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Photonic structure arrays generated using butterfly wing scales as biological units

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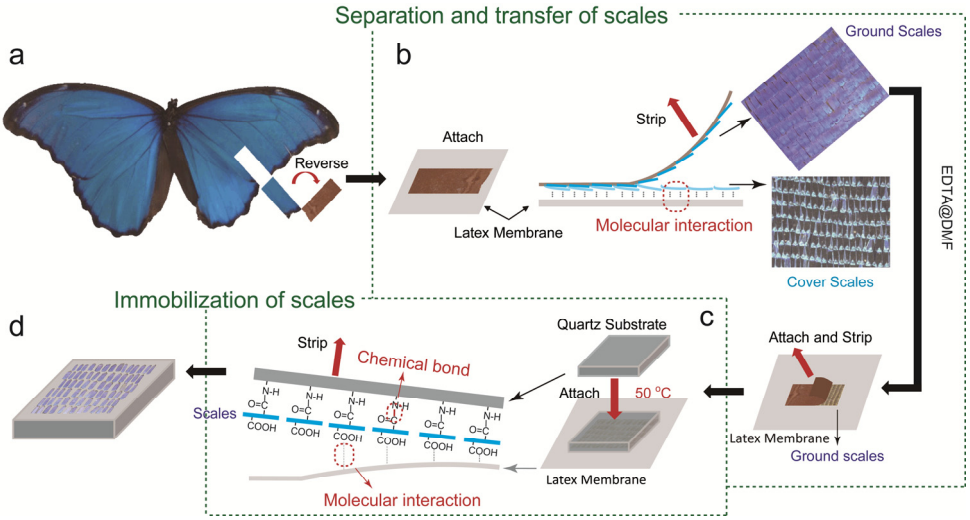
We report an effective process to transfer the scales of *Morpho* butterflies onto various substrates. Based on the difference in binding strength between molecular interactions and chemical bonds, this method provides photonic structure arrays with biological units, which is difficult to obtain otherwise.

Morpho butterflies are famous for their metallic blue colors,[1] which, as "structural colors", originate from the discrete multi-layers of cuticle and air equipped on the dorsal surface of butterflies' wing scales.[2] Such sub-micrometer textures are regarded as natural three-dimensional (3D) photonic structures that present blue colors visible from an ultra-long distance and generate a high-contrast color change with minimal movements as well.[1,2] These unique qualities have so far attracted considerable attention in terms of light manipulation.[3-6] For example, original *Morpho* butterfly scales can serve as photonic sensors for vapor detection[3] and optical resonators for visualizing mid-wave infrared radiation.[4,5] Also, the replication of these structures yields novel functional materials with excellent performance and low cost in many fields,[7-19] including the design of photoanodes,[9] surface-enhanced Raman scattering (SERS) substrates,[16] and smart hydrogels,[17,19] *et al*. Since hierarchical 3D photonic structures are still difficult to fabricate at present, all these works demonstrate the intriguing broad range of applications of such nature-designed unique photonic textures.

However, the natural bending, piling, and stacking modes of original butterfly scales are uncontrollable, which drastically affects the overall performance and scientific characterization of scales because of their strongly angle-dependent optical properties.[10,14,15] Moreover, many other wing parts except those desired scales (*e.g.*, wing membranes and the scales on the back



Scheme 1 Fabrication procedure for the biological PSAs. (a) Original *M. menelaus*. (b) Scale transfer process. A *M. menelaus* wing was first attached on a latex membrane and was then stripped off to separate the so-called "ground scales" from "cover scales". Ground scales were left on another latex membrane using the same attaching/stripping method after an additional EDTA treatment. (c) Scale immobilization process. An aminated quartz substrate was placed on these ground scales with chemical bonds formed under 50°C. (d) The quartz substrate was lifted off with the PSA of scales stuck on it.

