Microstructure and characteristics in the organic matrix layers of nacre

F. Song, X.H. Zhang, and Y.L. Bai
LNM, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

(Received 5 March 2002; accepted 11 April 2002)

The direct observation of a type of microstructure in the organic matrix layers of nacre was obtained with a transmission electron microscope. The microstructure, which is referred to as mineral bridge in the biomineralization, is nanoscale and randomly distributed in the layers. Statistical analysis gives the distribution laws and characteristics of mineral bridges in the organic matrix layers. The existence of mineral bridges in nacre was confirmed, and it was shown that the microarchitecture of nacre should be described as a "brick–bridge–mortar" arrangement rather than traditional "brick and mortar" one.

Nacre, one of several kinds of molluscan hard tissue, is considered as a ceramic composite containing 95 vol% interlocking aragonite platelets staggered in successive laminae and separated by a 5% organic matrix. Since it can give a conceptual guidance to the biomimetic design of synthetic materials, a great deal of attention has been attracted to the microstructure of nacre in recent years.[1–4] The traditional model of nacre is considered as a "brick and mortar" (BM) arrangement. It is the unique arrangement that is believed to result in lightweight materials with high mechanical performance.[5–8] However, the study of the microstructure of nacre has gained some significant developments in recent years. In particular, Schaffer *et al.*[9] clearly observed many nanopores in the interlamellar organic matrix sheets of nacre in terms of various microscopic observations and then gave a statistical distribution. Consequently, they supported the model of nacre growth that is based on mineral bridges between successive aragonite platelets. Furthermore, according to their transmission electron microscopy (TEM) micrograph, they stated that "these (gray in the micrograph) may be mineral bridges between the nacre plates, but it is difficult to be certain of this assignment." Here we describe direct observation of mineral bridges in the organic matrix layers of nacre. And by using statistical analysis, we obtain the characteristics and the distribution law of the microstructure. It is interesting that results presented in this paper are consistent with an earlier estimate.[9]

To reveal the microstructure of nacre, all observations of nacre were performed with an H-8100 TEM at an accelerating voltage of 200 kV. The testing samples are the nacre of *Haliotis iris* shell, an abalone shell from New Zealand. The keratin layer of the shell was

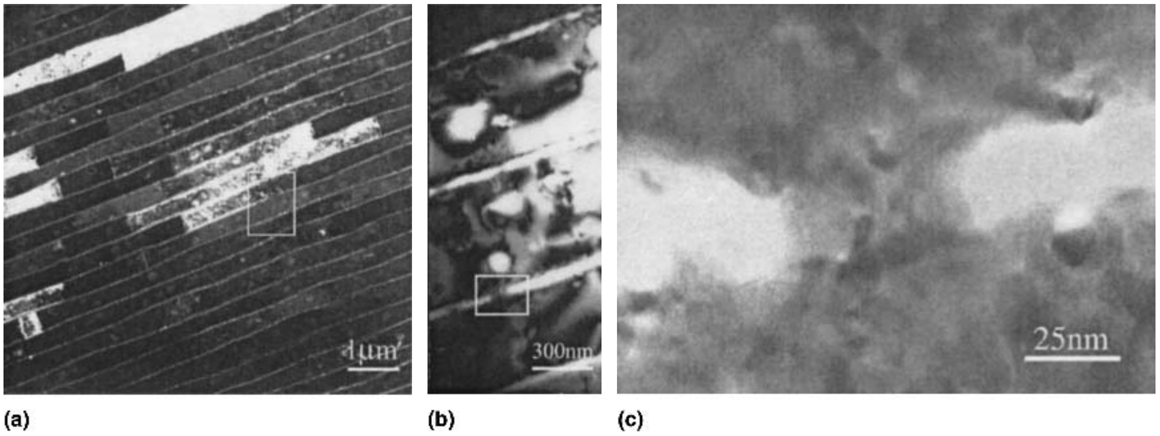

FIG. 1. (a) TEM image showing the microarchitecture of the cross sectional surface of nacre. It appears to be a traditional "brick and mortar" arrangement. (b) [boxed area in (a)] TEM image of the organic and inorganic layers on the cross sectional surface of nacre. There exist some mineral bridges in the organic matrix layers. The positions of the mineral bridges in the layers are random. (c) [boxed area in (b)] TEM image of a mineral bridge between two successive platelets of nacre. The appearance of mineral bridges approximates circular column.

mechanically worn off, and the residuary part, i.e., the nacre of the shell, was washed with distilled water and air dried at room temperature. Thin films vertical to the surface of the shell, i.e., parallel to the cross-sectional surface of the shell, were cut with a diamond saw, mechanically ground, and thin ion-beam milled at an angle of 10° to 50-μm thickness and then perforated under a voltage of 5.5 kV.

