $CaCO_3$ on the multilayered films. In natural nacre, the thickness of $CaCO_3$ layers is on the sub-micrometer scale. However, by conventional LbL method it is very difficult to obtain the "bricks" with a thickness larger than submicrometers. The main advantage of the method we proposed here is to obtain easily $CaCO_3$ layers from nanometer to submicrometer scale. Therefore, it is anticipated that this line of research may provide an efficient and controllable way for fabricating artifical nacre.

Experimental Section

Poly(ethylene imine) (PEI) (Mw = 750000), poly(acrylic acid) (PAA) (Mw = 24000), poly(diallyldimethylammonium chloride) (PDDA) (Mw = 400000), poly(allylamine hydrochloride) (PAH) (Mw = 65000), poly(4-styrene sulfonate) (PSS) (Mw = 70000), and $CaCl_2{\cdot}2H_2O$ were purchased from Aldrich. Polycationic diazoresins (DAR) was kindly provided by Prof. Yuping Dong (Beijing University of Science and Engineering).[18] The molecular weight (Mn) of the DAR was ca. 2640.

Preparation of artificial nacre with alternating organic/inorganic multilayers illustrated in Figure 1 involved two steps: (a) fabrication

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of DAR/PAA multilayered films and (b) preparation of the $CaCO_3$ nanolaminated structure. Cyclic repeat of the two steps two and four times resulted in two pieces of the (DAR/PAA)/CC) multilayers with two and four layers.

Fabrication of DAR/PAA Multilayered Films. The silicon wafer was cleaned by immersion in freshly prepared piranha solution (98% $H_2SO_4/H_2O_2 = 7:3$, v/v), heated for 1 h at 100 °C, and then rinsed throughly with distilled water. After being dried, the silicon wafer was immersed in aqueous solution with 0.9 vol % PEI for 20 min to obtain a positively charged surface and then dried by N_2. In general, the fabrication of DAR/PAA multilayered films included LbL assembly and post-UV irradiation. The positively charged substrate was alternately dipped into methanol solution of PAA and DAR (1 mg/mL) for 20 min, with intermediate methanol rinsing. Multilayered films were formed by repeating these two steps in a cyclic fashion. The negatively charged surface was produced by attaching PAA as the outermost layer. Next, the above fabricated films were exposed under UV light about 10 min to obtain the covalently attached multilayered films. The deposition process of the films was conducted in the dark to avoid the decomposition of the DAR.

Preparation of the $CaCO_3$ Layers. According to Cho's report,[30] two flasks were placed into a closed desiccator. One was covered by punched Parafilm (three holes) containing calcium chloride solution (40 mL, 2 mM), and the other contained fresh ammonium carbonate, about 2 g. The silicon wafer covered by DAR/PAA multilayered film was inverted and placed above the $CaCl_2$ solution. A $CaCO_3$ layer formed on the film/solution interface with the slow diffusion of CO_2 decomposed by $(NH_4)_2CO_3$ at room temperature. At the end, the wafer was rinsed by deionized water and dried in vacuum at 40 °C, and then the substrate was ready for fabrication of next DAR/PAA multilayered films.

Characterization. The samples were Au-coated prior to examination by a Hitachi S-4300 scanning electron microscope (SEM), fitted with a field emission source and operating at an accelerating voltage of 15 kV. X-ray diffraction (XRD) measurements were conducted using a Rigaku D/max-2400 powder X-ray diffractometer with Cu Kα radiation (40 kV, 120 mA), and 0.02° step and 2θ range of 20−60° were selected to analyze the crystal structure. FT-IR spectroscopic measurements were performed on an IFS-66v/S FT-IR spectrometer (Bruker), with scanning times of 32 and resolution of 4 cm^{-1}. The LbL films content in the artificial nacre was tested by thermogravimetric analysis (TGA) using a Netzsch Sta409 TGA analyzer, purged with nitrogen gas.