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side of butterfly wings) are redundant but occupy a large portion in the final fabricated products.[7-9] To take full advantage of these biological photonic structures and to further incorporate them into devices, a large number of butterfly scales should be efficiently transferred and immobilized onto target substrates without destroying the surface features of scales. This immobilization process may also help keep the fragile scales intact and flat during chemical heat treatment.[16-18] To date, unfortunately, there has not been such a satisfying method yet to fulfil this process. To be immobilized on target substrates (*e.g.*, quartz or silicon wafers), individual scales were either picked up tediously one by one for hours using a metallic needle,[15-18] or transferred using some adhesives but with their fine structures somewhat destroyed.[12] Such situation greatly hinders the development of novel functional materials or devices based on butterfly scales.[14-18]

Here, we report an effective method to efficiently transfer the scales of *Morpho menelaus* onto various substrates to form photonic structure arrays (PSAs, Scheme 1). This route is constructed based on the difference in the binding strength between molecular interactions and chemical bonds. We first used alkali-treated latex membranes to peel the scales off from the activated butterfly wing surface full of hydroxyl or carboxyl groups *via* van der Waals' forces and hydrogen bonds (Scale-transfer process, Scheme 1(b)). Then the scales from the latex membranes were immobilized onto aminated quartz or silicon substrates by forming chemical bonds (Scale-immobilization process, Scheme 1(c)). This method provides an important road toward the mass-production of butterfly wing scales in a broad range of areas such as optical displays, SERS substrates, and electro-optical components.[1-4,7-19]

Before the scale-transfer process, the surfaces of both latex membranes and scales need to be activated first as they do not contain enough active sites to generate effective interactions. Original surfaces of butterfly scales are composed of protein and chitin whose type and composition slightly vary in different scales.[20] Such surfaces were first activated *via* HNO_3 to expose more amino and hydroxyl groups. However, it should be noted that like many other butterfly species, *M. menelaus* has more than one layer of scales on its dorsal wing surface, denoted hereby as cover scales and ground scales, respectively (Supp. Fig. 1). The tiling of these two types of scales render *M. menelaus* iridescent metal-like colors.[21] Usually, these two layers were treated together to fabricate functional materials because of the lack of an effective method to separate them apart. Here, however, we have achieved this purpose by controlling the interactions between the surfaces of scales and latex membranes, generating two types of PSAs with different photonic units (Supp. Fig. 1).

To reveal such molecular interactions, we performed Fourier transform infrared spectroscopy (FTIR) measurement for both butterfly scales and latex membranes. For the butterfly cover scales treated with nitric acid (W2, Fig. 1(a)), the wide absorption peak at ~3283 cm^{-1} (stretching vibration mode of $–NH_2$ and –OH), the peaks at ~1652 and ~1539 cm^{-1} (C=O stretching and N–H bending mode, respectively), and the peaks showed in dotted eclipse (stretching vibration mode of C–N and C–O bonds)[22] were all higher than those in W1 (original scales), indicating that the

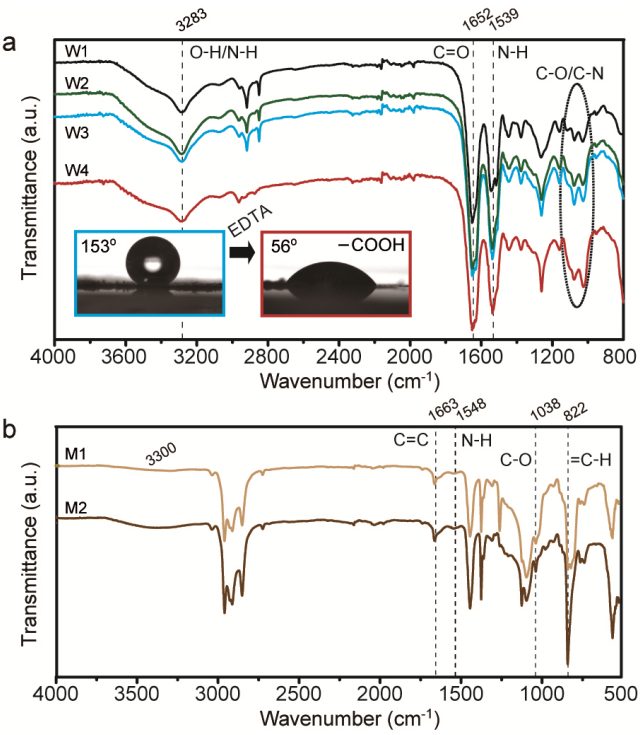

Fig. 1 Characterization of the scale transfer process. (a) FTIR spectra of original wings (W1), cover scales (W2) and ground scales treated using HNO_3 (W3), and ground scales treated with EDTA/DMF (W4). Inset shows the contact angle change of a droplet on the ground scales before and after the EDTA treatment. (b) FTIR spectra of latex membranes before (M1) and after alkali treatment (M2).

scales exposed more $–NH_2$, –OH, and –COOH groups after the activation process.