The microarchitecture of the cross-sectional surface of the nacre reveals a traditional BM arrangement [Fig. 1(a)]. However, when we focus on the mortars of nacre, we find that there do exist many nanoscale columns in the organic matrix layers [Fig. 1(b)]. The columns, which are traditionally referred to as a mineral bridge in the biomineralization, go through the mortar layers from one nacre platelet to the other [Fig. 1(c)]. The mineral bridges appear to be circular, and they stochastically come up in the organic matrix layers. We measured the diameter of the circular columns as 46 ± 8 nm, and the height of the mineral bridges is equal to the thickness of an organic matrix layer, 29 ± 4 nm, while the thickness of an aragonite platelet layer on the cross-sectional surface is 400 ± 30 nm.

To obtain the statistical characteristics of the mineral bridges in the organic matrix layers of nacre, we randomly chose some cross-sectional surfaces of nacre and selected 30 perfect platelets on the surfaces. By measuring the length of these platelets on the cross-sectional surfaces, we find that the average length approximately equals 4 μm [Fig. 2(a)]. By counting bridges on each of the chosen platelets, we obtained that the total bridges of the 30 platelets number 1169 and the average number on each platelet is approximately equal to 40 [Fig. 2(b)]. Further, on the cross-sectional surfaces we divide each of the chosen platelets into 16 equal units along the direction of organic matrix layer and separately add up the number of mineral bridges (on all chosen platelets) contained by each unit. A histogram of the number of the bridges on the platelets can be given [Fig. 2(c)]. Obviously, this histogram on average stands for the distribution of the number of mineral bridges of each of the platelets on the cross-sectional surface. We can approximately employ a curve to simulate the histogram [Fig. 2(c)]. However, this curve only stands for a joint marginal distribution law of the mineral bridges of a platelet of nacre and can be written as

$$f(x) = \frac{N_x}{\sqrt{2\pi\sigma}} \exp\left[-\frac{(x-\mu)^2}{2\sigma^2}\right] \quad , \tag{1}$$

where $N_x = 40$ is the average number of mineral bridges of each platelet on the cross-sectional surfaces, $\mu = 8$ and $\sigma = 2.6$ are approximately equal to the average value and standard deviation of the corresponding histogram, respectively, and x $(0 \leqslant x \leqslant 16)$ is a local coordinate from one end of a elected platelet to an arbitrary point in the platelet on the cross sectional surface. Its corresponding length is

