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Tunable alumina 2D photonic-crystal structures via biomineralization of peacock tail feathers

Yonggang Jiang [a, b], Rui Wang [a], Lin Feng [a, *], Jian Li [a], Zhonglie An [c], Deyuan Zhang [a]

[a] School of Mechanical Engineering and Automation, Beihang University, Xueyuan Road No. 37, Haidian District, Beijing 100191, PR China
[b] International Research Institute for Multidisciplinary Science, Beihang University, Xueyuan Road No. 37, Haidian District, Beijing 100191, PR China
[c] Department of Mechanical Systems Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo, 184-8588, Japan

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ABSTRACT

Peacock tail feathers with subtle periodic nanostructures exhibit diverse striking brilliancy, which can be applied as natural templates to fabricate artificial photonic crystals (PhCs) via a biomineralization method. Alumina photonic-crystal structures are successfully synthesized via an immersion and two-step calcination process. The lattice constants of the artificial PhCs are greatly reduced compared to their natural matrices. The lattice constants are tunable by modifying the final annealing conditions in the biomineralization process. The reflection spectra of the alumina photonic-crystal structures are measured, which is related to their material and structural parameters. This work suggests a facile fabrication process to construct alumina PhCs with a high-temperature resistance.

1. Introduction

Photonic-crystal (PhC) structures have aroused considerable interests in new generation optical and optoelectronic devices due to their ability to manipulate light propagation. Integrated optical circuits based on PhCs have been proposed for optical sensing and computation [1]. Photonic-crystal fibers are now finding applications in fiber-optic communications, fiber lasers, and highly sensitive sensors [2–4]. Various PhCs based sensors have been developed for detection of temperature, pressure, and chemicals [5–11]. Techniques such as electron beam lithography, nanoimprinting and colloidal self-assembly, etc. were used to construct artificial photonic crystals [12–14]. Electron beam lithography is a powerful technique for scientific research, with a critical limitation for mass-production. Gu et al. reported vapor-responsive colloidal PhC patterns by inkjet printing of mesoporous silica nanoparticle ink followed by self-assembly of the silica nanoparticles during drying procedure [15]. In order to obtain high-temperature PhCs, a sacrificial template method was used for fabrication of SiC Inverse Opal PCs [16,17], in which the templates were self-assembled polystyrene or silica spheres. The sacrificial template method is a feasible scheme to develop high-temperature PhCs, which is difficult to fabricate by micromachining techniques. As the self-assembly method is only appropriate for limited nanosphere templates, there remains a technological challenge to obtain complex high-temperature PhCs through a general low-cost method.

In nature, structural colors have been widely discovered in insects [18,19], birds [20,21], marine animals [22,23], reptiles [24], bacteria [25] and virus [26] and flowers [27]. In particular, the coloration mechanism in peacock tail feathers is attributed to 2-D photonic crystals, which is very ingenious and simple: controlling the lattice constant and the number of periods in the photonic-crystal structure. The mechanochromic response of the barbules in peacock tail feather was investigated for strain sensor applications [28]. In order to broaden the application of biological PhCs, it is very important to replace the sophisticated nanostructures of the biological templates into various functional materials. Inspired by the miscellaneous forms of biological species in nature, bio-replication was developed to fabricate optical materials with sophisticated structures analogous to biological species. As one of bio-replication approaches [29], biomineralization process was developed for synthesis of inorganic PhCs [30–32] from biological templates. Han et al. demonstrated an infiltration approach to incorporation of CdS or ZnO nanoparticles into the natural PhCs within peacock feathers [32]. Well-aligned ZnO nanorod arrays

* Corresponding author.
E-mail address: linfeng@buaa.edu.cn (L. Feng).

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were successfully derived from peacock feathers by a facile immersion and multi-step calcination process.

There is a strong demand to extend the biomineralization process to materials with high-temperature resistance such as alumina, SiC and other ceramics. Though previous literature described the biomineralization of alumina replicas from keratin fibers [33], how to retain the sophisticated 2D photonic structures remains a challenging issue. In this paper, we presents the fabrication of alumina nanorod based artificial PhCs with structures analogous to peacock tail feathers (*Pavo cristatus*) via the biomineralization process. The morphology and optical properties of the biomineralized PhCs are investigated in detail for optical sensor applications.

2. Materials and methods

The male peacock (*Pavo cristatus*) tail feather used in our experiments was purchased from Beijing Blue Peacock Farm (Shunyi District, Beijing). The barbs were manually cut from the rachis of the feathers for structural analysis, reflectance measurement and biomineralization. Individual barbs of the peacock tail feather were first immersed into an EDTA–DMF (approximately 1:10 v/v) suspension at 110 °C for 6 h to become activated and henceforth defined as the E/D feathers. The activated E/D feather were then immersed into the Al^{3+} precursor solution (a mixture of 4 mL $Al(NO_3)_3$ aqueous solution (1 mol/L) and 80 mL ethyl acetate) at at 80 °C for 4 h, and henceforth defined as the immersed feather. The samples were taken out after sufficient washing with DMF and then dryed at 100 °C for 15min. Finally, the immersed feathers were calcined in two-step annealing process in air: (1) The samples were heated up to 275 °C with a heating rate of 5 K/min and kept for 1 h; (2) the annealing temperature were increased from 275 °C to 570 °C with a heating rate of 1 K/min (10 K/min for comparison) and kept for 1.25 h. After burning off the template, the alumina replicas with well aligned nanorod structures were obtained.

