Controlled Replication of Butterfly Wings for Achieving Tunable Photonic Properties

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ABSTRACT

The fine structure of the wing scale of a *Morpho Peleides* butterfly was examined carefully, and the entire configuration was completely replicated by a uniform Al_2O_3 coating through a low-temperature ALD process. An inverted structure was achieved by removing the butterfly wing template at high temperature, forming a polycrystalline Al_2O_3 shell structure with precisely controlled thickness. Other than the copy of the morphology of the structure, the optical property, such as the existence of PBG, was also inherited by the alumina replica. Reflection peaks at the violet/blue range were detected on both original wings and their replica, while a simple alumina coating shifted the reflection peak to longer wavelength because of the change of periodicity and refraction index. The alumina replicas also exhibited similar functional structures as waveguide and beam splitter, which may be used as the building blocks for photonic ICs with high reproducibility and lower fabrication cost compared to traditional lithography techniques.

Nature provides abundant selections of micro- to nanostructures that can be used as templates for fabricating a wide range of photonic related structures.[1−6] Replication is a method of using biotemplates for achieving nanostructures made of more stable, harder, and high-temperature-tolerable inorganic materials that may have some designed functionalities for practical applications. Butterfly,[7,8] beetle,[9] and sea mouse[10] are the typical templates used for building photonic-related structures. Inorganic structures replicated from biological templates may combine the merits offered by both the material and biological structures. For practical applications, it is, however, still a challenge to replicate not only the morphological structures of the biotemplate but also its photonic performance. In this paper, we have replicated the photonic structures of butterfly wings using atomic layer deposition. The reflectance spectra measurement demonstrates that the replica preserves not only the photonic property of the original butterfly wing but also the tuneable color through precise control over the thickness of the inorganic layer. The structure of photonic "waveguide" and "beam splitter" have been illustrated, which demonstrate a new approach for fabricating photonic structures with a stop band in the UV to visible wavelength range. This discovery shows great potential in applying the replicated butterfly wing as the building blocks for photonic integrated circuits.

The beautiful colors exhibited by butterfly wings are usually contributed by two sources: pigments and periodical submicrometer structures, which are also referred to as "chemical" and "physical" colors, respectively.[7] For the purpose of structure and property replication, the "physical" color is the prerequisite for choosing the right type of butterfly templates. Previous research revealed that the blue color of the *Morpho* wings results from arrays of vertically aligned net-like skeleton structures.[11,12] Figure 1a shows a photo of a male *Morpho Peleides* butterfly that we used in our replication experiments. The uniform blue color covering the major area of the wings was from millions of the ordered scales, as shown in the optical microscopy image in Figure 1c. These scales can be removed from the wing surface and manipulated by microprobes for further characterization and investigation. A scanning electron microscopy (SEM) image of a single wing scale supported on a silicon substrate is shown in Figure 1b. The typical dimension of the scale is ∼150 μm in length and ∼60 μm in width. Thirty five to forty rows of lamellas align on the scale surface with almost an identical interspacing. A closer view of these lamellae is shown in Figure 1e. The lamellae are located ∼1.6 μm from each other and supported by cross-ribs, which dictate the interlamellae spacing and hold the lamellae ∼1 μm above the bottom surface of the scales.