Compared with cover scales, however, ground scales (W3) show less active sites even after the HNO_3 treatment. As shown by the FTIR spectra of W2 and W3 (Fig. 1(a)), the absorption peaks of ground scales (W3) at ~3283, ~1652, and ~1539 cm^{-1} were all weaker than those of cover scales (W2), indicating the less presence of $–NH_2$ and –OH groups at the ground scales' surface. As a result, the ground scales treated with HNO_3 still could not attach onto the latex membranes as their cover counterparts did (Supp. Fig. 2(a) and (b)). Therefore, we used ethylenediaminetetraacetic acid (EDTA)/N,N-dimethylformamide (DMF) solution to further increase the activation cites on these scales, because EDTA can react with ground scales' $–NH_2$ and –OH groups and introduce more –COOH groups.[11] As shown by the spectra of W3 and W4 in Fig. 1(a), the double peaks at ~2850 and ~2917 cm^{-1} were weakened in W4 because of the decreased number of the $–NH_2$ groups after the EDTA treatment, while the double peaks at ~1076 and ~1030 cm^{-1} were enhanced due to the increased number of C–O bonds from EDTA. We also conducted contact angle measurements in air ambient to study this modification (inset in Fig. 1(a)). The contact angle of a water droplet on the scales changed from 153° to 56° after the EDTA treatment for the scale surface, indicating the increase in the number of the hydrophilic –COOH groups. With such surfaces (W4 in Fig. 1(a)), the ground scales could be well transferred (Supp. Fig. 2(c)) *via* molecular interactions onto latex membranes. These membranes contain a large number of C=C groups from

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their main component polyisoprene and some –COOH and –NH_2 groups from protein,[23] which were further exposed by a pre-treatment in an aqueous solution of NaOH (Fig. 1(b)).

To immobilize the scales peeled off with latex membranes onto quartz substrates, we aminated the quartz surface by first using H_2SO_4/H_2O_2 to expose more –OH groups and subsequently applying (3-aminopropyl)triethoxysilane (APTES)/ethanol to introduce –NH_2 groups on the surface. As shown in Fig. 2(a), the contact angle of substrates changed from 32° to 16° after the H_2SO_4/H_2O_2 treatment and then to 43° after the exposure to APTES/ethanol solutions, suggesting the formation of amino groups.[24] Strong chemical bonds were then generated between the –NH_2 groups of APTES and –COOH of EDTA *via* a heat treatment at 50°C for 3 h, which immobilized the ground scales from the latex membrane on the quartz surface (Fig. 2(b) and (c)). Although such a process needs catalysts to accelerate the departure of the resulting H_2O in liquid phase conditions, our method was conducted in open air and the evaporation of water facilitated the formation of amide bonds as well. The as-fabricated biological