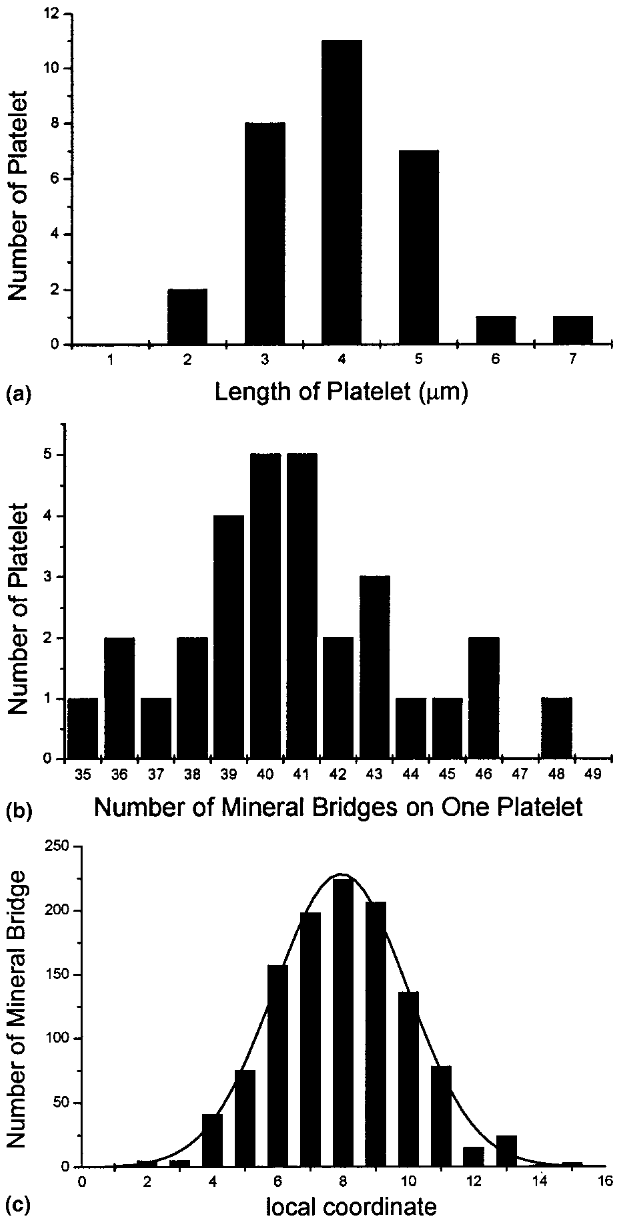

FIG. 2. (a) Histogram of the measured length of 30 platelets on the cross sectional surfaces of nacre. This distribution gives that the average length of a platelet on the surfaces is approximately equal to 4 μm. (b) Histogram of the measured number of mineral bridges of each of 30 platelets on the cross-sectional surfaces of nacre. It shows that the total number of mineral bridges of the tablets is 1169, and the average number of mineral bridges of each platelet on the surfaces is approximately equal to 40. (c) Histogram of the distribution of the number of mineral bridges along the length of platelet on the cross-sectional surfaces. The distribution reveals that most mineral bridges are concentrated on a central region of the platelet. The length of the central region is approximately equal to 1/3 the average length of the platelet on cross-sectional surfaces.

$$l = \frac{L}{n} x \quad , \tag{2}$$

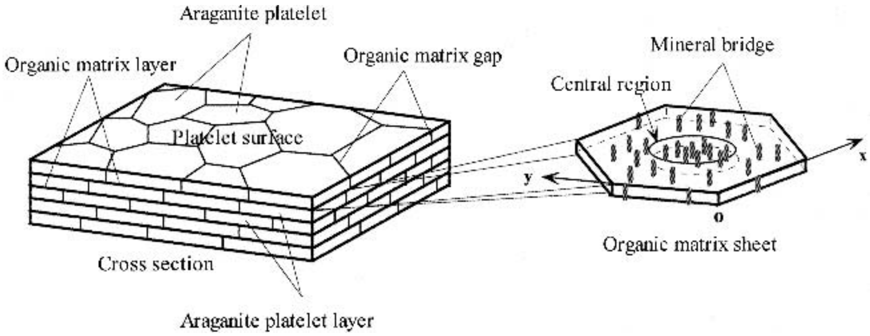

FIG. 3. Schematic illustration showing the structure of nacre, the mineral bridges in an organic matrix sheet, and the local coordinate system on the cross-sectional surfaces. The width of the sheet is taken as the average width of a platelet on the cross sectional surface, $L = 4$ μm.

where $L = 4$ μm is the average length of a platelet and $n = 16$ is the number of the divided units of a platelet on the cross sectional surface.

From Eq. (1), we have $\int_{\mu-\sigma}^{\mu+\sigma} f(x)\,\mathrm{d}x = 0.68N_x$. This indicates a feature of the distribution of the mineral bridges: there exists a central region along the length of each platelet on the cross-sectional surfaces in which the number of mineral bridges is 68% that of a whole platelet. The local coordinates of the central region are $(\mu - \sigma, \mu + \sigma) = (5.4, 10.6)$, and the length of the central region, 1.3 μm, is approximately equal to 1/3 the average length of the platelets on the cross-sectional surfaces. According to Eqs. (1) and (2), we can easily give the average bridge-to-bridge spacing between neighbor bridges of each platelet as

$$\langle s \rangle_{\mathrm{all}} = \frac{L}{n} \int_0^{16} x f(x)\,\mathrm{d}x \approx 80 \text{ nm} \quad , \tag{3}$$

while the average spacing in the central region is

$$\langle s \rangle_{\mathrm{center}} = \frac{L}{n} \int_{\mu-\sigma}^{\mu+\sigma} x f(x)\,\mathrm{d}x \approx 54 \text{ nm} \quad . \tag{4}$$

This is an indication that the average density of mineral bridges in the central region is higher than that in the whole platelet.

