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Aragonite $CaCO_3$ thin-film formation by cooperation of Mg^{2+} and organic polymer matrices

Ayae Sugawara and Takashi Kato*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. E-mail: kato@chiral.t.u-tokyo.ac.jp

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Aragonite thin films of calcium carbonate have been deposited on chitosan matrices by cooperation of chitosan, poly(aspartate) and $MgCl_2$ in $CaCO_3$ solution, and their double layered composite structures are obtained by the alternate operations of chitosan coating and thin-film crystallization.

Living organisms produce a great diversity of organic/inorganic composite materials by using interactions between biopolymers and inorganic substances. The nacre of mollusc shell, one of the most studied, has a laminated composite structure of $CaCO_3$ crystals in the aragonite polymorph and biological macromolecules such as chitin and silk-fibroin-like protein, which provides high mechanical strength and unusual optical properties.[1] Aragonite crystals are considered to enhance mechanical properties of the nacre owing to the absence of cleavage planes.[2] Polymorph control for aragonite crystals has been performed by the use of proteins extracted from shells,[3] synthetic polymers[4] and LB films.[5] A biofabrication method involving a biosystem, the mantle and shell of red abalone, led to the formation of flat aragonite films.[6] However, to our knowledge, no aragonite thin film has been formed by the use of simple polymers *in vitro*. Here, we report a synthetic approach to the fabrication of aragonite thin films which resemble a part of lamellar sheets in the nacre by using a cooperative effect of Mg^{2+} and organic polymers with simple repeating units.

For calcite and vaterite syntheses, thin films could be obtained on organic matrices such as polysaccharides[7,8] and aggregated amphiphilic molecules[9] in the presence of acid-rich macromolecules. In the present study, we selected poly(aspartate) (pAsp) as an organic additive. It was reported that aspartate-rich proteins are responsible for the controlled crystallization of $CaCO_3$ layers of shells.[1]

$CaCO_3$ was crystallized on chitosan matrices spin coated on glass substrates from supersaturated calcium hydrogen carbonate aqueous solution by slow evaporation of CO_2.† In the absence of additives, rhombohedral calcite crystals of size 10 μm were deposited, which suggests that the chitosan matrix does not solely exert any effects on the crystallization. In contrast, the addition of pAsp to the solution induced the deposition of thin film states of crystals with a homogeneous thickness, as shown in Fig. 1(a), for concentrations of pAsp between 4.4×10^{-4} and 1.0×10^{-2} wt%. The thickness of these films is *ca.* 1 μm. These thin films show circular symmetry around the center of nucleation. X-Ray diffraction patterns show that these crystals are mixtures of calcite, aragonite and vaterite [Fig. 2(a)]. The fraction of aragonite as well as vaterite increases with the concentration of pAsp.

To prepare thin films of high aragonite content, we added $MgCl_2$ ($Mg^{2+}/Ca^{2+} = 6$) to the solution in addition to pAsp as Mg^{2+} is known to induce aragonite formation.[10] Thin film crystals have also been deposited [Fig. 1(b)], although the appropriate concentration of pAsp is limited to *ca.* 4.4×10^{-4} wt%. The surface of the films is smoother than that without $MgCl_2$. X-Ray diffraction studies reveal that the fraction of aragonite in the films is 95 wt% or higher, and vaterite is absent [Fig. 2(b)]. By contrast, aragonite crystals with needle morphology were grown on chitosan matrices by the addition of $MgCl_2$