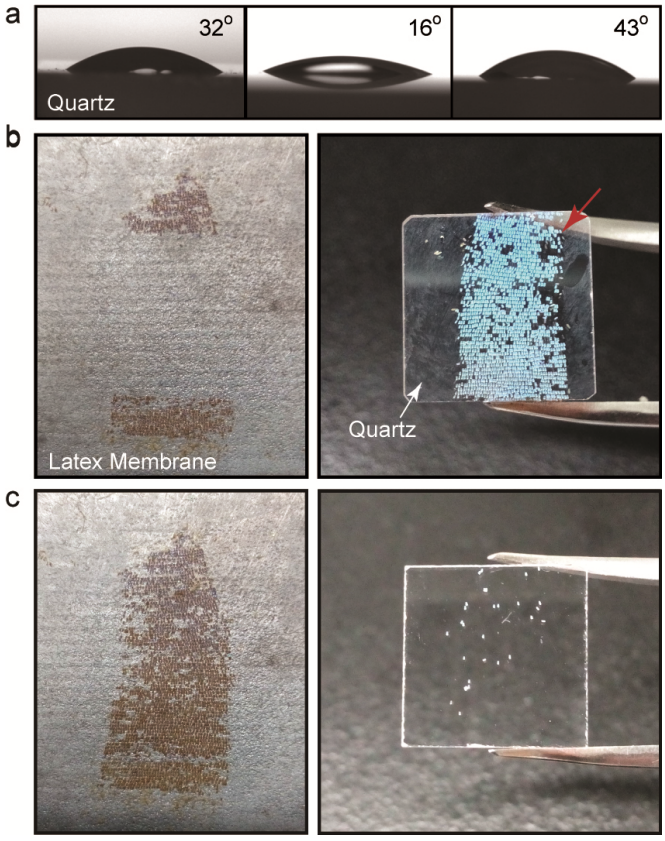

Fig. 2 Characterization of the scale immobilization process.(a) Contact angle measurement. Panels from left to right show a water droplet on the original quartz substrate, the substrate treated with H_2SO_4/H_2O_2, and the substrate subsequently exposed to APTES/ethanol, respectively. (b) and (c) show the possibility for the ground scales to be immobilized on the quartz surface with (b) or without (c) the heat treatment (50°C for 3 h), indicating the importance of forming chemical bonds.

PSAs could even be sonicated in water for 1 min (40 kHz, 240 W) with almost no scales detached, confirming that they were firmly attached to the substrate. In comparison, we immobilized the cover scales on quartz substrates without performing the EDTA/DMF and subsequent heat treatment. Results show that the flat back surface of cover scales provided a stronger interaction with quartz substrates than that with latex membrane, which makes the transfer possible. However, since no chemical bonds were formed between cover scales and quartz substrate in this case, the binding remains as molecular interactions and the cover scales can be easily shaken off by sonication (Supp. Fig. 3).

Interestingly, the optical property of these biological photonic structures can be further tuned by adjusting the process of present method (Supp. Fig. 4). Tunable colors have been achieved for butterfly wing scales[7,17-19] like for many other photonic structures.[25-27] For example, single-wing-scale/hydrogel hybrids can show a red-shift in their reflectance spectra with the increase in the distance between the "ridges" on each scale.[17] However, such hybrids inevitably contain water, bringing great difficulties in subsequent chemical or physical processes to convert these structures into other functional components (*i.e.*, metals or semiconductors).[15,16,18] In comparison, the blue PSAs on a quartz substrate changed their colors to cyan, and then to green, with the stretching of the latex membrane before the scale-immobilization process on quartz (Supp. Fig. 4(b)). Accordingly, their reflectance peaks moved from ~442 nm to ~487 nm, and then to ~518 nm, showing a red-shift of ~77 nm (Supp. Fig. 4(c)). This phenomenon is consistent with the experimental and simulation results reported in previous literatures,[17,19,28] where the reflectance peaks of scales could red-shift with the expansion of the scale lattice. This suggests the possibility (not confirmed yet) of the scale lattice expansion with the stretching of the latex membrane. Detailed statistical analysis of the relation between the lattice expansion and the membrane stretching is presently under way.

The PSAs can also be immobilized on other substrates, *e.g.*, on silicon wafers (Supp. Fig. 5) pre-treated *via* the same processes as the quartz substrates experienced. Moreover, the immobilized biological PSAs can be further replicated in various materials to form functional arrays. For example, they can be replicated in oxides by a wet-chemical plus calcination method (*e.g.*, ZnO, Supp. Fig. 6),[9,10,14,15,29] or in metals by a direct physical vapor deposition (PVD) process,[30] which can greatly broaden their applications. Figure 3 demonstrates an application (chemical detection) of Au PSAs as SERS substrates. These substrates were prepared *via* a simple ion sputtering process. Previous SERS substrates based on Au butterfly scales comprised either one tiny single scale with a small surface area or a whole butterfly wing with various scales tiling and overlapping each other.[16,30,31] In comparison, the SERS substrates prepared here can have their functional units efficiently separated and well defined. As shown in Fig. 3(b), the Raman signals of rhodamine 6G (R6G) collected on