Results and Discussion

The fabrication of artificial nacre involves two steps, as illustrated in Figure 1: (a) the fabrication of mortar layers composed of DAR and PAA multilayered films by LbL technique;[18] (b) the preparation of brick layers composed of $CaCO_3$ crystal (CC) via CO_2 gas diffusion method. In principle, cyclic repeat of the above two steps can result in fabrication of (DAR/PAA)/CC) multilayers with a controlled number of bilayers as shown in Figure 1c. Based on the above procedures, we have fabricated arifitical nacres with two and four layers by alternately repeating the cycle two and four times, respectively. SEM observation (Figure 2) of the cross section of artificial nacre reveals a multilayered structure similar to that of abalone shell.[3] Moreover, each $CaCO_3$ layer is dense and uniform with a thickness of about 300 nm, which agrees well with the report of Hansma and his co-workers.[31] The low magnified image of two layers (Figure 2a) shows that the surface is smooth, indicating that the DAR/PAA films can effectively facilitate the formation of $CaCO_3$ strata. A free-standing thin-film composite detached from the substrates inserted in Figure 2a suggests that artificial nacre film is flexible. The fact that the DAR/PAA films are not clearly disclosed in two adjacent layers from the magnified images (Figures 2b and 2d) may indicate that the organic matrixes are probably buried in the $CaCO_3$ layers, which is similar to that of natural abalone shell.

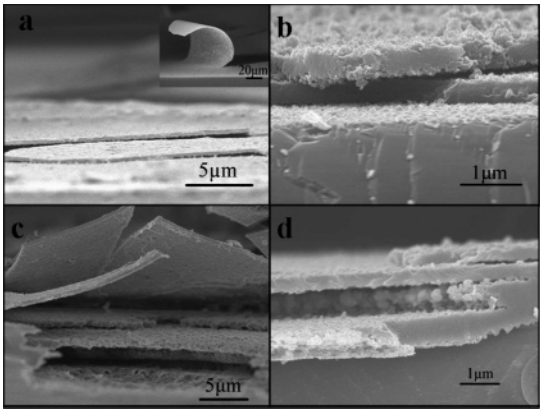

Figure 2. SEM images of the cross section of the artificial nacres with different layers prepared by cyclic fabrication of DAR/PAA multilayered films and $CaCO_3$ layers. (a) and (b) were prepared by alternately repeating steps (a) and (b) twice. (c) and (d) have the multilayered nanolaminated structure. The inserted image in (a) is a free-standing film of $(DAR/PAA)_6/CaCO_3$ composite.

The polymorph of $CaCO_3$ strata in artificial nacre is confirmed as a mixture of calcite, vaterite, and aragonite,[32] by XRD diffraction and FT-IR spectroscopy. The XRD pattern of the sample shown in Figure 3a displays not only the diffraction peaks (2θ [deg]) of vaterite and calcite but also those of aragonite. The diffraction peaks of vaterite are 20.9°, 24.8°, 27.0°, and 32.7°, correlating to the (*hkl*) indices (004), (110), (112), and (114), respectively. The diffraction peaks of calcite are identified at 20.9° (012) and 24.8° (104). Although the (021) crystal face of aragonite at 27.4° (012) is covered by the vaterite (112) crystal face, the existence of aragonite can still be identified by the weak diffraction peak at 26.1° corresponding to aragonite (111) crystal face. The structure identification is also supported by the characteristic vibration bands in FT-IR spectroscopy, as shown in Figure 3b: 745 and 848 cm^{-1} for vaterite, 712 cm^{-1} for calcite,[33] and 699 cm^{-1} for aragonite.[10a] The mixture of three polymorphs of $CaCO_3$ crystal suggests that there is crystalline transformation in the process of the formation of $CaCO_3$ strata.

In natural nacre, the mortar content is about from 5 to 10%, rendering the abalone shell great hardness and toughness. So the content control of man-made mortar is very

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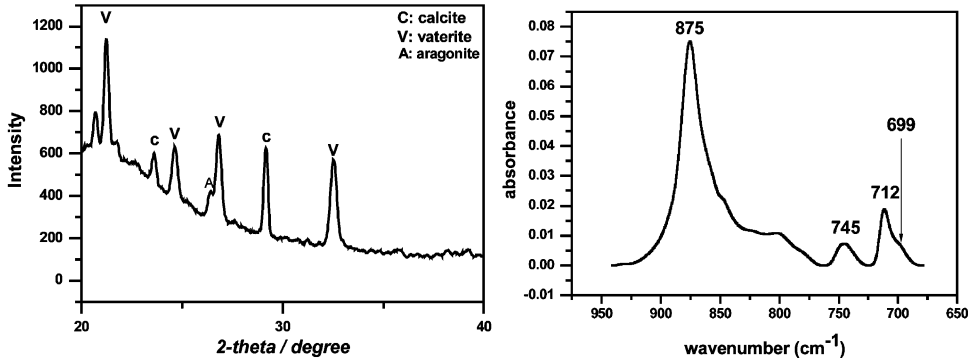

Figure 3. XRD diffraction pattern and FT-IR spectroscopy of artificial nacre by cyclic fabrication of DAR/PAA multilayered films and $CaCO_3$ layers.

