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Short communication

A humidity sensitive two-dimensional tunable amorphous photonic structure in the outer layer of bivalve ligament from *Sunset Siliqua*

Weigang Zhang [a,*], Gangsheng Zhang [b]

[a] College of Materials and Chemical Engineering, Chuzhou University, Chuzhou 239000, PR China
[b] College of Material Science and Technology, Guangxi University, Nanning 530004, PR China

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ABSTRACT

A humidity sensitive two-dimensional tunable amorphous photonic structure (2D TAPS) in the outer layer of bivalve ligament from *Sunset Siliqua* (OLLS) was reported in this paper. The structural color and microstructure of OLLS were investigated by reflection spectra and scanning electron microscopy, respectively. The results indicate that the reflection peak wavelength of the wet OLLS blue-shifts from 454 nm to 392 nm with the increasing of air drying time from 0 to 40 min, while the reflectivity decreases gradually and vanishes at last, relevant color changes from blue to black background color. The structural color in the OLLS is produced by a two-dimensional amorphous photonic structure consisting of aligned protein fibers, in which the diameter of protein fiber and the inter-fiber spacing are 101 ± 12 nm. Water can reversibly tune the reflection peak wavelength and reflectivity of this photonic structure, and the regulation achieved through dynamically tuning the interaction between inter-fiber spacing and average refractive index.

1. Introduction

Tunable photonic structures had generated ongoing research interest since it was discovered by Weissman in 1996 [1] for their important applications in the fields of optical transducers and high sensitive detectors [2,3]. From our knowledge, humidity-, electrical-, magnetic-, and thermo-sensitive one- or three-dimensional tunable photonic structures have been discovered [1,4–7]. But there are few previous studies about two-dimensional tunable photonic structure [8,9], and only one paper about humidity sensitive two-dimensional tunable photonic structure consisting of aligned aragonite fibers and proteins has been reported by our research group [10]. In addition, the photonic structure reported in this work is more interesting because it is only consisted of aligned protein fibers.

The structure of bivalve ligament includes three layers: inner layer, outer layer, and periostracum from the ventral to dorsal [11] (Fig. 1). Zhang discovered blue and golden structural colors in the inner layers of bivalve ligaments from *Pinctada maxima* and *Lutraria maximum*, respectively, and confirmed that these structural colors were caused by two-dimensional amorphous photonic structures [12,13]. But the structural color and photonic structure in the outer layer of bivalve ligament have not been reported, because the outer layer of bivalve ligament is covered by inner layer and periostracum, and its structural color is difficult to be discovered.

In this paper, the microstructure and reflection spectra of OLLS in different wet states were systematically investigated. We first discovered blue structural color in wet OLLS, and confirmed that this color was caused by a two-dimensional amorphous photonic structure consisting of aligned protein fibers. Water can reversibly tune the reflection peak wavelength and reflectivity of this photonic structure, revealing that OLLS is a new kind of humidity sensitive 2D TAPS.

2. Experimental

2.1. Materials

Samples of *Sunset Siliqua* were obtained from Guangxi in southern China. After removing the soft body, the shells were washed with distilled water and dried at room temperature for 5 days. Then we carefully removed the ligament. Next, using a single blade, we broke the ligament in different directions for SEM observation, and using a few ligaments to strip inner layer for optical observation and reflection spectra measurement.

2.2. Characterization

Optical photos of the ligament were taken using a GL-99 stereomicroscope, which was connected to a CCD camera, light source power was 70 W of HL2013 quartz lamp, and the angle between incident light and observation surface was 60°. The reflection spectra of OLLS were measured using an AvaSpec-2048 fiber optical spectrometer with analyzing software of Avasoft 7.1. A halogen–tungsten lamp and a

* Corresponding author.
E-mail address: abczwg15@163.com (W. Zhang).

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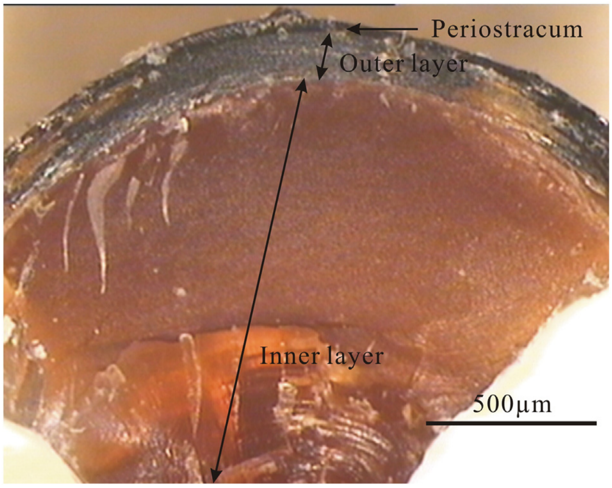

Fig. 1. Optical photo of transverse section of the ligament in *Sunset Siliqua*.

reflection probe were used as light source and probe, respectively. The incident light and the test surface were perpendicular, the distance between the probe and the test surface was about 1 mm, and the probe surface area was about 1 mm^2. A white board was used as a reference for the reflectivity. The microstructure of the ligament was observed by using an S-3400 scanning electron microscope (SEM) operated at 30 kV accelerating voltage.