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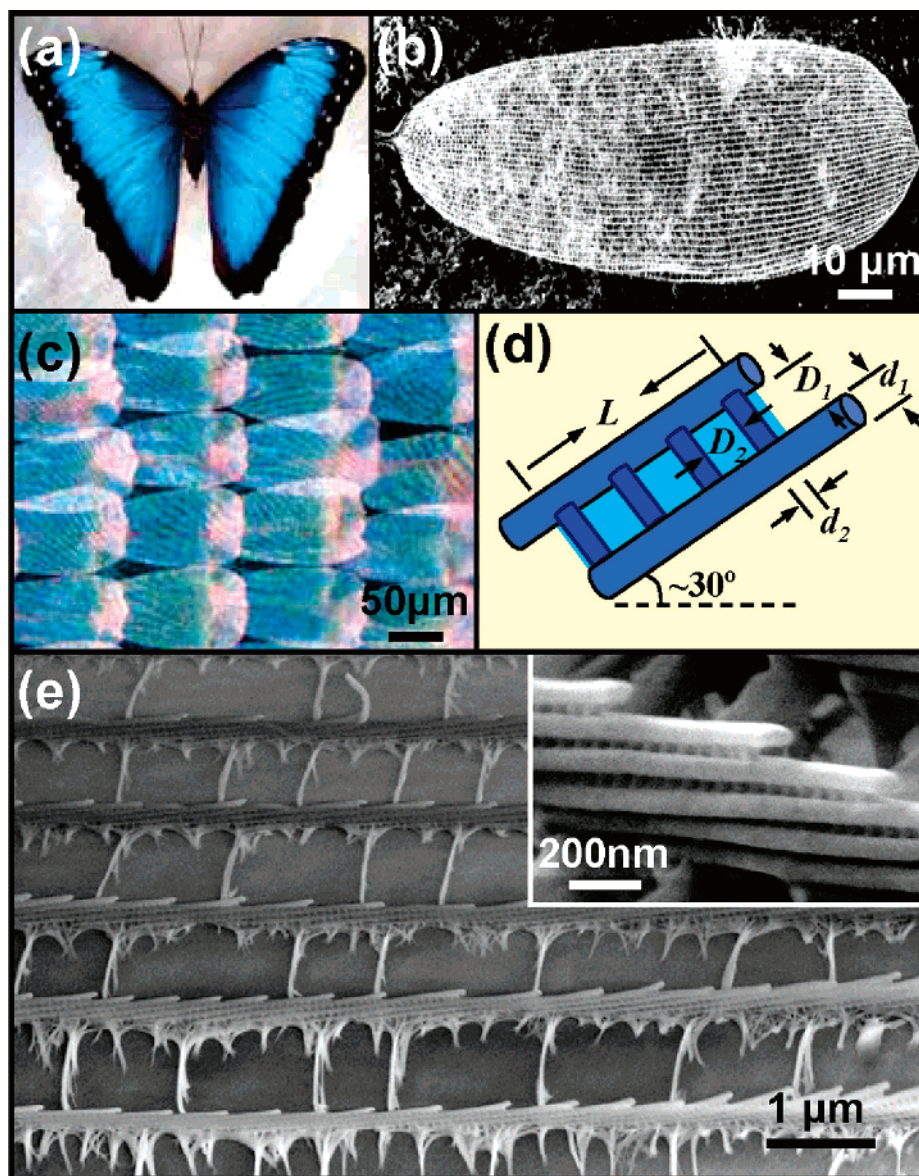§ Both authors contributed equally to this work.

Figure 1. Morphology and structure of the original butterfly wing scales (*Peleides Morpho*). (a) A photo of the butterfly. (b) A low-magnification SEM image of a single butterfly wing scale on silicon substrate showing the stripe structure. (c) An optical microscope image of the butterfly wing scales from the blue area. (d) The schematic of a "unit cell" on the lamellae that responsible for the scattered colorful light. (e) A SEM image taken on the scale surface showing the structure of the lamellae. The inset is a higher resolution SEM image showing the periodic nanostructures on a lamella.

The detail of the periodic structure on a lamella is shown by a higher magnification SEM image in the inset of Figure 1e, of which one "unit cell" is illustrated schematically in Figure 1d. The cylindrical main ribs are $\sim$1.6 μm in length (L) and $\sim$100 nm in diameter (d_1) with $\sim$60 nm of interdistance (D_1). Two adjacent ribs are bound together by a row of smaller sub-ribs with a diameter of $\sim$20 nm (d_2), which remain $\sim$50 nm (D_2) away from each other. This configuration constructs a 2D array of 50 nm $\times$ 60 nm rectangular squares surrounded by organic nanometer-scale cylinders (the main and sub-ribs) with a periodicity of $\sim$160 nm ($D_1 + d_1$) along its length direction and $\sim$70 nm ($D_2 + d_2$) along the main ribs. Although the entire lamella is perpendicular to the scale surface, the "unit cells" are largely tilted and the angle between the main ribs and the horizontal plane is only $\sim$30°. This long-range ordered organic structure

with a very small periodicity can be considered as 2D photonic crystal slab, and the brilliant blue color was attributed to the existence of the photonic band gap (PBG) in this structure.[13−15]