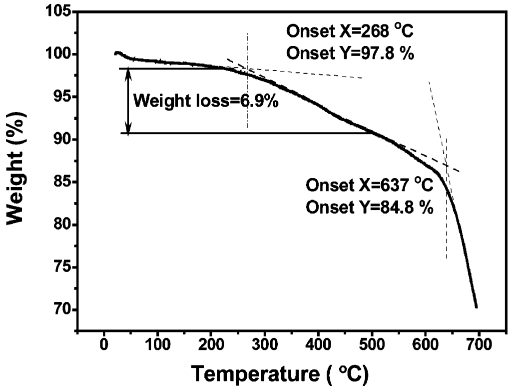

Figure 4. Thermogravimetric analysis of $(DAR/PAA)_6$−$CaCO_3$ films.

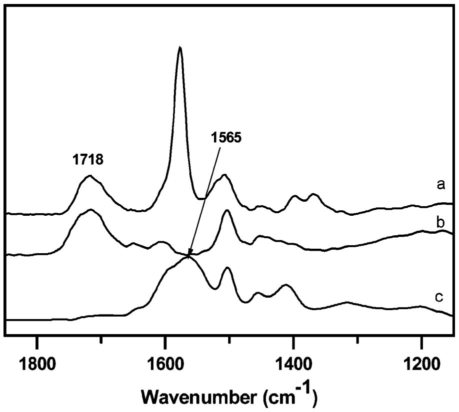

Figure 5. FT-IR spectra of the $(DAR/PAA)_6$ multilayered film: (a) before exposure under UV light; (b) after exposure under UV light; (c) after immersion in $CaCl_2$ solution.

important for the property of artificial nacre. We have employed thermogravimetric analysis (TGA) to determine the weight content of organic and inorganic material in the artificial nacre fabricated in this way. As shown in Figure 4, the weight loss is about 6.9% from 267 to 500 °C, which is attributed to the decomposition of DAR/PAA films. Further increasing of the temperature results in the decomposition of $CaCO_3$, and at 637 °C the decomposition becomes strong.[34] Therefore, the weight content of DAR/PAA films in artificial nacre is high enough to meet the requirement in mimicking the mortar in the abalone shell. Moreover, because the LbL technique allows buildup of the films with controlled thickness and composition, we may expect that the weight content of DAR/PAA films in the artificial nacre can be easily adjusted by selecting the deposition conditions.

It should be noted that DAR/PAA film is a good candidate for fabricating mortar based on several advantages as follows. First, the cross-linked structure between DAR and PAA under irradiation of UV light endows the DAR/PAA films with enough stability, which may function as the insoluble organic framework in nacre. Second, the necessary negatively charged surface of the artificial mortar can be prepared by selectively attaching PAA at the outmost layer of DAR/PAA films, thus providing the negatively charged surface which is required for the epitaxial nucleation of $CaCO_3$ crystals.[4] Finally, the adsorption of PAA readily on various solid substrates guarantees the next fabrication of the DAR/PAA films on former $CaCO_3$ layers, resulting in the formation of periodic man-made mortars. In this study, DAR/PAA mutlilayered films with six bilayers have been fabricated by the LbL technique in methanol solution, followed by photochemical cross-linking upon UV irradiation. Because of PAA as the outmost layer, the strong peak at the 1718 cm^{-1} in the corresponding FT-IR spectra shown in Firgure 5a,b reveal the abundant existence of carboxylic acid on the surface of DAR/PAA films not only before but also after UV irradiation. Actually, we have tried several systems such as PAH/PAA, PSS/PAH, and PDDA/PAA. With biomineralization by decomposition of $(NH_4)_2CO_3$, one layer of $CaCO_3$ can be grown onto the multilayer thin film of these systems. After fabricating multilayer on the $CaCO_3$ layer and undertaking biomineralization once again, the formed $CaCO_3$ can peel from the substrate.

