Bio-Inspired Functional Materials Templated From Nature Materials†

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Abstract

Inspired from nature materials with hierarchical structures, many functional materials are developed based on the templating synthesis method. This review will introduce the way to fabricate novel functional materials based on nature bio-structures with a great diversity of morphologies, in State Key Lab of Metal Matrix Composites, Shanghai Jiao Tong University. We present the idea and methods of obtaining multi-scale porous materials by using wood, agricultural wastes and butterfly wing scales as bio-templates. We change their original components into our desired materials with original morphologies faithfully kept. Properties of the obtained materials are studied in details. Based on these results, we discuss the possibility of using these materials in light control, environment issues, and solar energy conversion field. This work has great values on the development on structural function materials in the near future.

Keywords: bio-inspired, nature materials, functional materials

1. Introduction

Scientists are always amazed by the nature materials, which are characterized by unique structures and morphologies. Inspired by nature, scientists struggle to fabricate artificial structures with certain functions in a biomimetic way. There has been a great interest in using nature materials with subtle hierarchical structures as nature templates to fabricate biomorphic inorganic materials. In this review, the latest developments in this field done by our group will be discussed. The review is organized into four parts. In the first part, versatile inorganic materials using different wood issues as templates will be discussed. The second part will give an overview on the utilization of agricultural waste to fabricate novel functional materials. The third part will give an intensive review on the latest developments on how to create inorganic materials with unusual structural specialty and complexity using the butterfly wings as the templates. Finally, we will give the summary, expectation and our own perspectives on these active areas.

2. Bio-Inspired Materials Converted From Wood

As a group of the plant, wood is a heterogeneous, hygroscopic, cellular and anisotropic material, composed of fibers of cellulose and hemicellulose held together by lignin. Wood exhibits microstructural features ranging from mm (growth ring patterns) via μm (tracheidal cell patterns, macro- and microfibril cell wall textures) down to nm scale (molecular cellulose fibers and membrane structures of cell walls). Since all the cell walls in the wood link together to form a frame, the body of the wood is then divided into innumerable rooms by this frame. After being heated in high temperature, the mixed biopolymers in the cell walls decomposed into carbon and gases. This gives rise to a porous carbon frame with the morphology derived from its wood template. Our work convinced that the porous carbon wood microstructure has many favorable characteristics such as stable coefficient of friction, good electromagnetic shielding properties, excellent far infrared property and high damping capacity. These outstanding properties of the wood can be attributed to its rational

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Generally, wood ceramics are fabricated through three steps: (i) formation of bio-carbon template by pyrolyzing the wood materials; (ii) infiltration of the bio-carbon template with ceramic precursors; (iii) calcination to form ceramics and remove organic materials. Carbides and carbide composites are most reported due to carbonaceous nature of the wood template, but a range of ceramic materials, including oxides, nitrides, and zeolites, were also produced by employing proper precursors and reaction routes. The general schemes for fabricating wood ceramics are illustrated as follows.

2.1 Carbides with wood microstructures

We converted wood carbon frameworks into morph-genetic SiC/C ceramics through methyl organic silicone resin infiltration followed by a high-temperature reaction. The process was investigated and it was revealed that the methyl organic silicone resin was first thermal decomposed into silicon compounds between 400 and 650°C, and then reacted with the carbon preform to form crystalline SiC after 1400°C sintering. Metal carbides can be synthesized using metal-containing sols as precursors. For example, TiC ceramic was produced by infiltrating tetrabutyl titanate sol into wood template in our group. The sol was first thermally decomposed into TiO₂, and then converted to TiC by reacting with the carbon cellular wall. Fig. 1 are images showing microstructures of several wood species and corresponding TiC wood ceramics prepared by infiltration with Ti-containing sols.

2.2 Oxides with wood microstructures

In section 2.1, we have studied the wood-templated carbon ceramics, SiC ceramics, Si/SiC/C and SiOC/C composites, metal/carbon composites to preserve wood’s structures. Can we remove the carbon inside wood and reserve the wood structure intactly to prepare wood-templated oxide ceramics? Till the beginning of this research, the research both domestic and overseas to this question was still very rare, and the preparation technique of oxide ceramics was not mature and still at an exploratory stage.

There are millions of species of trees all over the world and they all contain unique structures. So by making good use of these natural treasures, different metal oxides with a wide range of pore size can be made. The synthesis scheme proposed here is an example of general and simple approach. It can be expanded to other oxides through changing inorganic precursors. Our team has prepared wood-templated metal oxides (e.g. NiO, ZnO, Co₃O₄), rare earth metal oxide (e.g. Y₂O₃, Ce₂O₃) and composite oxide successfully by the wood-templating method. In other kinds of wood-templated oxides, we also find controllable hierarchical porous structures that will be reported later. The following are several typical examples of our work.