Such a delicate structure given by nature contains $\sim$100-nm-scale PBG structures with the stop band in the visible light range, which are still very costly to be made by current techniques. By utilizing such a structure as a template and coating it uniformly with an inorganic dielectric material, it may be possible to fabricate PBG structures with high-reproducibility and low-cost. However, because of the C-, H-, and O-based organic skeleton of the wing, a moderate replication condition is required, such as noncorrosive environment, proper pH value, and mild temperature. Here we used atomic layer deposition (ALD) technique to replicate the wing structure by Al_2O_3, which was carried out at 100
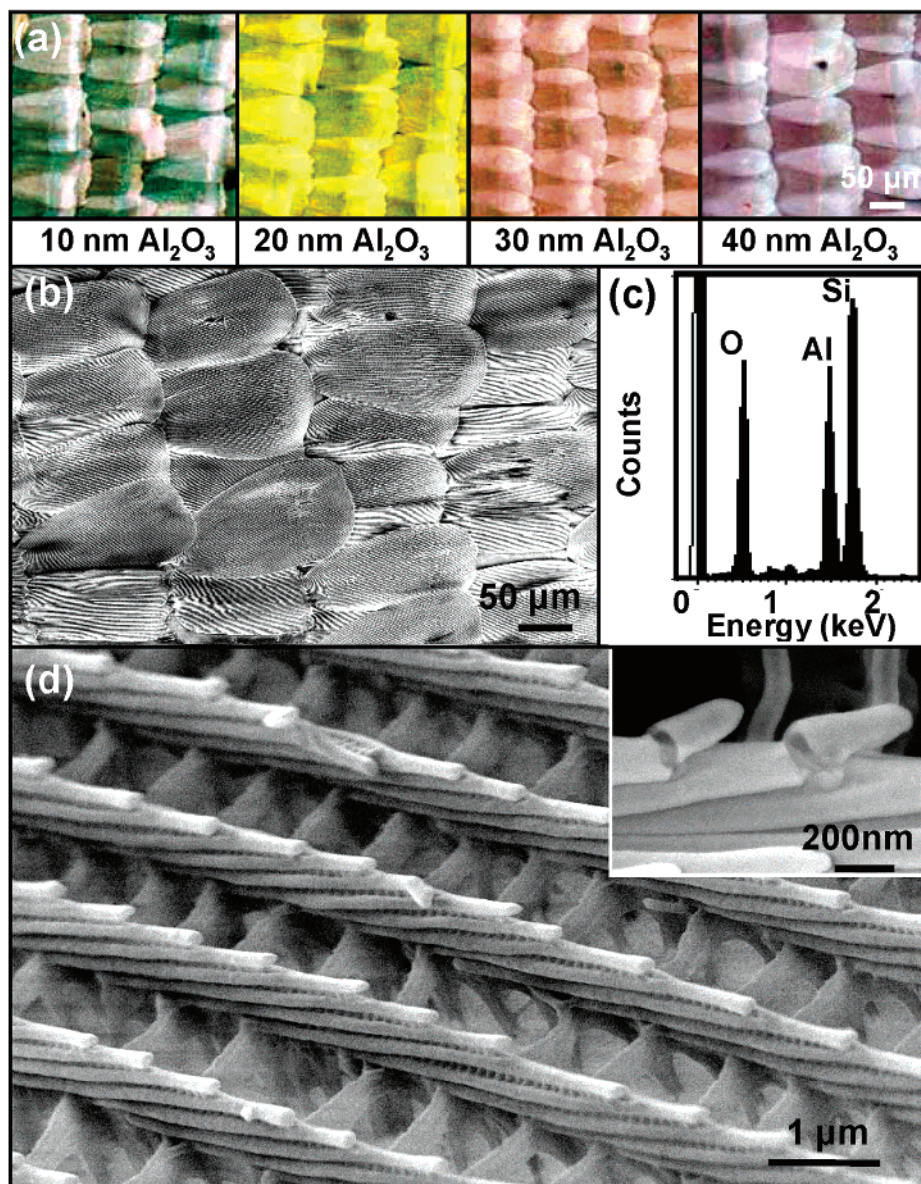
Figure 2. Images of the alumina replicas of the butterfly wing scales. (a) An optical microscope image of the alumina coated butterfly wing scales, of which the color changed from original blue to pink. (b) A low-magnification SEM image of the alumina replicas of the butterfly wing scales on silicon substrate after the butterfly template was completely removed. (c) The energy dispersive X-ray (EDX) spectrum of the alumina replica shown in part b. (d) A higher magnification SEM image of an alumina replicated scale, where the replica exhibits exactly the same fine structures. (e) A SEM image of two broken rib tips on an alumina replica.

°C. The ALD deposition was performed in a Savannah 100 Atomic Layer Deposition system manufactured by Cambridge NanoTech Inc. Two precursors for Al_2O_3 deposition were 99.9999% $Al(CH_3)_3$ (TMA) purchased from Aldrich and deionized H_2O with a resistivity of ~18 MΩ. During the replicating, the thickness of the Al_2O_3 layer could be controlled very well by varying the cycles of deposition, where the growth rate was 1 Å per cycle.