To confirm that the DAR/PAA films can afford the negatively charged surface for the $CaCO_3$ nucleation as the mortar in abalone shell, we used FT-IR and the energy-dispersive X-ray spectra (EDAX) to identify the adsorption of Ca^{2+} on the DAR/PAA film. The vanishment of the peak at 1718 cm^{-1} and the emergence of a peak at 1565 cm^{-1} in the FT-IR spectra, as shown in Figure 5c, indicate the ionization of COOH in the DAR/PAA film after immersion in $CaCl_2$ solution. Further EDAX analysis of this film reveals that there is about 86% weight content of calcium at the surface of DAR/PAA film, which may suggest the higher concentration of Ca^{2+} near the DAR/PAA surface than in the bulk solution. In the process of slow CO_2 diffusion decomposed by $(NH_4)_2CO_3$ at room temperature, the nucleation of $CaCO_3$ crystal primarily happens on the surface of DAR/PAA films and then grows to $CaCO_3$ strata with the

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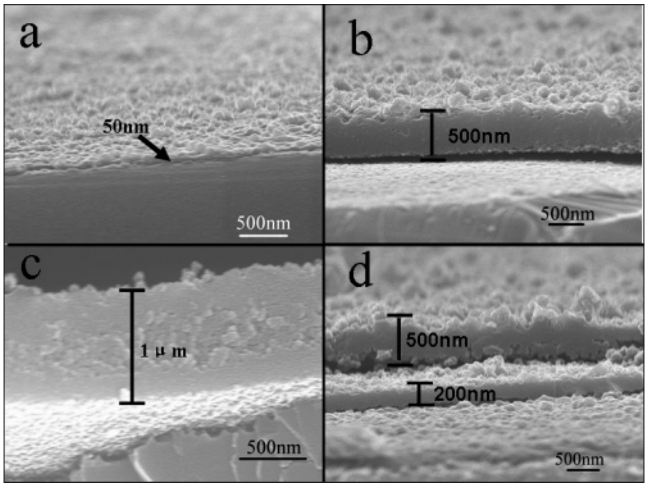

Figure 6. SEM images of the cross section of $CaCO_3$ nanolaminated structure with different thicknesses by controlling the diffusion times of CO_2. The thicknesses of one layer as shown in (a), (b), and (c) are 50 nm, 500 nm, and 1 μm, corresponding to the diffusion times 4, 14, and 20 h, respectively. The two layers as shown in (d) were fabricated by diffusing CO_2 gas 10 and 14 h, respectively.

diffusion of more CO_2.[35] Because of the crystallization that takes place in $CaCl_2$ solution, the layer of calcium ion will spontaneously form at the end of overgrowth of $CaCO_3$ stratum, which offers a positively charged surface for the next fabrication of DAR/PAA multilayered film.

It should be pointed out that the thickness of the $CaCO_3$ films can be effectively controlled by varying the diffusion time of CO_2 because the $CaCO_3$ crystallization depends on the value of CO_2 diffusion. Figures 6a−6c show the cross-section images of $CaCO_3$ films prepared with different diffusion times. As predicted, the $CaCO_3$ strata with different thicknesses, 50 nm, 500 nm, and 1 μm, were obtained, corresponding to the diffusion times, 4, 14, and 20 h, respectively. To examine the influence of the prior $CaCO_3$ layer on the fabrication of the next $CaCO_3$ layer, two different diffusion times, 10 and 14 h, have been selected to prepare the $CaCO_3$ films. The SEM image of the cross section of two-layer films shown in Figure 6d shows that the thicknesses of two $CaCO_3$ strata are about 200 and 500 nm, respectively. In other words, this result suggests that the thickness of each $CaCO_3$ strata can be controlled by adjusting the diffusion time of CO_2.

Conclusion

In summary, we have developed a method for mimicking artificial nacre with regular alternating brick-and-mortar structure by cyclic repeats of LbL deposition and $CaCO_3$ stratum formation. The thickness of the layered $CaCO_3$ can be controlled by selecting the diffusion time of CO_2. Moreover, the content of organic mortar may be adjusted by controlling the bilayer number of multilayered films. Further investigation is underway for controlling the crystalline transformation in the process of the formation of $CaCO_3$ strata to render the formation of one selective polymorph. It is greatly anticipated that this line of study may open a new avenue for mimicking the structure of natural nacre.

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