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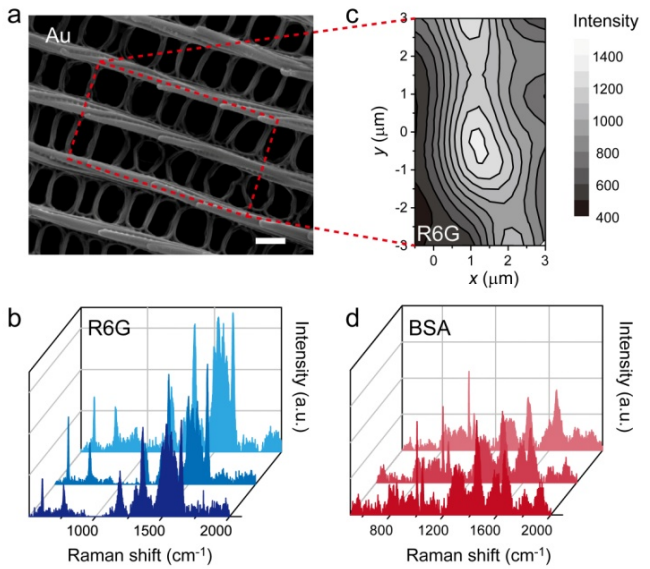

Fig. 3 Chemical detection using Au scale arrays as SERS substrates. (a) SEM image of a Au scale as an array unit. Scale bar: 1 μm. (b) Raman spectra of R6G (10^{-6} M) collected on various array units. (c) provides a mapping result of Raman signals of R6G at 1650 cm^{-1}. The rectangle of broken line in (a) schematically denotes the scanned area. (d) Raman spectra of BSA (50 μg mL^{-1}) on various array units.

three individual scales are reproducible, while thousands of such scales can be simultaneously generated and well-arranged on a support. For bio-detection, we studied the Raman signals of an aqueous solution of bovine serum albumin (BSA) dripped on Au scale arrays. Compared with previous BSA detections (~66 μg mL^{-1}) using electron-beam lithographed Au nanoparticles as SERS substrates,[32] the Raman signals of BSA collected on our Au scale arrays are comparable in terms of Raman enhancement effect and signal reproducibility. Since there are no high-tech equipments involved in preparing these Au scale arrays, the process reported here may generate high quality SERS substrates with low cost for chemical detections.

Conclusions

We have successfully separated and transferred various *M. menelaus*' wing scales onto different substrates, constituting orderly biological photonic structure arrays for the first time. The process is fulfilled by the step-by-step modification of the bonding between the scales and various substrates that successively bearing them. Moreover, the as-fabricated PSAs can be further replicated into other functional materials, which greatly extends the reach of the applications of these novel PSAs. This method has thus paved the way for the use of butterfly wing scales as optic or plasmonic devices/sensors, where large quantity, well separation, and well arrangement of these biological PSA units are required. Such PSAs as bio-templates are now being replicated into more kinds of functional materials for the applications in photovoltaic devices, colorimetric sensors, and SERS substrates, *et al*..

Methods

M. menelaus specimens were purchased from Shanghai Qiuyu Co. Ltd.. Concentrated sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2) solution, APTES, sodium hydroxide (NaOH), concentrated nitric acid (HNO_3), EDTA, and DMF of analytical grade were purchased from Sinopharm Chemical Reagent Co. Ltd., China, and were used as received. R6G of reagent grade was bought from Sigma-Aldrich. BSA powders of molecular biology grade were purchased from Aladdin Industrial Inc.

Quartz substrates were provided by Yixing Gaoke Co. Ltd., China. They were first soaked in a soap solution and sonicated for several minutes to remove organic residues, and were then rinsed with distilled water. The cleaned substrates were immersed in a mixture of 98 wt% H_2SO_4 and 50 wt% H_2O_2 with a volume ratio of 7:3, kept at 80°C for 40 min to expose their surface hydroxyls, and rinsed in distilled water for several times. The activated substrates were subsequently placed into an ethanol solution of APTES with a volume concentration of 1:15 and kept at 50°C for 2 h to graft amino groups onto the substrates. After the reaction, the substrates were washed with ethanol and distilled water successively and dried in vacuum.