Fig. 2(a) and (b) show the cross-sectional morphologies of carbonized Paulownia and Paulownia-templated bulk Fe₂O₃ calcined at 600°C. Vessels of about 50 μm in diameter and fibers of about 10 μm in diameter can be observed in Fig. 2(a). Two kinds of pores can also be found in Fig. 2(b) with similar pore size and arrangement as original Paulownia, which illustrates that Fe₂O₃ preserves wood’s hierarchical macroporous structures well.

The enlarged TEM image of ultrasonic dispersing Fir-templated Fe₂O₃ calcined at 600°C is shown in Fig. 3(a). Whiskered structures can be found in this sample. The SAED (Selected Area Electron Diffraction) of the whisker was inserted in image (a). It illu-
minimizes the crystalline hematite phase of the Fir-templated Fe₂O₃. On the other hand, coexistence of the diffraction rings and spots at the SAED photo shows that more than one grain exists in the small diffraction area. In addition, different darkness on the same diffraction ring elucidates the anisotropic diffraction. Image (b) shows the cellulose microfibrils and lamella of microfibrils of Poplar. S1 and S2 are the outer layer and middle layer of the secondary wall. The two layers are composed of microfibrils seen as the whiskered shape in image. S1 has dense microfibrils and S2 has sparse microfibrils. Various woods have similar wood cell composition. The characters of S1 and S2 of Poplar are very like the morphology of Fir-templated Fe₂O₃ in image (a), which proves that Fe₂O₃ preserve the microfibrils of wood cell wall and realize the replication in nanometer scale.

Fig. 4(a) and (b) show the cross-sectional morphologies of carbonized Pine and Pine-templated bulk NiO calcined at 600°C. A NiO fiber assembly can be observed in Fig. 4(b) along the longitudinal section, which was derived from long and channel-like tracheid cells with the functions of conducting water and supporting in Pine shown in Fig. 4 (a). The pits, through which the Ni-precursor penetrated efficiently, were also preserved by NiO pointed out by arrow in Fig. 4 (b). As can be seen, the original cellular anatomy of Pine template is retained integrally in NiO.

Cr₂O₃ ceramic was synthesized by immersing wood in chromium nitrate solution. These ceramics not only inherited the specific microstructures of the original wood, also possessed a characteristic IR absorption peak, which indicating the potential application in IR absorption devices. Hierarchically porous manganese oxide wood ceramic was also produced using manganese nitrate as the precursor. An overall collapse in IR adsorption spectra was also observed with increasing calcination temperature, related to the effect of nanoscale pore structures. Hierarchically porous zinc oxides fabricated from Fir tissues show high sensitivity and selectivity to H₂S vapor. Higher porosity and surface area can provide more surface adsorption positions and reacting areas for oxygen and test gases and help gases transfer more quickly, which could lead to the increase of gas response.

2.3 Metal/carbon composites with wood microstructures

Not only are the iron oxides, metal/carbon composites prepared from wood templates also been fabricated and characterized. Aluminas alloys are known for their high specific strength, good cast ability, low thermal expansion and high corrosion resistance. The wear rates for the materials increase with increasing the applied load and the test temperature. The carbon-frame in the composites divided the Al alloy into innumerable sections. It can help the Al matrix improve its dry friction behaviors. The coefficient of friction for the materials usually increases with increasing applied load and test temperature. Moreover, during the course of wearing, the coefficient of friction curves for the composites were more smooth and straight than the Al alloy. This demonstrates the more stable friction state for the composites.

3. Bio-Inspired Materials Converted From Agricultural Wastes

An agricultural establishment produces many types of wastes in its daily operations. Agricultural waste materials particularly those containing cellulose shows potential metal bio-sorption capacity. The basic components of the agricultural waste materials biomass include hemicellulose, lignin, extractives, lipids, proteins, simple sugars etc., which is very similar to the wood tissues. To loose the environment pressure and increase the economic value of these wastes, re-using them is a very urgent topic. Studies reveal that various agricultural waste materials such
Rice husk, a by-product of the rice milling industry, accounts for about 20% of the whole rice. With the estimated annual rice production of 500 million tons in developing countries, approximately 100 million tons of rice husk is available annually for utilization in these countries alone. However, the amount of rice husk available is far in excess of any local uses and, thus, has posed disposal problems. In our research, rice husk was chosen to be applied as a template material due to its high porous structure, special components and its local availability at almost no cost. The objectives of this study was to determine selected electromagnetic wave absorption properties of different sorbents made from rice husk by different routes of preparation. 