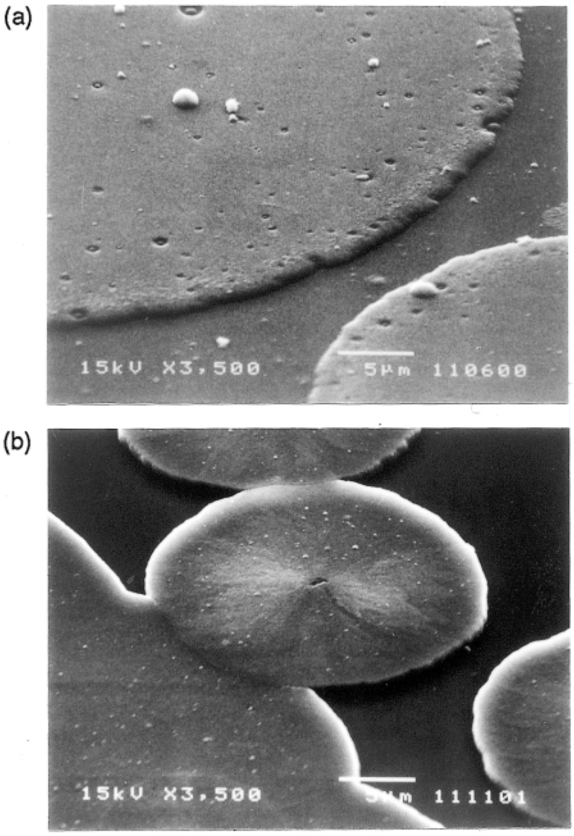

Fig. 1 Scanning electron micrographs of $CaCO_3$ thin films grown on chitosan matrices in the presence of pAsp (4.4×10^{-4} wt%): (a) in the absence of $MgCl_2$ and (b) in the presence of $MgCl_2$ ($Mg^{2+}/Ca^{2+} = 6$).

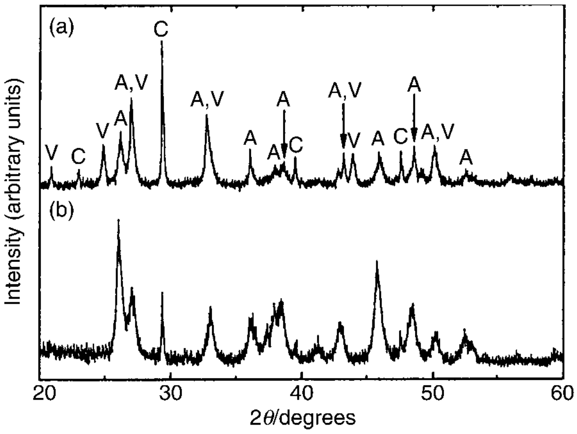

Fig. 2 X-Ray diffraction patterns of $CaCO_3$ thin films grown on chitosan matrices in the presence of pAsp (4.4×10^{-4} wt%): (a) in the absence of $MgCl_2$ and (b) in the presence of $MgCl_2$ ($Mg^{2+}/Ca^{2+} = 6$); aragonite (A), calcite (C) and vaterite (V).

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in the absence of pAsp. These results show that selective aragonite deposition by the addition of $MgCl_2$ and the formation of thin film crystals by chitosan and pAsp are compatible for aragonite thin-film formation. Furthermore, the stability of the film was so high that no flaking was observed upon microwave irradiation while needle-like aragonite crystals obtained with $MgCl_2$ in the absence of pAsp were observed to detach under such conditions.‡

By alternate operations of chitosan spin coating and aragonite crystallization,§ we could prepare double layered composite films of aragonite and chitosan. Fig. 3 shows an example of such a film; the upper aragonite layer has successfully grown on the underlying layer. It is expected that multi-layered composite materials resembling the nacreous structure can be prepared if adequate control is provided.

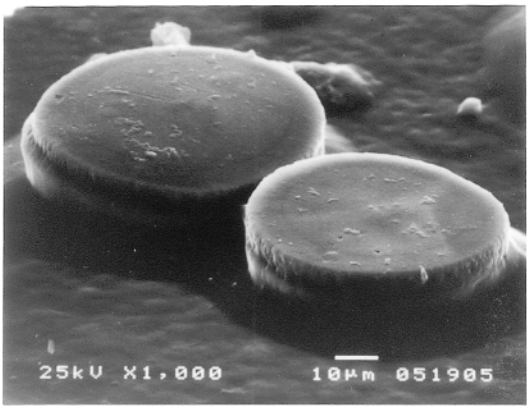

Fig. 3 Scanning electron micrograph of double layered aragonite thin films grown on a chitosan matrix in the presence of pAsp (4.4×10^{-4} wt%) and $MgCl_2$ ($Mg^{2+}/Ca^{2+} = 6$) by alternate spin coating and crystallization.

