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Study of the surface microstructure and optical properties of pearls induced growing by rare earth cerium

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ABSTRACT

We investigated the influence of rare earth element (REE) Ce on the surface microstructure and luster of pearls in the scaled of micro and nanometer range by means of scanning electronic microscopy (SEM),reflect and Raman spectra. We found that the pearls in control group without adding REE dosage are mainly build up by spindly aragonite blocks, while the REE pearls are made up by pseudo-hexagonal blocks that are the most idea blocks in crystallography. The luster of REE pearls is stronger than that of the control pearls. And the reflect intensity also is largely enhanced than that of the control pearls. The intensity of Raman vibration peak from REE pearls is almost two times than that of the control pearls. The results show that an appropriate quantity of REE Ce will promote the growth of pearls, and enhanced the lustrous of pearls significantly.

KEYWORDS

Freshwater pearls;
Rare earth elements;
Scanning electronic microscopy (SEM);
Aragonite blocks.

INTRODUCTION

Pearls are largely found of people because of they beautiful color and luster. They are widely used in adornments, such as pearl necklaces, bracelets, and eardrops. Their optical beauty of elegance and soft luster is closely related to the micro-structure of pearls. Pearls are mainly composed of aragonite calcium carbonate (94.7%~96.0%) and onchiolin (3.1%~4.6%). The aragonite blocks and organics uniformly cementated together show sand texture under optical microscopy[1,4,7,8]. Pearls surface can be classified to four levels microstructure; that is mosaic blocks, small plates, microstructure and pearls layer. The mosaic blocks are the smallest unit cell of structure, almost as thick as a small block. The blocks are the basic unit cell of pearls layer by which they arranged in two dimensions to build up pearl layer[6]. The surface gloss of pearls is a complicated effect of reflection, refraction and interference of light shining on the multi-layer complex surface of pearls.

For 20 yearls, rare earth elements (REE) have been widely used in agriculture, forest, animal husbandry, freshwater livestock, forage and medicine[2,3,5,9]. In the present work, we investigated the influence of REE on the microstructure and surface gloss of pearls surface by means of observing surface microstructure, analyze the reflection spectrum and Raman spectrum of fresh water and REE pearls.

EXPERIMENT MATERIAL AND METHODS

Experimental materials

Test pearl bivalves. Healthy freshwater pearl bivalves, 1-2 years old, 7.0-8.0 cm long, and weighing 20-30 g, were purchased from a bivalves culturing field in Xiangcheng section of Suzhou city, Jiangsu Province. They were temporarily kept in fully aeration tap water box for two weeks.

Preparation of the rare earth standard additive solution

A Ce $(NO_3)_3$ stock solution of 0.600 mg/ml was prepared by dissolving 0.31g white powder cerium oxide (CeO_2, 99.99%, bought in Beijing Youyan rare new material limited company) in aqueous nitric acid (HNO_3; 2 ML), then was diluted with water to give a different additive solution.

Experimental method

Pearl bivalves were cultured accepting static water culture method. They were randomly divided into two parallel groups, that is one control group and a test group. The concentration of Ce $(NO_3)_3$ in the groups was levels of 0 and 1.0 mg/l. Each rare concentration set two parallel groups. To simulate open water, 100 L vessels containing 40 L of freshwater served as culturing vessels, each vessel consisting of 12 bivalves. During cultural, the pH value in water was kept at 7.5-7.8, the concentration of Ca^{2+} was 20 mg/l, the dissolved oxygen content was 7.5-8.2 mg/l, and the temperature was in the range 18-22 °C. The bivalves were fed with home-made feed once a day; the water was changed every 15 days. After 45 days of culturing, six bivalves were randomly selected from each group, and were dissected in an ice-box to extract their pearls, dry by air. The pearls were immersed 5% NaOH solution for 15 mins to remove organics and imputity on pearls, then immersed 5% EDTA solution for 5 and 30 mins, finally rinsed with deionized water and dried in air. The pearls were analyzed by UV-visible spectroscopy (UV-3600) and Raman spectroscopy (RENISHAW). After evaporation gold film, they were observed by field emission scanning electron microscopy (HitachiS4700).