Fig. 5 shows the procedure of nickel-loaded composites preparation. Rice husk were elementarily carbonized at 800°C. Hereinafter, the product was called black rice husk, the primary components of which were amorphous SiO₂ and carbon. In a sol-gel process, black rice husk was impregnated in nickel nitrate solutions of different concentration chosen as the precursor of nickel for 24 h. This procedure was carried out for the purpose of obtaining higher dispersion of nickel nitrate in black rice husk. Non- and nickel-loaded black rice husk was milled to powders, and then mixed well with 15 wt% phenolic resin powder chosen as a curing agent in a stainless steel vessel. Finally the mixture was molded into disk specimens with 115mm in diameter and thickness, respectively. In these molding processes, various pressures (12, 16 and 20 MPa) were applied on the mixture for initial 20 min, and then solidification of the mixture was continued free from compression for 12 h. Secondary carbonization was carried out at the temperatures of 800°C, 1200°C and 1400°C to yield nickel-loaded carbon matrix composites. The influence of carbonization temperature, molding pressure, nickel loading and the porous structure on the as-synthesized rice husk composites are discussed, which are summarized in Table 1.

The SE of a material is defined as the ratio between the incoming power (Pᵢ) and outgoing powder (Pₒ) of an electromagnetic wave. In general, SE is expressed in decibels (dB). Table 1 summarizes the electromagnetic SE at 500 MHz, 1 GHz and 1.5 GHz and the conductivity of the composites sintered at 800°C and above at room temperature. It can be seen that the nickel-impregnated samples had significantly higher SE values (at least 10 dB better) than the untreated samples at all sintering temperatures except 800°C. Even at 800°C the nickel impregnated sample shows slightly better SE values than the untreated sample at all frequencies tested here. Moreover the SE of the nickel treated samples increases with increasing of the sintering temperature significantly and steadily from 800°C to 1200°C. For the untreated composites, the SE does not seem to increase significantly with the increase of the sintering temperature from 800°C to 1400°C even though the SiO₂ was replaced by SiC at 1400°C. The SE values were 47.5 dB, 44.4 dB and 47.7 dB for the samples sintered at 800°C and 51.9 dB, 44.3 dB, 41.8 dB for the samples sintered at 1400°C at 500 MHz, 1 GHz and 1.5 GHz, respectively.

Table 1 Constituents, thickness, SE and electrical conductivity of nickel-impregnated and untreated composites as a function of heat treatment temperature.
More details please refer to our published work.

Except rice husks, coconut shells were also utilized to enhance the electromagnetic wave absorption properties of the composites. Scanning electron microscopy (SEM) image reveals that both porous carbons and C(Co) nanocomposite are characterized with a hierarchical porous structure. It can be observed from Fig. 6a that the C(Co) nanocomposite is constructed with separate carbon tubes with about 10 μm diameter. Little pores with 1-2 μm diameter are distributed uniformly on the walls of the carbon tubes.

Porous materials have better impedance match with free space than corresponding solid materials for their low effective permittivity. The electromagnetic waves can easily irradiate into the porous structure, and then dissipate in the composite. Moreover, the porous structure definitely increases interfacial areas throughout the composite, enhances the chance of multi-reflection, and leads to the improved energy loss. In conclusion, porous C(Co) composites exhibit excellent electromagnetic absorption properties, which are attributed to the well impedance match between porous structure and free air, the strong interfacial polarization relaxation loss and Ohmic loss. The porous carbon-based composites have advantages in being light weight and having effective absorption performance and may become attractive candidates for electromagnetic absorption materials.

4. Bio-Inspired Materials Converted From Butterfly Wings

Occurred on the earth in Tertiary period 25 million years ago, the butterfly family possesses the largest number of species (about 100,000 species). A butterfly’s wing is a uniquely visual exhibition, not only of the aesthetics of nature, but of the machinery of evolution and of inspiration of research. They are made of scales which are quite small and form two or more layers over the wing membrane. Different forms of butterfly microstructures have been categorized based on the nature of structural reflection, scattering and diffraction by H. Ghiradella. To distinguish these species, a main method is to identify the narrow difference of the colors and structures between different wing scales. The scales are of a thin plate-like form, whose typical dimensions are 100 μm in length, 50 μm in width, and about 0.5 μm in thickness, which cover the wing like tiles on a roof or a dense tapestry.

Fabrication the similar hierarchical microstructures shown above in the butterfly wings in lab by using a manmade assembly synthesis route is an extremely difficult task, since the formation mechanisms are tremendously complex. Therefore, we turned towards naturally occurring photonic structures for inspiration and several nanofabrication techniques have been developed to replicate natural photonic structures in butterfly wings. Chemical synthesis permits the manipulation of matter at the molecular level. Better control of the particle size, shape, and size distribution can be achieved in particle synthesis. To benefit from the advantages of chemical processing, several carefully designed approaches to fabricate butterfly wings replicas have been studied in our group recently. Here, three typical functional butterfly wings replicas with various properties are shown below.