3. Results and discussion

3.1. Color observation

We can see blue color from wet OLLS, but it will disappear in the dry state (Fig. 2). Also the blue color of OLLS will gradually become darker or lighter with the incident light direction changing, revealing that the blue color of OLLS belongs to a structural color.

3.2. Structural characterization

The SEM images clearly show that the ligament is comprised of three layers (Fig. 3a). The outer layer has fibrous structure (Fig. 3b and c), in which the fiber's diameter is highly uniform with an average value of 101 ± 12 nm (Fig. 3c). The IR results of the outer layer of ligament indicated that the fibers are protein fibers [14]. Since close packing of the protein fibers and no other materials fill, the inter-fiber spacing and the diameters of the protein fibers are equal (Fig. 3c). We can also see that the protein fibers are packed in short-range order (Fig. 3c), revealing that the OLLS resembles a two-dimensional amorphous photonic structure with short-range order. However, the OLLS is comprised of only one kind of medium of protein, and do not have the condition to present structural color, so the OLLS in the dry state can only show the black background color.

3.3. Reflection spectra

We can see from the reflection spectra of wet OLLS (0 min) the reflection peak wavelength at 454 nm, which belongs to the blue light range, so the performance of the corresponding color is blue. This is consistent with the above optical observation. The trend of reflection peaks are divided into two stages as the drying time increases from 0 to 40 min (Fig. 4). First stage (0–20 min), the reflectivity decreases gradually, but the reflection peak wavelength does not change in this stage. Second stage (20–40 min), the reflection peak wavelength blue-shifts from 454 nm to 392 nm, while the reflectivity decreases gradually and vanishes at last, the reflection spectra approximates a horizontal line and there is no obvious reflection peak at this time, so the corresponding color can only present black background color.

3.4. Mechanism discussion

In order to reveal the effect of wet state on the structural color of OLLS, the swelling test of the cross-section of OLLS was operated. The expansion rate of OLLS was calculated at 62% by measuring the cross-sectional thickness in dry and wet states, respectively.

Swelling test shows that the water can obviously tune the microstructure of OLLS, we speculate the process of expansion as shown in Fig. 5. When the OLLS is in wet state, the structure will fill with water, which makes the structure comprised of two kinds of mediums of protein and water. So it has the condition to present structural color. The inter-fiber spacing increases from 101 nm (P_1) to 164 nm [$P_2 = 101 \times (1 + 62\%)$] with the effect of swelling. Using this parameter and the following formulas of photonic band gap, the reflection peak wavelength of wet OLLS is calculated at 456 nm, which belongs to the blue light range, and nearly equal to the measured reflection peak wavelength. The measured and calculated results indicated that the blue structural color in the wet OLLS is produced by a two-dimensional amorphous photonic structure consisting of aligned protein fibers and water.

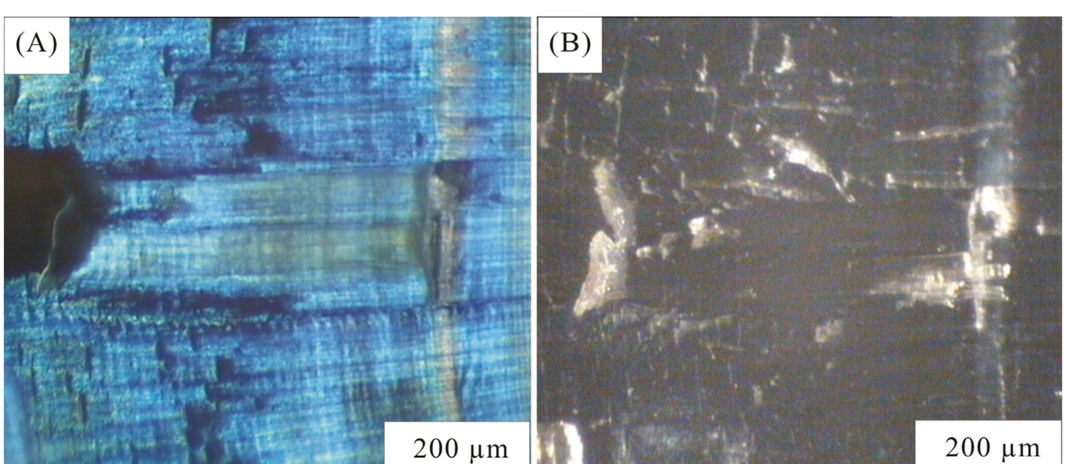

Fig. 2. Optical photos of OLLS in different states: (A) wet state and (B) dry state.