RESULTS AND DISCUSSION

Pearls sampled in the control bivalves group (no REE) were found to be with smooth surface and good luster by naked eyes. The typical morphology and surface microstructure was observed by SEM, as shown in Figure 1(a). There are many spindle-shaped or fish-like shaped thin slices proximately parallel aligned on the surface of pearls. The slices take an orientation of 30º with respect to horizontal direction. The length of slices is in a large of 1~3 μm, width 0.8~0.3 μm. The ratio of the long and short axes is about 3:1. From the gaps and ridges between the slices, it is evident that the

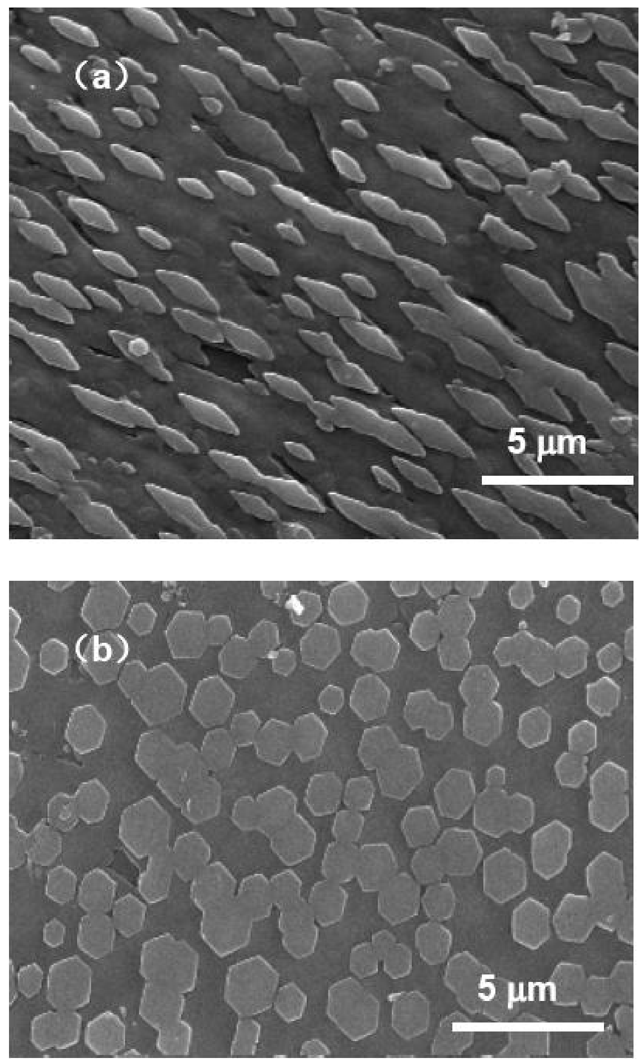

Figure 1: (a) The typical SEM pictures of pearls in the control group. Many rhombus or spindly crystal slices are uniformly located on the surface with an angle of 30° to horizontal. (b) Many regular hexagonal blocks are seen on the top surface, without any overlap or aggregation. Each block has a perfect regular hexagonal structure

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subsurface is also composed of spindly with same aligned direction. These show that the growth style is characteristic of a growth of layer- structured.

Typical SEM images of pearls sampled from the REE test group with a Ce concentration of 1.0 mg/l is shown in Figure 1(b). The surface luster of pearls was found to be largely increased, and the surface microstructure took large change. Many regular hexagonal blocks are seen on the top surface, without any overlap or aggregation. Each block has a perfect regular hexagonal structure. A profile of the REE pearls, confirming that the pearls are built up from microlayers composed of ordered hexagonal blocks in a layer by layer manner, without any dislocations or faults, each microlayer corresponding to the thickness of the blocks. Each block, even the smallest, has a perfect regular hexagonal shape, free from breakages or fragments. Moreover, the subsurface is a smooth plane as a result of a highly ordered and compact packing of the hexagonal blocks, devoid of any gaps or ridges. Moreover, unlike the pearls from the control group, these changes show a phase transition in the microstructure of the pearls that was induced by the presence of Ce.

The reflection spectrum collected from the samples is shown in Figure 2. The samples of the natural and the REE pearls were mounted under the 5×dry objective of a microscope and an aperture was used to illuminate an area of 0.07mm with unpolarized light at normal incidence, respectively. A polarization insensitive spectrometer (USB2000) was used to analysis the reflection light. As expected, distinct differences were noted in the two spectra. There are four main peaks in the two samples at 430 (blue), 519 nm (green), 588 nm (orange) and 620 nm (red), respectively. The intensity of 519 nm in natural pearl is only a half that of the REE pearls, and the two other peaks at 588 nm and 620 nm are smeared together. The reflected peaks observed in two samples agree with the mircrostructure of the two samples. The natural pearls have a mesa structure, and their surfaces are very rough, on which lights would take a diffuse reflection than produce interference. Additionally, the grooves and micro-caves may produce strong diffraction effect. As a result, the natural pearls have weak iridescence color. On the contrary, the REE pearl has a planar layered structure; the smooth surface could not only give a strong reflection light, but also produce a strong interference. The enhanced intensity at 519 nm of REE pearls is mainly originated from the Bragg scatter effect on the planar layered microstructure. Therefore, the brighter color of the REE pearls is a combined effect of interference, reflection, and diffraction on their super-nacre layers.