4.1 Optical functional oxides templated from butterfly wings

The beautiful colors exhibited by butterfly wings are usually contributed by two sources: pigments and chitin periodical structures, which are also referred to as "chemical" and "physical" colors, respectively. Physical colors, i.e., structural colors, are essential topics since they can be modulated by the materials’ dielectric coefficients and their internal submicrostructures. Hence, to study the properties of butterfly replica, which are synthesized using different functional materials e.g., Al₂O₃ and ZnO with natural
butterfly as biotemplates, attracted great attention. However, some key features of the structural color, including iridescence, are unfortunately not reported in these works, which questions whether the obtained replica color is an inherited structural one or not.

It is generally believed that an obvious response to the imposed electromagnetic (EM) wave needs a big refractive index (RI) difference between the two materials that compose the photonic crystals (PCs). As compared to the air, the RI of the original chitin, previously reported ZnO, and Al₂O₃ is 1.57, 1.94, and 1.75 at 1.06 μm, respectively. To see what will happen by making the butterfly fossils with some higher RI materials is quite interesting to us. In this letter, we choose ZrO₂ to prepare the butterfly PCs. ZrO₂ has a RI of 2.12 at 1.08 μm, which is at least 9%, 21%, and 35% higher than ZnO, Al₂O₃, and chitin, respectively.

ZrO₂ is a high dielectric constant material with excellent optical properties. It has also been reported that ZrO₂ possesses a small thermal expansion coefficient, a very low thermal decomposition temperature, and a well metallic workability in high temperature, which makes it easy to be utilized in present fabrications. The butterfly wings we chose as biotemplate are from Euploea macleiber (Cramer, the family of Danaidae). The upper surface of its either wing has a prominent large shining metallic blue patch in the whole area. The wings are covered by chitin scales, as thousands of tiny flat platelets lying in rows. All the scales are fixed by peg-and-socket attachments. Scales with the size of about 100 μm in length, 50 μm in width, and 0.5 μm in thickness, form the flat plates overlapping over the membrane like roof tiles when viewed under a microscope.

Intact ZrO₂ replica, which is large in size has been synthesized by using natural butterfly wings as templates. Microstructure characters of original butterfly wing scales are maintained faithfully in this biomorphic ZrO₂. All replicas can reflect iridescent visible lights, which can even be observed by naked eyes, shown in Fig. 7. These ZrO₂ fossils with high RI can reflect the visible lights so strongly that the colors can be clearly observed directly even by naked eyes. In addition, iridescent colors can be seen in different observation positions from Fig. 4b-d, confirming a good inheritance of the structural colors. Optical microscope investigations indicate that colors reflected by one single scale are different from those done by the overlapped two or even more scales. Colors are not only determined by materials’ refractive index, observation angle, and the structure of every single scale, but also by its piled number and modes. With the increase in the number of piled scales, the color is not simply red-shifted or blue-shifted, which is the most direct and powerful evidence for structural colors.

Fig. 8 presents the micrographs of the ZrO₂ replica. Here, Fig. 8(a)-(c) are taken using a digital optical microscope at various regions under different magnifications. The system is carefully checked using standard color cards to avoid the color distortion. Fig. 8(d) and (e) are the field-emission scanning electron microscope images. These scales have clearly identifiable ridges with parallel cross ribs between them, which preserve the original structures well. Fig. 8(f) presents an X-ray diffraction (Cu Kα) result of the replica, which confirms the as-synthesized products to be ZrO₂. The ZrO₂ fossil presents blue, brown, or red under the investigation of the optical microscope. It should be noted here that colors in the middle of one single scale and in overlapped
edges are different. This property is the same as the original wings and faded ones, but different in colors and clarities, indicating a structural color nature of this phenomenon. Points A–E marked in Fig. 8(a) and (b) show the optical images of the overlapped area of two or more scales. Colors are determined by the number of overlapped scales. It can be seen that the color is not only simply redshifted or blueshifted with the increase in piled numbers. Instead, the color changed from brown (one single scale), to blue (two piled up, see A, B, D), to yellow (three piled up, see C), and finally to red (four piled up, see E). Because of the length of this letter, more detailed results and analysis will be presented elsewhere.