The morphology of biomineralized barbules on the barbs were characterized by using a scanning electron microscope (S4800, Hitachi High-Technologies Co. Hitachi City, Japan) equipped with an energy dispersive spectroscopy (EDS) analyzer. The samples were sputtered with a thin Au layer on the surface to prevent charging. The microstructures of biomineralized alumina replicas were characterized by an X-ray diffractometer (XRD, D/max 2200 P C, Rigaku, Japan). The diffraction scanning scope ranged from 10 deg to 100 deg at a scanning speed of 6 deg/min using Cu-Kα radiation.

The reflection spectra of the specimens were measured using a reflectivity measurement setup comprising of an optical microscope (Olympus BX-51, Olympus Co. Tokyo, Japan), a white light source (HL2000, Ideaoptics, Shanghai, China), and a spectrometer (USB2000+VIS-NIR, Ocean Optics, Florida, America). The resolution of the spectrometer is 1.5 nm with a range from 350 nm to 1000 nm.

3. Results and discussions

The barbules branched on the barb of a green peacock tail feather were trimmed using a diamond cutter. Fig. 2 illustrates the cross-sectional SEM micrographs of natural peacock tail feather barbules and samples after biomineralization. As shown in Fig. 2(a) and (b), the cross-sectional micrographs reveal that the barbule consists of a medullar core enclosed by a cortex layer. Periodically-aligned melanin rod arrays beneath the surface keratin form 2D photonic-crystal structure. The 2D photonic-crystal structure shows a rectangular lattice, and the changes in lattice constants (rod spacing) and number of periods (melanin rod layers) along the direction normal to the cortex surface result in the variation of the color.

The biomineralization process was demonstrated using the peacock tail feathers as the biotemplates to produce alumina nanorods. Fig. 2(c) and (d) illustrates the biomineralized samples with a heating rate of 10 K/min in the 2nd step of the annealing process. It is clearly seen that the 2D photonic-crystal structure retained after the biomineralization process, though the dimensions of the barbules are significantly decreased. As shown in Fig. 2(d), the well-aligned alumina nanorods exhibit a typical length of 300–400 nm and a diameter of 35 nm on average, indicating that shrinkage occurred as a result of the high-temperature calcination at 570 °C. The air-holes between the nanorods almost disappear, which probably originates from the shrinkage and distortion of melanin rods induced by the high heating rate. As a result, the heating rate was decreased to 1 K/min. The identical morphology for the barbules and the synthesized alumina was clearly manifested from the high-resolution SEM images as shown in Fig. 2(e) and (f). In the annealing process of immersed feather, we take advantage of the different decomposition temperature of keratin and melanin. Keratin will decompose before melanin, and the initially heated keratin will gradually wrap the melanin rod. As a result, the 2D photonic crystal structure consisting of melanin rods is maintained during the first annealing process. In the second annealing process, the formation of alumina and the decomposition of melanin rod process simultaneously. The alumina rods squeeze in this process and causes structural distortion, which is significantly affected by the heating rate. Therefore, the lattice constants of the alumina replica can be modified by the heating rate in the second annealing process.

As shown in Fig. 3(a), the EDS result indicates that the biomineralized samples contain a large amount of aluminium and oxide elements. The elements of sulfur, calcium, and sodium are originated from the nature peacock tail feather. In immersed feather, on-site precipitation is formed due to the low solvation of Al^{3+} in EA, leading to the precise replication of the peacock tail feather with alumina. It is reported that the pyrolysis of keratin starts at 243 °C, and the melanin are pyrolyzed at a temperature range of 470 °C–570 °C as schematically illustrated in Fig. 1 [32]. The XRD pattern shown in Fig. 3(b) indicates that amorphous Al_2O_3 is formed by annealing at 570 °C. After annealing the alumina at an elevated temperature of 800 °C for 1 h, γ- Al_2O_3 is formed with characteristic diffraction peaks at 19.33°, 31.82°, and 66.49° [34].

Fig. 4(a) illustrates the schematic diagram of the 2D photonic structure of the peacock tail feather and the replicated alumina nanorod arrays. a_x and a_y refer to the lattice constants in directions parallel and normal to the cortex surface, respectively. In addition to the lattice constants, the diameters of melanin (or alumina) rods and air hole were also measured using an image processing software (ImageJ, National Institutes of Health, America). As shown in Fig. 4(b), the lattice constants are $a_x = 122$ nm, $a_y = 164$ nm for green barbules, while the lattice constants are $a_x = 38$, $a_y = 41$ for the alumina nanorod arrays shown in Fig. 2(f). It should be noted that the measured lattice constants are averaged values and they are not perfect 2D photonic crystal compared to engineering materials. The shrinkage ratio of the alumina replica to its natural template can be modified by the heating rate in the annealing process.

Fig. 5(a) illustrates the measured reflection spectrum for green barbules at normal incidence, which shows a reflectivity peak at a wavelength of approximately 500 nm with a narrower bandwidth. In the case that 2D photonic crystal is illuminated by white light at normal incidence, the peak wavelength is expressed by $\lambda = 2dn_e$, where d is the interplanar spacing of the planes, and n_e is the effective refractive index. The lattice constants ($a_x = 122$ nm,