Thermoresponsive Photonic Crystal: Synergistic Effect of Poly(*N*-isopropylacrylamide)-*co*-acrylic Acid and *Morpho* Butterfly Wing

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S *Supporting Information*

ABSTRACT: In this work, we report a simple method to fabricate smart polymers engineered with hierarchical photonic structures of *Morpho* butterfly wing to present high performance that are capable of color tunability over temperature. The materials were assembled by combining functional temperature responsivity of poly(*N*-isopropylacryla-mide)-*co*-acrylic acid (PNIPAm-*co*-AAc) with the biological photonic crystal (PC) structure of *Morpho* butterfly wing, and then the synergistic effect between the functional polymer and the natural PC structure was created. Their cooperativity is instantiated in the phase transition of PNIPAm-*co*-AAc (varying with the change of temperature) that can alter the nanostructure of PCs, which further leads to the reversible spectrum response property of the modified hierarchical photonic structures. The cost-effective biomimetic technique presented here highlights the bright prospect of fabrication of more stimuli-responsive functional materials via coassembling smart polymers and biohier-archical structures, and it will be an important platform for the development of nanosmart biomaterials.

KEYWORDS: *biomaterials, temperature-responsive, photonic crystals, polymerization, functional polymers*
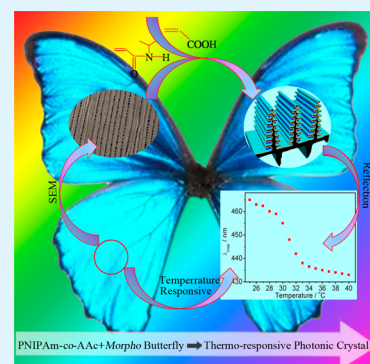
■ INTRODUCTION

Photonic crystals (PCs), which are composed of periodic arrays of contrasting refractive index materials, have shown an increasing number of applications in ever-widening areas of science and technology, such as gas-based nonlinear optics,[1] atom and particle guidance,[2] nanocavity laser,[3] and ultrahigh nonlinearities,[4] since it was independently presented by John[5] and Yablonovitch[6] in 1987. In the last few decades, a series of photonic-sensing materials (e.g., Bragg mirrors,[7] Bragg stacks,[8] colloidal crystals,[9,10] and nanostructure arrays[11]) have been successfully fabricated artificially. Although innovative, these designs are difficult to adapt to measurements and fabrication with high intelligence in low cost. Specifically, fabrication of color tunable PCs under external stimuli (e.g., temperature,[12,13] magnetic field,[13] pH,[14,15] or mechanical force[16]) is of great significance in future sensor, biological detection, and photonic switch. However, it is still a great challenge to realize it.

Recent research shows that those unique features might be achieved if we move the design space away from the last 30 years of artificial fabrication technology to adapt instead the 5 million year old design features of the iridescent wings of the tropical *Morpho* butterfly.[17] As a natural PC structure, the iridescence of the butterfly wing (BW) is ascribed to the combined effects of light interference on the horizontal lamellae and light diffraction on the vertical ridges of the scales[17,18] as well as to the cooperation of chitin and air-spaces within a scale.[19] Therefore, the unique hierarchical biological photonic structures are believed to demonstrate outstanding perform-

ance. Potyrailo et al. reported that *Morpho* BWs indicated a highly selective reflectance spectrum response to a series of vapors because of their hierarchical PC structures.[18] Recently, smart polymer functionalized natural PCs of the butterfly wing have shown a great potential for the design of multifunctional PCs. Zhang et al. presented a pH-tunable PC on the basis of the electrostatic interaction between the $-NH_3^+$ of chitosan and the $-COO^-$ groups of polymethylacrylic acid,[14] which is a successful hierarchical photonic structure, and it can be expected to indicate high tunable performance with the stimulus of varying pH. Miyako et al. reported that poly(3-hexylthiophene)-modified-CNT functionalized BW can present the photothermal property under the laser radiation.[20] Nevertheless, to the best of our knowledge, no further research on the synergistic effect of smart polymer and natural PC structures has been reported.

In this article, for the first time, we report a novel thermoresponsive PC of hierarchical structures by coassembling temperature-responsive poly(*N*-isopropylacrylamide) (PNIPAm)-*co*-acrylic acid (AAc) and *Morpho* butterfly wings (PNIPAm-*co*-AAc-PC) together. Specifically, by forming hydrogen bonding with hierarchical BW, AAc acts as a bridge between NIPAm and biological PC, which further promotes the formation of the synergistic effect between PNIPAm layers and

natural photonic structures. Subsequently, the temperature-responsive PNIPAm could induce the transformation of PC structure on the basis of a surface bonding between PNIPAm and *Morpho* BW. The following theoretical analysis validates that only the volume change of PNIPAm-*co*-AAc induces transformation of the wing scale nanostructure, which brings about the temperature-responsive property of the obtained PNIPAm-*co*-AAc-PC. The unique temperature-induced color change can be detected by reflectance spectra indicating that the thermoresponsive PC is capable of converting thermal energy (temperature) into a characteristic optical signal. Therefore, our work provides an effective method to prepare tunable PCs with hierarchical structures on the basis of the design of the synergistic effect between smart polymers and natural PC structures.