Reflection measurements were then performed in the visible and near-infrared wavelength regions to reveal the light interaction with the replicated structures. They were taken on UV-visible-near infrared microspectrophotometer. The incident angle is vertical to the surface of the substrate, as shown in red microspectrophotometer. The incident angle is around 650 nm, indicating the existence of a photonic band gap in the replicated structure. The reflection spectrum of the ZrO2 replica. A and B are the natural butterfly wings.

Fig. 8a. To B, a main peak around 600–700 nm, explaining the brown color we saw at single scale area in Fig. 8(a). To A, a peak around 350–450 nm confirms the violet to blue colors we viewed directly at points A, B, and D, in Fig. 8a and b. To B, a main peak around 600–700 nm explain the brown color we saw at single scale area in Fig. 8a-c.

Fig. 9(b) presents the microarea spectrum of the ZrO2 replica. A and B are the two areas representing two piled up wing scales and their single scale counterpart, respectively. To A, a peak around 350–450 nm confirms the violet to blue colors we viewed directly at points A, B, and D, in Fig. 8(a) and 8(b). To B, a main peak around 600–700 nm explain the brown color we saw at single scale area in Fig. 8(a)-(c).

To reconstruct these experimental results, we theoretically calculated the reflection spectrum using a finitedifference time-domain (FDTD) method. The model based on the wing scale we used, as well as the calculated results, is presented in the right inset of Fig. 9(a). The calculated results agree well with the reflection data of B area in Fig. 9(b), which is measured at a single scale simulated directly by our calculation model. It should be noted that the replicas in this work are composed of submicrometer ZrO2 particles, which can induce additional diffuse reflection because of their granular surfaces. Moreover, the scale replica’s surface is not perfectly flat, which may also produce deviations between the experimental and calculated results.

According to these results, we found that with the increase in the RI, a stronger modulation of the periodic submicrostructure to visible EM wave is obtained, giving rise to some phenomena that have not been reported before. Under this RI modulation, the structural color is not sensitive to the layer thickness of the replica anymore. Instead, it can simply be modified by scale-pile numbers, or by collection along various directions, which loosens the preconditions for this replica family to be prepared and broadly applied. Since the reflection peak will shift to long wavelength with the increase in the materials’ dielectric constant, colors of the replica, which locate in visible wavelength range, can be further changed or modulated via functional or ferroelectric materials. The present fabrication of large-area and colored replica has great potential applications in display screens, spectroscopes, detectors, and so on. Since there are so many kinds of butterflies with thousands of different microstructures, it is possible to find a
suitable structure that meets our demands for certain applications.

4.2 Novel gas sensors inspired from butterfly wings

By introducing natural butterfly wings as templates, well-organized porous hierarchical SnO$_2$ replicas with controllable wall thickness were fabricated, on the basis of the control over the impregnants concentration and the immersing time. As far as we know, SnO$_2$ with the large bandgap (E$_g$ = 3.6 eV, at 300 K), has been the most typical and promising choice for a metal oxides sensors based gas sensor.

The gas sensing properties were evaluated according to the resistance variation under a direct current (dc) voltage of 5 V by using ethanol as the target gas. To avoid structural damage, the samples were cut into small fragments and then mixed with appropriate adhesives to adhere onto a flat alumina substrate, which is attached with two gold electrodes having a gap of about 1 mm. The fittings were then sintered at 500°C for 1 h in air and aged at 350°C for 7 days. Gas sensing experiments were carried out in a gas flow apparatus equipped with an external heating facility. The sample gases used were ethanol diluted in dry air. The gas flow was switched between the sample gas and dry air while the electrical resistance of the SnO$_2$ sheet was measured continuously on an electrometer.

FESEM images in Fig. 10 show the well-organized porous hierarchical architecture of the target product SnO$_2$ and the corresponding natural butterfly wings. They are covered by a large number of overlapping SnO$_2$ scales and chitin scales (Fig. 10(a) and (e)), respectively. On each scale (Fig. 10(b), and (f)) the parallel-aligned ridges are divided into numerous uniform windows (macropores) by the periodic aligned pillars between them. A higher magnification image (Fig. 10(c), and (g)) clearly exhibits that the ridges are stacked stepwise by multi-layers of lamellas, which are supported by a mass of ordered-aligned nano-scaled microribs. The cross sections of scales (Fig. 10(d), and (h)) reveal that the pillars are orderly standing on the substrate layers and extend to the top parallel ridges, and thus well-organized macroporous frameworks are produced. In conclusion, the unique architecture of the target product SnO$_2$ (Fig. 10(a)–(d)) is faithfully inherited from that of the natural butterfly wings (Fig. 10(e)–(h)) from the nanoto micro-scales, despite some dimensional shrinkage.