Latex membranes from condoms (Donless^{RT}, China) were first washed with ethanol to get rid of lubricants. These membranes were then immersed in a 9 wt% NaOH water solution at 50°C for 1 min to increase their stickiness. After the alkali treatment, the latex membranes were rinsed with distilled water for several times and cut into pieces with a square shape of ~3 cm×3 cm in size.

An original butterfly wing was first immersed in a diluted HNO_3 ethanol solution (9 vol%) at 50°C for 6 h to expose its amino and hydroxyl groups, and was washed with distilled water afterwards. Then, the wing was carefully placed on the latex membrane and flattened with a forceps. The extra water was soaked up using filter paper. After waiting for 30 min under room condition, the wing thoroughly dried up. We subsequently used the forceps to slowly strip the wing substrate off and left the cover scales on the latex membrane. The remaining wing bearing ground scales was further treated with an activation medium prepared by dispersing 1 g EDTA in 10 mL DMF at 110°C for 5 h, and washed with DMF and distilled water successively afterwards. Again, this treated wing was attached on another latex membrane and the wing substrate was stripped off, leaving the ground scales on the latex membrane. PSAs with two various types of biological units were thus obtained.

Scanning electron microscopy (SEM) was carried out on a field emission SEM (Quanta 250, FEI). Optical images were taken using an optical microscope (VHX-600, Keyence). Reflectance spectra were measured on a spectrometer (Maya

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2000, Ocean Optics) using a non-polarized xenon light source. FTIR measurements were conducted using a Fourier transform infrared spectrometer (Nicolet 6700, Thermo Fisher). Contact angles were recorded with an optical contact angle measurement device (OCA20 from Dataphysics).

As SERS substrates, Au scale arrays were prepared by sputtering Au (~20 nm in thickness) onto the scale arrays immobilized on quartz substrates using an ion sputter & carbon coating unit (E-1045, Hitachi). A R6G ethanol solution (10^{-6} M×100 μL) and a BSA water solution (50 μg mL^{-1}×100 μL) were dripped onto the surfaces of two various Au arrays and dried at 30°C, respectively. The Raman measurements were conducted on a Raman spectrometer (LabRAM HR Evolution, Horiba) equipped with a ×50 objective lens and operated using a 532 nm laser. The laser beam was ~2 μm in diameter. The Raman mapping of R6G was conducted using the Raman shift peak of 1650 cm^{-1}.

Acknowledgements

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Differences between two kinds of PSAs on quartz substrates; Attachment ability of various scales on latex membrane; Necessarity of forming chemical bonds during the immobilization process; Reflectance change of bio-PSAs by stretching latex membranes; PSAs immobilized on Si wafers; ZnO PSAs].

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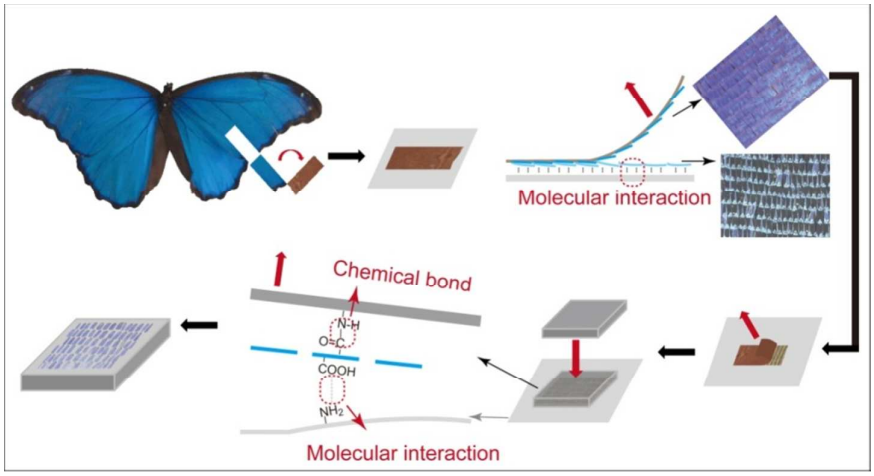
Photonic structure arrays generated using butterfly wing scales as biological units



Photonic structure arrays composed of biological units have been generated via a binding difference between molecular interactions and chemical bonds.

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