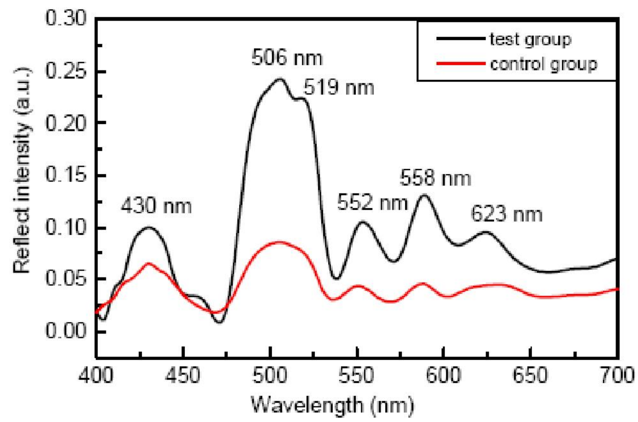

Figure 2 : The reflection spectrum collected from the samples

Figure 3 is the Raman spectrum of the pearls sampled in the REE Ce and the control groups. The measurement was operated on a confocal Raman spectrometer using a He-Ne laser with a wavelength of 632.8 cm^{-1}, scanning time 10 s, scanning range 105.24~3505.60 cm^{-1} and the resolution of ±1 cm^{-1}. There are four strong Raman vibration peaks positioned at 706, 1082, 1132 and 1520 cm^{-1} for both kinds of the pearls. Where, the peak of 1082 cm^{-1} attributes the symmetrical vibration of Co_3^{2-} anion, and peak of 706 cm^{-1} belongs to the anti- symmetrical vibration of Co_3^{2-} anion. They are both the Raman vibrations peaks for aragonite blocks[2,3,7,9]. The intensity of the former is about two times than that of the latter, indicating that the vibration of double bond is much stronger than that of the single bond. In addition, the peak at 1082 cm^{-1} of the REE pearls is also much stronger than that of the control pearls. It shows that REE Ce can enhance the luster of pearls. The peaks of 1132 and 1520 cm^{-1} are the typical all trans conjugated double bond caused by carotenoid. The peak of 1132 cm^{-1} belongs to the stretch out and draw back vibration (ν_2) of C-C single band, and 1527 cm^{-1} is attributed to the stretch out and draw back vibration (ν_1) of C-C double band. The ratio of the relative intensity of the two peaks is basically unchanged. It is suggest that the ratio (0.0~3.7) is closely related to the color of pearls. The larger the ratio, the deeper color of pearls is[2].

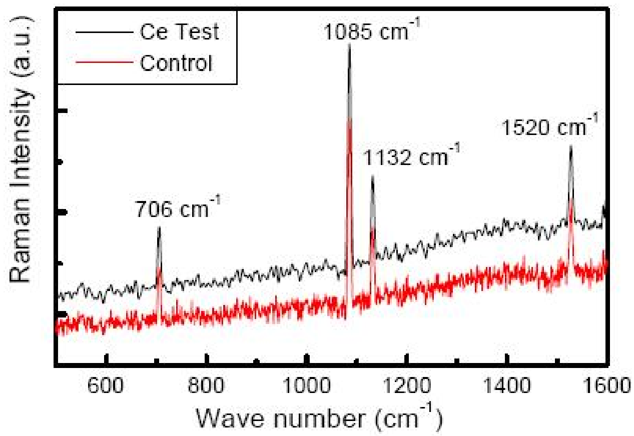

Figure 3 : The SEM picture of pearls with 1.5 mg/l REE Ce. The aragonite crystals on pearls surface varies from regular hexagon to round, suggesting that it may do unfavorable for pearls growth if the REE concentration large than the threshold

The aragonite crystals on pearls surface varies from regular hexagon to round, suggesting that it may do unfavorable for pearls growth if the REE concentration large than the threshold.

The shape of the aragonite crystals blocks composed superficial microstructure of pearls changes from spindly to perfect regular hexagonal sheets, suggesting that the microstructure of pearls is strongly influenced by REE Ce. The glossiness changes accordingly with the microstructure, the pearls with the regular hexagonal structure displaying the highest glossiness. Since the growth conditions, such as the water temperature, the pH, and the feeds, were kept constant in the test groups, apart from the Ce concentration, it can be concluded that the microstructure of pearls is greatly modulated by the presence of Ce.

CONCLUSION

We have studied the effects of REE Ce on the superficial microscopic structure of pearls. We found that the control pearls surface were mainly build up by spindly aragonite blocks, while the REE pearls surface were chiefly composed of the regular hexagonal aragonite blocks that is the most idea blocks in crystalics. The intensity of reflect and Raman vibration from the REE pearls is much stronger than that of the control pearls. Also, the luster of the REE pearls is largely enhanced than that of the control pearls. The results show that an appropriate quantity of Ce will promote the growth of pearls, and enhanced the lustrous of pearls significantly.

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