More details of SnO$_2$ scale (Fig. 12(a)–(c)) reveal the connective hollow interiors and thin walls. It is obvious that the pillars (Fig. 12(a)) are indeed fastigiated hollowtubers, and the lamellas (Fig. 12(b)) stacked on the ridges are interconnected tubes with a diameter of about 188 nm. The substrate layer (Fig. 12(c)) is piled in two parallel thinlayers. Thus the well-organized hierarchical architecture is actually composed of thin, conformal and continuous walls with thickness around 32 nm, which provides convincingevidence of the nanocoating process. Energy-
dispersive x-ray (EDX) spectroscopy (Fig. 12(d)) demonstrates that the walls are indeed composed of Sn and O elements, which is in accord with the above XRD results.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images (Fig. 13) provide further insight into the morphology and microstructure of the biomorphic SnO$_2$ (the target product). The long dark rows (Fig. 13(a)) are the ridges orderly stacked by parallel tubes. The ordered microribs are also clearly seen as parallel dark rods of about 130 nm in diameter on each ridge. Between the ridges are the fastigiated hollow tubers. The top view and the cross section of the ridge in high magnification (Fig. 13(b) and (c), respectively) clearly exhibit the hollow interiors with thin walls. The wall thickness is about 31 nm according to the tip of the tube with a diameter of about 183 nm (Fig. 13(d)), which is close to the result of FESEM. The higher magnification image (Fig. 13(e)) reveals that the well-organized porous hierarchical architecture is actually assembled by the nanocrystallites with an average size of about 7.0 nm, which is in accord with the XRD results. The selected area electron diffraction (SAED) pattern (inset in Fig. 13(e)) indicates that the assembled units of the biomorphic SnO$_2$ are polycrystalline in nature and the diffraction rings are indexed to (110), (101), (200), (211) and (301) planes of rutile SnO$_2$, respectively. The HRTEM image (Fig. 13(f)) reveals the further microstructure of the SnO$_2$ nanocrystallites. The spacings between two adjacent lattice planes are about 0.3418 and 0.2677 nm, corresponding to (110) and (101) planes of rutile SnO$_2$.

The nano-scaled porous structures of the biomorphic SnO$_2$ and the contrasting sample are characterized by nitrogen adsorption–desorption measurements. The adsorption–desorption isotherms are displayed in Fig. 14(a). The isotherm shape of the biomorphic SnO$_2$ is typical of an H3-type type-IV isotherm, while that of the contrasting sample is typical of H2-type type-IV. The presence of a hysteresis loops in the isotherms is associated with the filling and the emptying of mesopores by capillary condensation. The BET (Brunauer–Emmett–Teller) surface areas are calculated to be 514.12 m$^2$g$^{-1}$ for the biomorphic SnO$_2$ and 14.12 m$^2$g$^{-1}$ for the contrasting sample. The pore size distributions investigated by the BJH (Barrett–Joyner–Halenda) method are shown in Fig. 14(b), indicating both the two samples are mesoporous structures. The pore size of the biomorphic SnO$_2$ is distributed from 2 to 50 nm, centered on 4.6 nm, while that of the contrasting sample has a narrow distribution centered on 10.5 nm. Despite of the lower peak value, the biomorphic SnO$_2$ has much higher pore volume (0.159 cm$^3$g$^{-1}$) than that of the contrasting sample (0.059 cm$^3$g$^{-1}$). Based on these results, it is obvious that the biomorphic SnO$_2$ assembled by nanoparticles into the unique porous hierarchical architecture, possesses higher BET surface area and contains more mesopores, which are preponderant for better surface accessibility and more convenient gas transmission.

From the above investigation, the fine porous lightweight skeleton was faithfully inherited from that of natural butterfly wings via the ethanol-assisting sol–gel soaking process followed by a calcination treatment. Rutile SnO$_2$ nanocrystallites could be assembled to form interconnected tubes, fastigiated hollow tubers, and double-layered substrates, which are further orderly organized into a unique porous hierarchical architecture with connective hollow interiors and thin mesoporous walls. In view of the small...
grain size and the unique hierarchical architecture, it can be expected that the biomorphic SnO₂ would possess good gas sensing properties. The sensing mechanism could be described as gas surface chemisorption and electron acceptance, resulting in the change of the sensor’s resistance. Usually, oxygen molecules from ambient air are adsorbed on the surface of SnO₂ particles to form oxygen ions (O⁻, O₂⁻ and O₂⁻²) by trapping electrons from the conduction band, which gives rise to a high resistance state. Upon exposure to ethanol, the adsorbed oxygen ions (O⁻, O₂⁻ and O₂⁻²) react with the reducing gas to release electrons back into the conduction band, which reduces the resistance. Herein, the gas sensitivity (S) is defined as $S = R_a / R_g$, where $R_a$ and $R_g$ are the sensor’s resistance in air and in ethanol, respectively. The response (rise) or recovery (decay) time is defined as the time needed to reach 90% of the total signal change. The sensing experiments were carried out at 170°C under an ambient relative humidity of 25%.