With the coating of Al_2O_3 layer, the color of the butterfly wing was also changed. By increasing the coating thickness from 10 to 40 nm with a 10 nm interval, the reflected color shifted from original blue to green, yellow, orange, and eventually pink. A series of optical microscope images of the wing scales coated with a 10-, 20-, 30-, and 40-nm-thick Al_2O_3 layer is shown in Figure 2a. This red-shift is due to

the surface film enhanced reflection of a particular wavelength that is determined by the thickness of the film and its refraction index.

After coating an Al_2O_3 layer, the original butterfly template can then be completely removed by annealing the sample to 800 °C for 3 h in atmosphere. Under such a high temperature, the organic wings were burned out with the existence of oxygen. Meanwhile, the amorphous Al_2O_3 shell was gradually crystallized into a more robust polycrystalline shell structure, with crystal grain sizes smaller than 3 nm. Owing to the excellent uniformity of the alumina film, both the large-scale arrangement of the wing scales and the nanometer-scale periodic structures are perfectly preserved after this vigorous template removing process. As shown in Figure 2b, the alumina replicas of wing scales exhibit the same
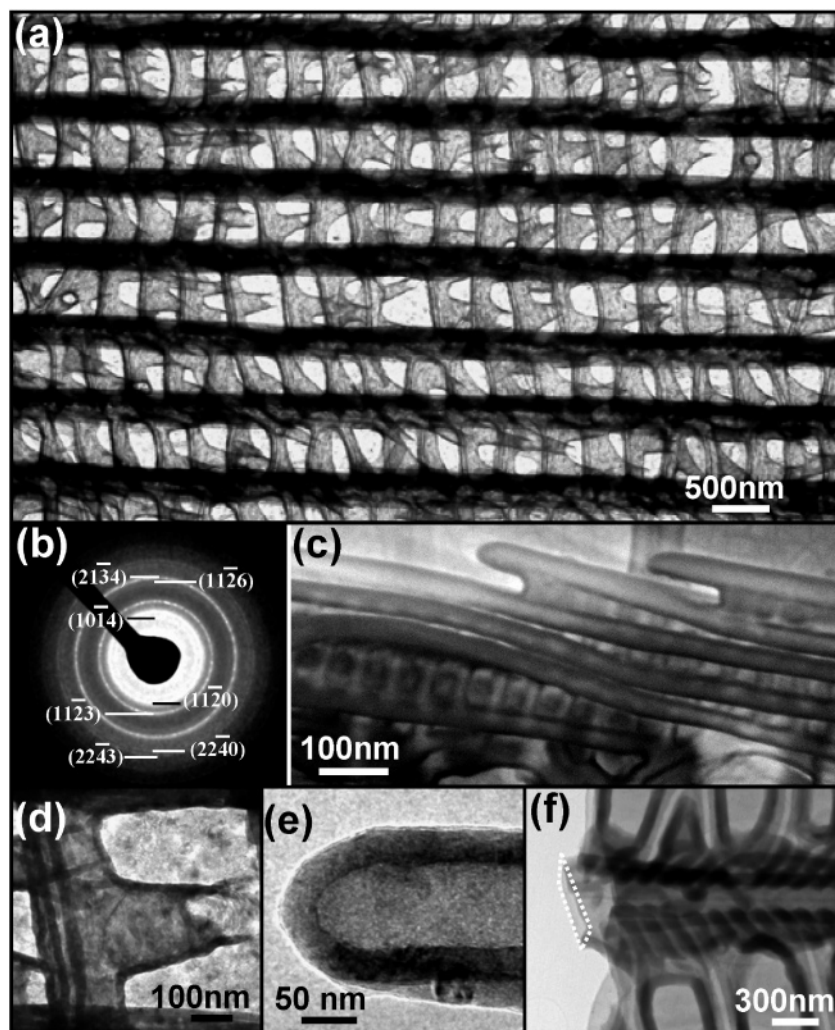
Figure 3. TEM characterizations of the alumina replicas of butterfly wing scales. (a) A low-magnification TEM image corresponding to the typical structure of an alumina replicated scale. (b) Select area electron diffraction (SAED) pattern of the alumina replica. Calculation of the plane distance demonstrated that the alumina is the α-Al_2O_3. (c) A higher magnification TEM image showing the hollow periodic lamella structure. (d) A TEM image of a supporting cross rib replica. (e) A TEM image of a replicated rib tip, where the coating thickness clearly measured. (f) A TEM image of a broken edge of a lamella showing a hollow channel under the ribs.

shape, orientation, and distribution as their "parent" scales. The chemical composition of the coating layer is presented by the energy dispersive X-ray (EDX) spectrum (Figure 2c), where only O and Al elements were detected from replicated scales (Si signal is from the supporting silicon substrate). The detailed structure of the alumina replica can be clearly observed from a higher resolution SEM image, as shown in Figure 2d. The main and sub-ribs on the lamellae as well as the supporting cross ribs were well preserved without any distortion or broken surface. It should be noticed that all of the ribs are hollow alumina cavity at this stage. A broken tip shown in the inset of Figure 2d clearly reveals this tubular rib structure.