The characteristics of mineral bridges of the platelets above are only for the cross-sectional surface of nacre. Fortunately, the structure of all cross-sectional surfaces of nacre is statistically the same and the distributions of the mineral bridges on the cross-sectional surfaces are statistically independent each other (Fig. 3). So, from Eq. (1), we can grossly write a joint distribution density function of mineral bridges on the whole platelet as

$$g(x, y) = \frac{N}{2\pi\sigma^2} \exp\left[-\frac{(x-\mu)^2 + (y-\mu)^2}{2\sigma^2} \right] \quad , \tag{5}$$

where $N \approx N_x N_y = 1600$ is the average total number of the bridges on one platelet and x and y ($0 \leqslant x, y \leqslant 16$) are local coordinates, the origin of which is one end of the platelet on the cross-sectional surface, and satisfy Eq. (2). From Eq. (5), we have $\int_{\mu-\sigma}^{\mu+\sigma}\int_{\mu-\sigma}^{\mu+\sigma} g(x, y)\,\mathrm{d}x\,\mathrm{d}y \approx 0.46\,N$. This shows that in each platelet of nacre exists a central region, in which the number of mineral bridges is about 46% that of the whole platelet, while the area of the central region is approximately equal to 1/9 total area of the platelet.

We also determined that the surface area of one side of a platelet approximates 16 μm^2. So the average densities of mineral bridges on each platelet and its central region are about 100 and 414 μm^{-2}, respectively. And we reckoned that total cross-sectional area of the mineral bridges on one whole platelet is about 2.7 μm^2. Such an area of the mineral bridges is approximately equal to 1/6 that of the platelet itself. This is an indication that the organic matrix layer of nacre should be considered as a fiber-reinforced composite, in which the matrix is part of the organism and the fibers are mineral bridges, rather than a pure organic matrix material as tradition when studying the mechanical properties of nacre (Fig. 3). Therefore, the microarchitecture of nacre should be referred to as a "brick–bridge–mortar" arrangement instead of traditional "brick–mortar" one. In addition, it has also been reported that the crystallographic orientations of 3–10 successive platelets on cross-sectional surfaces of nacre can remain the same.[10] So, all these investigations may suggest a bit tangled "brick–bridge–mortar" structure for nacre.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundations of China (Grant 10072067) and the Natural Science Foundation of Chinese Academy of Sciences (Grant KJCX2-SW-L2).

REFERENCES

1. A.H. Heuer, D.J. Fink, V.J. Laraia, J.L. Arias, P.D. Calvert, K. Kendall, G.L. Messing, J. Blackwell, P.C. Rieke, D.H. Thompson, A.P. Wheeler, A. Veis, and A.I. Caplan, Science **255,** 1098 (1992).

2. T. Kato, Adv. Mater. **12,** 1543 (2000).
3. N. Almqvist, N.H. Thompson, B.L. Smith, G.D. Stucky, D.E. Morse, and P.K. Hansma, Mater. Sci. Eng. C **7,** 37 (1999).
4. L. Addadi and S. Weiner, Nature **389,** 912 (1997).
5. J.D. Currey, Proc. R. Soc. London, Ser. B **196,** 443 (1977).
6. A.P. Jackson, J.F.V. Vincent, and R.M. Turner, Proc. R. Soc. London, Ser. B **234,** 415 (1988).
7. R.Z. Wang, H.B. Wen, F.Z. Cui, H.B. Zhang, and H.D. Li, J. Mater. Sci. **30,** 2299 (1995).
8. B.L. Smith, T.E. Schaffer, M. Viani, J.B. Thompson, N.A. Frederick, J. Kindt, A. Belcher, G.D. Stucky, D.E. Morse, and P.K. Hansma, Nature **399,** 761 (1999).
9. T.E. Schaffer, C. Ionecu-Zanetti, R. Proksch, M. Fritz, D.A. Walters, N. Almqvist, C.M. Zaremba, A.M. Belcher, B.L. Smith, G.D. Stucky, D.E. Morse, and P.K. Hansma, Chem. Mater. **9,** 1731 (1997).
10. Q.L. Feng, F.Z. Cui, G. Pu, R.Z. Wang, and H.D. Li, Mater. Sci. Eng. C **11,** 19 (2000).