EXPERIMENTAL SECTION

Materials. The *Morpho* butterfly was supplied by Shanghai Dieyu Biological Technology Co., Ltd. *N*-Isopropylacrylamide (NIPAm) was purchased from Shanghai TCI (Tokyo Chemical Industry) and was used as received. Ethylene glycol dimethyl acrylate (EDGMA) and acrylic acid (AAc) were obtained from Aladdin Chemistry Co., Ltd. 2,2′-Azobis (isobutyronitrile) (AIBN), NaCl, HCl, $NaH_2PO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 12H_2O$, NaOH, and absolute alcohol were purchased from Sinopharm Chemical Reagent Co., Ltd. AIBN and AAc were distilled before use to remove the polymerization inhibitor.

Amination of Butterfly Wings. The original butterfly wings were pretreated by dipping in absolute alcohol for 0.5 h and were then immersed in 6 wt % HCl aqueous solution for 3 h. Subsequently, the resultant BWs were washed with distilled water and ethanol. After drying under the natural conditions at room temperature, as-prepared BWs were carefully dipped into a 10 wt % NaOH aqueous solution at 60 °C for 15 min to switch the surface chitin of the original BWs into chitosan.

Preparation of PNIPAm-*co*-AAc-PCs. The modified BWs were immersed in a 5 mL anhydrous ethanol solution containing 16 mmol NIPAm monomer, 8 mmol AAc, 6 mmol cross-linking agent EGDMA, and 0.01g initiator AIBN (6.1 mmol) at room temperature, and the process lasted for 24 h, which would be helpful for the complete soakage of amination-BWs in the precursor solution. Then, we brought out the biotemplate and removed excess surface liquid with filter paper through a capillary. Next, the polymerization was carried out on the surface of the amination-BWs when the temperature increased from room temperature to 65 °C. After polymerization for 24 h, the temperature-responsive photonic crystals with hierarchical structures were obtained.

Sample Characterization. The morphologies of the samples were analyzed by a field-emission scanning electron microscope (FE-SEM, JEOR JSM-6700F) at an accelerating voltage of 10 kV. Fourier transform infrared spectra (FTIR) of the products were recorded on KBr pellets with a TENSOR 27 FTIR spectrometer (Bruker) in the absorption mode with resolution of 2 cm^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were made on an ESCALABMK spectrometer using the electrostatic lens mode with a pass energy of 100 eV. Al Kα radiation was used as the excitation source. Thermal gravimetric analysis (TGA) was conducted on a SMP/PF7548/MET/600W instrument from 25 to 600 °C with a heating rate of 10 °C·min^{-1}. The digital optical photographs of the butterfly wings were taken using an OLYMPUS BX51 optical microscope.

Characterization of Temperature-Responsive Properties. A Cary 500 UV−vis−NIR microspectrophotometer was used to investigate the temperature-responsive optical property, equipped with the 89090A temperature controller and Peltier heating device. The temperature was recorded in the range of 25−40 °C, and the spectrum data was collected every 1 °C after waiting 5 min at each temperature for stabilization.

RESULTS AND DISCUSSION

Our design is inspired by the photonic nanoarchitecture of *Morpho* butterfly scales (Figure 1) and suggests a strategy for
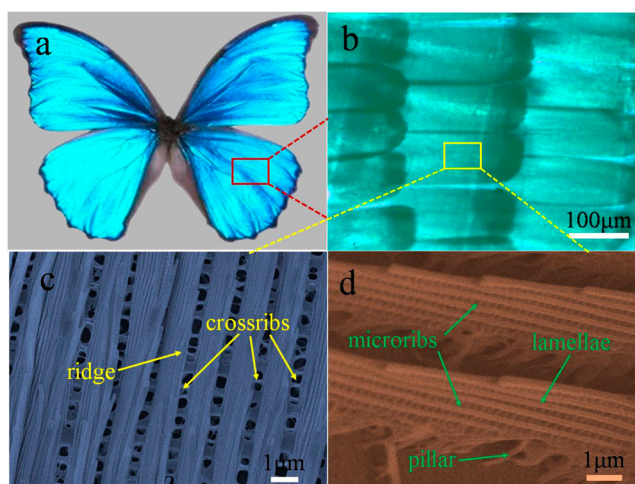

Figure 1. Appearance and structures of the butterfly with one-dimensional photonic crystal structure. (a) Digital photo of overall view of natural *Morpho* butterfly, (b) optical microscopy image of the wing scales, and SEM images from (c) a vertical view and (d) a horizontal view.

the development of tunable PCs with hierarchical structures. The shining blue *Morpho* BWs (Figure 1a) comprise alternating layers of rectangle-like scales (slight round in the front part). Uniformly and densely, these scales are arranged on the surface of the wings regularly, with a dimension of 150 μm in length and 80 μm in width (Figure 1b). Within iridescent BW scales, PC structures are formed through the periodic configuration of cuticle and air-spaces, as revealed in Figure 1c and d. Each scale is composed of many ridges in stripes (Figure 1c), which are supported by crossribs and which are aligned along the scale longitudinal direction. From the cross section view of these ridges (Figure 1d), we can see that the ridges about 2 μm high are stacked with seven-layer lamellae, each of which is around 100 nm thick and which is connected by several microribs to sustain the porous architecture (Figure S1 of the Supporting Information). All the ridges, ribs, and lamellae are supported by columnar pillars, which are formed by a single epithelial cell that secretes the inner layers of the cuticle. The color is caused by multilayer stacks with alternating chitin layers and air.