Further characterization of this replication results was carried out by transmission electron microscopy (TEM). Because the alumina replicas of the wing scales were flexible and robust, they could be transferred to and manipulated on TEM grids without destroying their fine structures. Figure 3a showed a low-magnification TEM image taken on an alumina replica. The dark rows were the lamellae perpen-

dicular to the projection screen. Between them are the supporting cross ribs, each of which had one or two legs standing on the bottom surface and exhibiting a hollow body. The crystal structure of the annealed alumina film was characterized by selected area electron diffraction (SAED). The polycrystalline structure was confirmed by the diffraction rings shown in Figure 3b.

The perpendicular lamella structure can only be viewed after tilting the sample. As shown in Figure 2c, the hollow ribs, sub-ribs, and even the thin film in the inter-rib spaces could be clearly distinguished, which indicates that the air space inside the alumina shell preserves the identical shapes and dimensions as the original template. Consequently, this structure could be considered as an inversed two-dimensional (2D) photonic crystal (PC) slab, where periodic air space with particular shapes were confined and surrounded by a dielectric outer shell. This configuration is similar to the inverse opal structure converted from opal structure. The construction details are shown by higher resolution TEM images in Figures 3d−f. Figure 3d showed a one-leg
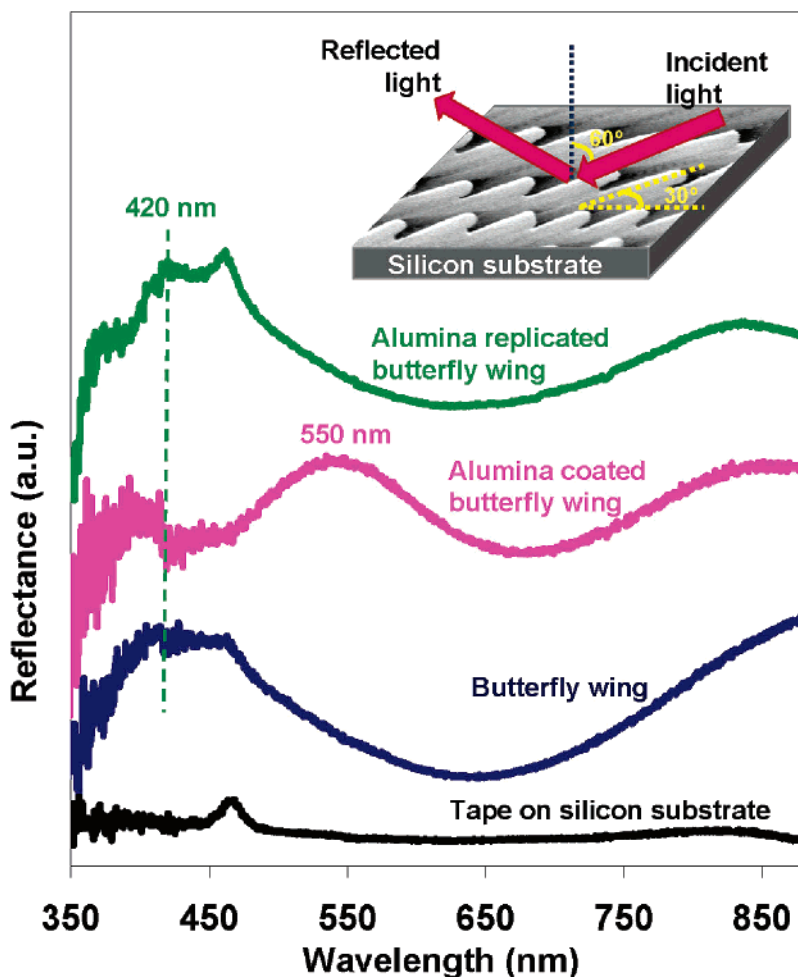
Figure 4. Reflectance spectra of the original butterfly wings, alumina coated wings, alumina replicas, and the carbon tape background in UV−visible light range. The inset is the schematic of reflection measurement setup.

supporting cross rib. Because the alumina layer grew simultaneously around both the ribs and the bottom surface, the contacting junction was actually one seamless continuous shell. This resulted in the robustness of the replica even with a thickness of only tens of nanometers. The tip of the main rib was shown in Figure 3e, where the thickness of the alumina layer can be easily measured to be 41 nm, corresponding to the result of 400 cycles of ALD growth. The uneven contrast distribution was resulted from the random crystal orientations of the polycrystalline alumina shell. A broken edge of a lamella row was shown in Figure 3f, which displayed a big open channel that connects all of the main ribs at their bottom side. As indicated by a white dashed box, the channel is ∼400 nm wide. This configuration would allow a further infiltration of other high-index materials into the periodic air space so as to achieve a largely tunable PBG on the same type of structure.