In summary, we have succeeded, for the first time, in the formation of aragonite thin films with a controlled homogeneous thickness. Double layer films have also been fabricated by the cooperative effect of $MgCl_2$ and functionalized organic polymers. These results offer potential for the design of high-performance organic/inorganic composite materials by simple synthetic procedures.

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Notes and references

† Crystals were grown from supersaturated calcium hydrogen carbonate solution in the presence of poly-L-(aspartic acid) sodium salt (DP = 360) (pAsp) and/or $MgCl_2$ at 30 °C. The detailed synthetic procedure has been described previously.[7] Polymorphs of $CaCO_3$ were studied by X-ray diffraction measurements. The fraction of aragonite in the crystals was calculated from the diffraction peak areas using a calibration curve obtained from crystal mixtures with known ratios of the polymorphs.

‡ The stability of the crystals formed on the matrix polymers was tested by microwave irradiation at 140 W for 30 min for the films placed in water.

§ After preparation of the aragonite thin films, chitosan was spin coated on them, and then $CaCO_3$ was subsequently crystallized.

1 S. Mann, in *Inorganic Materials*, ed. D. W. Bruce and D. O'Hare, Wiley, Chichester, 2nd edn., 1996, p. 255; L. Addadi and S. Weiner, *Proc. Natl. Acad. Sci. USA*, 1985, **82**, 4110; L. Addadi and S. Weiner, *Nature*, 1997, **389**, 912; N. Watabe, *J. Ultrastruct. Res.*, 1965, **12**, 351; I. A. Aksay, M. Trau, S. Manne, I. Honma, N. Yao, L. Zhou, P. Fenter, P. M. Eisenberger and S. M. Gruner, *Science*, 1996, **273**, 892.
2 S. Weiner and L. Addadi, *J. Mater. Chem.*, 1997, **7**, 689.
3 A. M. Belcher, X. H. Wu, R. J. Christensen, P. K. Hansma, G. D. Stucky and D. E. Morse, *Nature*, 1996, **381**, 56; G. Falini, S. Albeck, S. Weiner and L. Addadi, *Science*, 1996, **271**, 67.
4 Y. Levi, S. Albeck, A. Brack, S. Weiner and L. Addadi, *Chem. Eur. J.*, 1998, **4**, 389.
5 A. L. Litvin, S. Valiyaveettil, D. L. Kaplan and S. Mann, *Adv. Mater.*, 1997, **9**, 124.
6 M. Fritz, A. M. Belcher, M. Radmacher, D. A. Walters, P. K. Hansma, G. D. Stucky, D. E. Morse and S. Mann, *Nature*, 1994, **371**, 49.
7 T. Kato, T. Suzuki, T. Amamiya, T. Irie, M. Komiyama and H. Yui, *Supramol. Sci.*, 1998, **5**, 411; T. Kato and T. Amamiya, *Chem. Lett.*, 1999, 199.
8 S. Zhang and K. E. Gonsalves, *Langmuir*, 1998, **14**, 6761.
9 G. Xu, N. Yao, I. A. Aksay and J. T. Groves, *J. Am. Chem. Soc.*, 1998, **120**, 11 977.
10 Y. Kitano, *Bull. Chem. Soc. Jpn.*, 1962, **35**, 1973; D. Walsh and S. Mann, *Nature*, 1995, **377**, 320; G. Falini, S. Fermani, M. Gazzano and A. Ripamonti, *Chem. Eur. J.*, 1997, **3**, 1807; G. Falini, M. Gazzano and A. Ripamonti, *J. Cryst. Growth*, 1994, **137**, 577; N. Wada, K. Yamashita and T. Umegaki, *J. Colloid Interface Sci.*, 1999, **212**, 357.

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