The biomorphic porous hierarchy was constructed by a layer of flexural wall that was assembled by SnO₂ nanocrystallites with diameter of around 7.0 nm. The wall thickness was tunable under the control of the impregnants concentration as well as the immersing time. The biomorphic SnO₂ showed good sensing to ethanol and formaldehyde, due to its small nanocrystalline building blocks and unique porous hierarchical architecture. As shown in Fig. 15, the real-time sensing response of the sensors to ethanol (at 170°C) and formaldehyde (at 210°C), respectively. The responses are reversible with fast response and recovery, and increase with increasing gas concentration. To a fixed gas concentration, the response increases sharply with decreasing wall thickness: $S_{SnO₂-3} < S_{SnO₂-2} < S_{SnO₂-1}$. Fig. 15(c) and (d) shows the response variation of the sensors exposed to ethanol (at 170°C) and formaldehyde (at 210°C) at different concentrations, respectively.

Despite the different wall thickness, the as-fabricated biomorphic SnO₂ exhibited the same grain size of about 7.0 nm, well-organized macroporous frameworks, similar BET surface area and pore size distribution. Benefiting from the small grain size effect and the well-organized porous hierarchy facilitating gas diffusion, the biomorphic SnO₂ showed good ethanol and formaldehyde sensing properties. The highest responses to 50 ppm ethanol and formaldehyde are about 49.8 and 30.4, respectively. It is more noticeable that the response of the biomorphic SnO₂ increased with the decreasing wall thickness despite the same grain sizes and similar microstructures.

The response dependence should be ascribed to the increasing difficulty of the gas diffusion into inner grains via Knudsen diffusion with the increasing wall thickness, which is similar to that in thin films.

4.2 High light harvest efficiency photoanode derived from butterfly wings

The discovery that butterfly wings have scales that act as tiny solar collectors has led us to design a more efficient solar cell that could be used for powering homes, businesses, and other applications in the future. In the study, we note that scientists are searching for new materials to improve light-harvesting in so-called dye-sensitized solar cells, also known as Gratzel cells for inventor Michael Gratzel. These cells have the highest light-conversion efficiencies among all solar cells.

We studied a novel photoanode structure inspired by butterfly wing scales with potential application on dye-sensitized solar cell in this paper. Quasi-honeycomb like structure (QHS), shallow concavities structure (SCS), and cross-ribbing structure (CRS) were synthesized onto a fluorine-doped tin-oxide-coated glass substrate using butterfly wings as biotemplates separately, details of the process was shown in Fig. 16. The as-synthesized photoanodes are divided into four layers: glass substrates, F:SnO₂ conductive layer, anatase film, and titania film with butterfly wing microstructures.

*Papilio* paris is a species of beautiful swallowtail butterfly found in South China. Upperside of the wings is black, irrorated with dark green scales, which on the outer portion of the forewing coalesce and form an incomplete post discal narrow band.
On the hind wing, there is a conspicuous upper discal shining blue patch. The other specie of butterfly used in our work as contrast is Thaumantis diorens, the upper wings of which are brown black. A four-level observation method was adopted in studying the morphology of butterfly wings. The first level deals with the macroscopic aspect of the butterfly wings, as the left column of Fig. 17 shows. The second level is the optical microscopy observation level, as images a and d in Fig. 17 show. Fig. 1a shows the area taken from the matte black wings of Papilio paris. The optical image (Fig. 1d) is from the shining patch on the hind wings. The outline and color of the scales can be clearly identified in these images. FESEM was used to study the fine structures (the third and fourth level) of the wing scales. For FESEM measurement, all the samples were stuck to microscope stubs with double-sided carbon tape and then coated by a thin, sputtered gold layer to provide a conducting surface and avoid charging effects. It should be noted that previous studies have proven that there is no significant distortion of the scale geometry during this process. The low-magnification images of the scales from blue and black areas on the wings are shown in images b and e in Fig. 17. The scale morphologies are totally different, i.e., the blue shining scales (Fig. 17e) on the patch presents one layer of scales with rounded endings, the arrangement of which on the wing resembles that of shingles on a roof. By contrast, the matte black scales (Fig. 17b) are more elongated and have a deep zigzag ending, composed usually of three to five fingerlike features.