The success of the replication was not only on the morphologies but also on the optical property. Blue diffraction light can be observed on the alumina replica at a higher glancing angle. Angular reflection measurements were performed in the visible and near-infrared wavelength regions to reveal the light interaction with the replicated structures. In order to remove the multi-scale interacting effect, the scale replicas were transferred one by one onto a black carbon

tape supported by silicon substrate, which was chosen to minimize the substrate effect. The scales were manipulated by a microprobe to a side-by-side arrangement with the same orientation and covered an area of ∼1 mm². As discovered by previous SEM characterization, the main ribs on lamellae are aligned ∼30° with the horizontal surface. To achieve maximum interaction between the incident light and lamella lattice, the reflectance was measured at 60° to the normal direction with the incident beam parallel to the lamella rows, as illustrated in the inset of Figure 4. Therefore, the incident light was propagating along the main rib direction and fully interacting with the periodic arrays of the sub-ribs that were separated by ∼50 nm.

Under the configuration described above, the reflectance was measured on the original butterfly wings, alumina coated wings, and alumina replicas. The corresponding spectra were summarized in Figure 4. The reflectance of the carbon tape on silicon substrate was also recorded to eliminate background signal, such as the sharp peak at 461 nm. The original butterfly wing exhibited the highest reflection at ∼390 nm, which was in UV region. However, the relatively large reflectance in the short visible wavelength region contributed to its nature violet/blue color. After a 40-nm-thick alumina coating, the reflection peak red-shifted to ∼600 nm, indicating a red/pink color according to our earlier observation
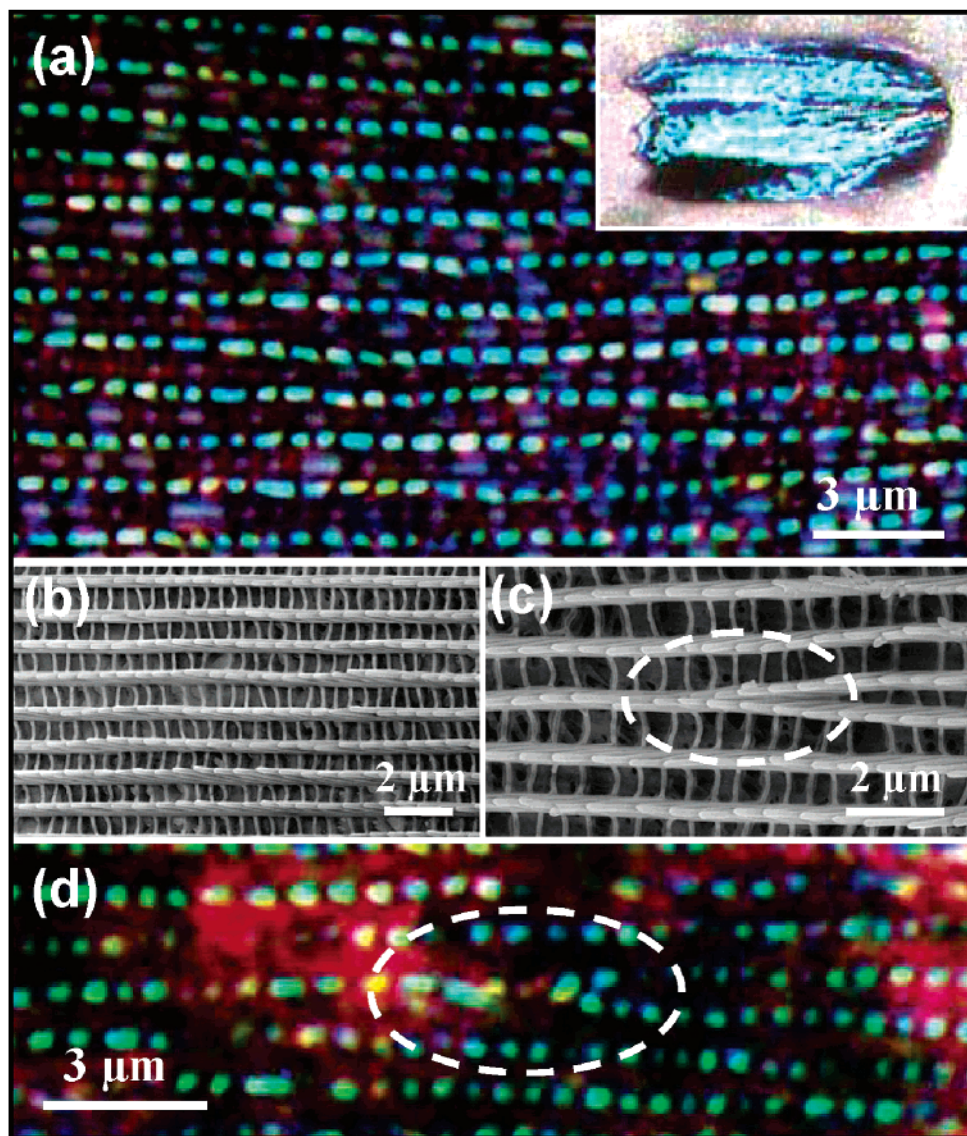
Figure 5. "Waveguide" properties of the alumina replicas. (a) A dark field optical microscope image of an alumina replica of the lamella rows; the inset is an optical image of an individual scale. (b) The SEM image of the replica structure corresponding to optical microscopy image shown in part a. (c) The SEM image of the bifurcated lamella structure. (d) The corresponding dark field optical microscope image showing the potential application as a beam splitter.

(Figure 2a). The alumina replica, which can also be considered as an inverse butterfly wing, shows almost the same reflection spectrum as that from the original butterfly wing, while the reflection peak was located at ∼420 nm. The appearance of this peak reveals the existence of a PBG in the replicated structure, where the original organic lamella lattice was replaced by air and covered by alumina matrix. It should be noticed that in the experimental setup the 2D PC slabs (lamellae) were perpendicular to the substrate surface so that the incident light was propagating in the 2D PC plane. Light with wavelength inside the stop-band would be reflected and recorded. Consequently, unlike other angular reflectance characterization, where the 2D PC slab was always parallel to the substrate, these reflection peaks were able to directly reveal the wavelength range of the stop band without angle-related shifting.[16]

One of the important applications of 2D PCs is as a waveguide, which is normally realized by introducing an artificial line defect into a perfect 2D PC slab. Because of the high requirement of the light guiding efficiency in optical communication and computing, PC waveguides are very sensitive to defects so that they have to be fabricated line by line or even point by point using lithography.[17,18] This is a rather complex and expensive process. On the basis of 2D PC slabs, more sophisticated photonic integrated circuits (IC), an integration of light emitters, waveguides, splitters, and detectors that generate, modulate, and process light signals or perform logical computations, have been in perspective for years.[19,20] Although the prediction of the photonic IC's performance is very optimistic, fabrication techniques and integration methods are still immature. Nevertheless, as many other cases, when the view was switched from pure man-made techniques to nature, solutions might have already been there for millions of years. In our replication investigation, the structure of waveguides and beam splitter, two key

components of a photonic IC, have been discovered from the replicas of butterfly wing scales.

Recall the nano/microstructure of the lamellae, the repeating unit was 50 nm × 60 nm rectangular square surrounded by the ribs. The main ribs with bigger size were similar to line defects in the 2D matrix of periodic nanosquares. After replication, the ribs became air nanocylinders in alumina shells, while their bottoms were all connected by a big channel (Figure 3c and f). Light with a certain wavelength could propagate inside the channel and be confined by the nanosquare matrix due to the existence of the PBG. This statement can be supported by the dark-field optical microscopy image, which is formed by the spreading/scattered light (top incoming light source) to highlight fine structures from the background. The inset of Figure 5a is such an image of an individual scale replica, where the blue light was strongly reflected. The light-propagating traces can be clearly observed in the higher resolution image, as shown in Figure 5a. The bright blue/violet dashed lines were the lamellae rows perpendicular to the observing plane, of which the corresponding SEM image is shown in Figure 5b. This brilliant color indicates different optical property of the lamella compared to the supporting sheet. It is foreseeable that as long as the replica is covered by another selected dielectric material to achieve a good reflection at the alumina interface, light would be trapped inside the hollow main ribs with the wavelength corresponding to the PBG of the nanosquare matrix so as to realize a 2D PC waveguide array.