In this paper, we will focus on the fourth level, i.e., the surface and internal hierarchical structures of the scale, because they are responsible for the structural colors of the wings. Medium-magnification FESEM images (images c and f in Fig. 17) reveal that the structures of the blue and black scales have more obvious differences in the micron range. The black scales exhibit a complicated network structure called “quasi-honeycomb-like structure” (QHS), whereas the scanning electron micrographs of scales taken from the wings’ blue patch regions show that their surfaces comprise a regular two-dimensional array of shallow concavities structure (SCS) of about 5 μm in width and 10 μm in length. These concaves are responsible for the blue coloration of male butterflies according to the similar research doing by P. Vukušić.

The as-synthesized titania photoanode microstructures were shown in Fig. 18 with corresponding FFT images on the lower left-hand corner. The samples shown in the left column are synthesized in the lower concentration solution, while the right column samples are soaked in higher concentration. The morphology changes greatly, which are shown in the QHS (images a and b in Fig. 18). In Fig. 18b, the interspaces in the QHS are filled with titania particles, and the surface characters of the quasi-honeycomb structures are covered up. The changes are reflected on the corresponding FFT images, that is the diffuse ring pattern (shown in Fig. 18a inset) disappeared in Fig. 18b inset. By contrast, the spindle shape FFT from SCS are kept in the titania films, and the surface characters of the quasi-honeycomb structures are covered up. The changes are reflected on the corresponding FFT images, that is the diffuse ring pattern (shown in Fig. 18a inset) disappeared in Fig. 18b inset. By contrast, the spindle shape FFT from SCS are kept in the titania films, for the concavities are inherited in the titania films integrally, even the continued submicrometer drapes between the longitudinal ridges. The fill factors are nearly the same except the full filled sample (QHS-18 replica). It means that the morphology characteristics are maintained well, which is corroborated by the FFT results shown in Fig. 18.
The transmission spectra measurements in the UV-vis range are shown in Fig. 19a. The wing substrates and scales contain nearly the same amounts of pigments, especially the melanin, the differences in the transmission spectra are due to the diversity of the wings microstructures. The blue scales have higher transmissibility in longer wavelength, and the black ones with the CRS take second place, then the QHS ones take the third. According to the absorbance function shown below, $A(\lambda) = 1 - R(\lambda) - T(\lambda)$, with $A(\lambda)$ being the absorbance, $T(\lambda)$ the transmittance, and $R(\lambda)$ the reflectance. For the black wing, reflectance is virtually constant throughout the whole spectral range. The QHS scales with different microstructures (SCS, CRS, QHS) exhibited quite different absorption characteristics. The CRS titania replica film has a higher absorptivity than the normal anatase film in longer wavelength. The blue wings replica shows a lower absorptive peak around 450 nm, and as a result the film appeared a little yellow. It is heart-stirring that the QHS titania replica film has a remarkable increase in the absorption curve. Compared with the normal anatase film and CRS replica, the characteristic band-edge absorption position of the titania film with QHS is red-shifted to nearly 420 nm, because of the scatter and diffuse effect caused by the QHS in the titania replica film. This is similar to what happened in the original butterfly wings. Two main factors could influence the absorption spectra, one is the microstructures of the film, and the other is the remainder composing the film. All the samples were synthesized at the same condition, so the components of the film (TiO$_2$) would have the same properties, especially the crystal structures.

In conclusion, the butterfly wing scales templating procedure is a facile and economic design for the synthesis of hierarchically periodic microstructure titania photoanode without the need for complicated experimental conditions or equipments, such as photo lithography adopted. The quasi-honeycomb
structure titania replica photoanode has a perfect light absorptivity and higher surface area, which give great advantages to the light harvesting efficiency and dye sorption. This structure gives the butterfly ultrablackness wings, so it is convincing that we could obtain potential ultra-absorptivity photoanode adopting the quasi-honeycomb structure. The successfully synthesized butterfly wing microstructure titania photoanode we obtained not only gives us new ideas to DSC researches in technology and theory but also opens a short cut to the photothermal, photocatalyzed, and photosensitized devices research. Also, the fabrication method may be applied to other chitin substrate template and metal oxide systems that could eventually lead to the production of optical, magnetic, or electric devices or components as building blocks for nanoelectronic, magnetic, or photonic integrated systems.

5. Summary

As described in this review, significant developments have been made in Bio-inspired materials using nature materials as templates during the last years. The field continues to grow internationally and contribute to new interdisciplinary areas concerned with the synthesis, self-assembly and processing of organized matter across arrange of length scales. Bio-inspired materials, as the result of learning from nature, will change our life styles and bring us to a higher level of civilization. The fabrication method may be applied to other nature substrate template and inorganic systems that could eventually lead to the production of optical, magnetic, or electric devices or components as building blocks for nanoelectronic, magnetic, or photonic integrated systems.

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