More importantly, the split of lamella could be generally observed when the scale became wider, as shown in Figure 5c. This configuration naturally forms a beam-splitting device in nanometer scale when the lamella rows are considered as waveguides. The light trace of the splitter is shown in Figure 5d. The splitting junction structure and the corresponding light distribution are highlighted by white dashed circles in Figure 5c and d, respectively. At the splitting point, the bright dot first became wider and then split into two separated rows of dots exactly following the lamella structure. By arranging these two basic components, the waveguides and beam splitters, a complex photonic IC could be realized with an improved efficiency. A single blue *Morpho* butterfly can supply millions of such scales, which will provide a feasible mass production of such photonic IC building blocks.

In summary, the fine structure of the wing scale of a *Morpho Peleides* butterfly was examined carefully and the entire configuration was completely replicated by a uniform Al_2O_3 coating through a low-temperature ALD process. An inverted structure was achieved by removing the butterfly wing template at high temperature, forming a polycrystalline Al_2O_3 shell structure with precisely controlled thickness. Other than the copy of the morphology of the structure, the optical property, such as the existence of PBG, was also inherited by the alumina replica. Reflection peaks at the violet/blue range were detected on both original wings and their replica; while a simple alumina coating shifted the reflection peak to longer wavelength because of the change of periodicity and refraction index. The alumina replicas also exhibited similar functional structures as waveguide and beam splitter, which may be used as the building blocks for photonic ICs with high reproducibility and lower fabrication cost comparing to traditional lithography techniques.

References

(1) Davis, S. A.; Burkett, S. L.; Mendelson, N. H.; Mann, S. *Nature* **1997**, *385*, 420−423.
(2) Cook, G.; Timms, P. L.; Spickermann, C. G. *Angew. Chem., Int. Ed.* **2003**, *42*, 557−559.
(3) Seshadri, R.; Meldrum, F. *Adv. Mater.* **2000**, *12*, 1149−1151.
(4) Chia, S. Y.; Urano, J.; Tamanoi, F.; Dunn, B.; Zink, J. I. *J. Am. Chem. Soc.* **2000**, *122*, 6488−6489.
(5) Yang, D.; Qi, L. M.; Ma, J. M. *Adv. Mater.* **2002**, *14*, 1543−1546.
(6) Dong, A. G.; Wang, Y. J.; Tang, Y.; Ren, N.; Zhang, Y. H.; Yue, J. H.; Gao, Z. *Adv. Mater.* **2002**, *14*, 926−929.
(7) Vukusic, P.; Sambles, J. R.; Lawrence, C. R. *Nature* **2000**, *404*, 457.
(8) Biro, L. P.; Balint, Z.; Kertesz, K.; Vertesy, Z.; Mark, G. I.; Horvath, Z. E.; Balazs, J.; Mehn, D.; Kiricsi, I.; Lousse, V.; Vigneron, J. P. *Phys. Rev. E* **2003**, *67*, 021907.
(9) Parker, A. R.; Welch, V. L.; Driver, D.; Martini, N. *Nature* **2003**, *426*, 786−787.
(10) Parker, A. R.; McPhedran, R. C.; McKenzie, D. R.; Botten, L. C.; Nicorovici, N.-A. P. *Nature* **2001**, *409*, 36.
(11) Mohan, S. *Chem. Rev.* **1999**, *99*, 1935−1962.
(12) Ghiradella, H. *Appl. Opt.* **1991**, *30*, 3492−3500.
(13) Brink, D. J.; Lee, M. E. *Appl. Opt.* **1996**, *35*, 1950−1955.
(14) Kinoshita, S.; Yoshioka, S.; Kawagoe, K. *Proc. R. Soc. London, Ser. B* **2002**, *269*, 1417−1421.
(15) Yoshioka, S.; Kinoshita, S. *Proc. R. Soc. London, Ser. B* **2004**, *271*, 581−587.
(16) Astratov, V. N.; Whittaker, D. M.; Culshaw, I. S.; Stevenson, R. M.; Skolnick, M. S.; Krauss, T. F.; De La Rue, R. M. *Phys. Rev. B* **1999**, *60*, R16255−R16258.
(17) Joannopoulos, J. D.; Villeneuve, P. R.; Fan, S. *Nature* **1997**, *386*, 143−149.
(18) Lin, S.-Y.; Fleming, J. G.; Chow, E. *MRS Bull.* **2001**, *26*, 627−631.
(19) Noda, S.; Yamamoto, N.; Imada, M.; Kobayashi, H.; Okano, M.; *J. Lightwave Technol.* **1999**, *17*, 1948−1955.
(20) Tanaka, Y.; Sugimoto, Y.; Ikeda, N.; Nakamura, H.; Kanamoto, K.; Asakawa, K.; Inoue, K. *Appl. Phys. Lett.* **2005**, *86*, 141104.

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