Deacetylation of the wing template has been crucial in most biotemplating processes, since the results show that more than 83% of the components in the wing scales is chitin, which is made of units of *N*-acetylglucosamine.[21] Accordingly, the chitin/chitosan chemistry becomes necessary because people need to expose free active groups, such as amino groups, to facilitate the biotemplating fabrication process.[21−23] It has been reported that the chitin/chitosan chemistry is beneficial for the polymer to coat homogeneously on the natural hierarchical

Scheme 1. Overall Synthesis of Thermoresponsive PCs from *Morpho* BWs[a]
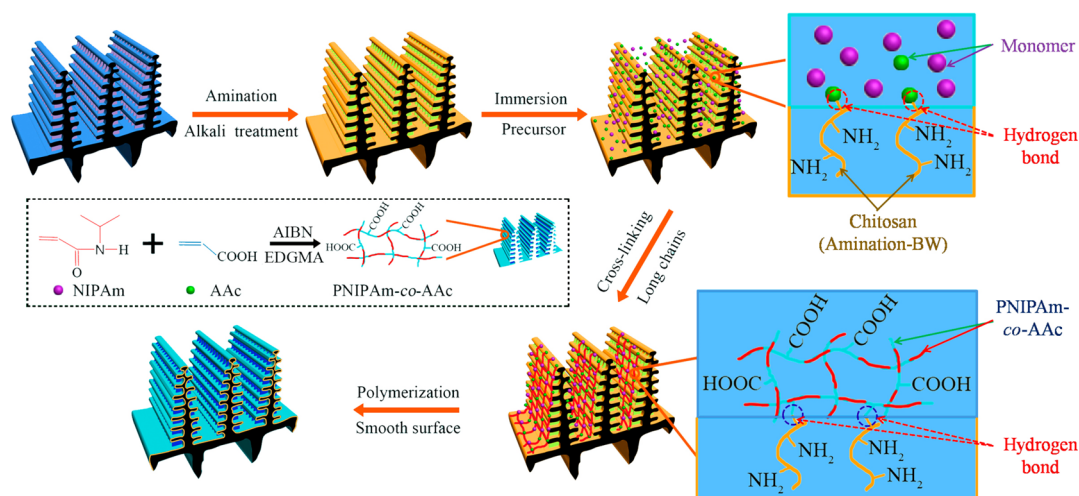
[a]The biotemplate indicates the PC structure, and the amination process was used to expose more free active reaction groups. AAc was introduced to fix on the biotemplate, and NIPAm provided the temperature-responsive property.

photonic structures. In 2013, Zhang et al. successfully fabricated a pH-tunable PC through the deposition of polymethylacrylic acid (PMAA) onto a *Morpho* butterfly wing template by using a surface bonding and polymerization route.[14] The pH-responsive property was achieved by the change of chemical bond between −NH$_2$ of chitosan and −COOH of PMAA in their system. In our study, we focus on providing a platform for the fabrication of more stimuli-responsive functional materials via coassembling smart polymers and biohierarchical structure. Indispensably, an essential requirement for the objective is the realization of stimuli-responsive property without the component transformation of natural substrate (mainly −NH$_2$ of chitosan). Accurately, in our system, physical volume variation induced phase transition of smart polymers was designed to change the biological hierarchical PC structure. Barely, acting as a bridge to connect smart polymers with the natural PC structure, a chemical bond between −NH$_2$ of chitosan and −COOH of polymer has no influence on PC structure.

In Scheme 1, we illustrate the overall process of thermoresponsive PCs synthesis from *Morpho* BWs. First, the chitin/chitosan chemistry (amination) of BW was implemented by alkali treatment. Then, AAc was introduced to fix on the wing scales, generating the hydrogen bonding between the carboxyl groups of AAc and the amino groups of the amination-BW. Subsequently, the PNIPAm-*co*-AAc could be obtained by the polymerization of −C=C− between AAc and NIPAm. Finally, the temperature-responsive copolymer was perfectly introduced onto the PCs of hierarchical structures by in situ polymerization. Notably, the hydrogen bonding between polymer and wing scales plays a crucial role in the uniform coating. In the control experiment, we can prove that the single PNIPAm dispersion on the biotemplate is not uniform, as evidenced by Figure S2 of the Supporting Information, because there is no reaction site for the formation of hydrogen bonding between the groups of NIPAm and the amino groups.[21] SEM images indicate that the PNIPAm-*co*-AAc with fine hierarchical photonic structures has been successfully fabricated because of the hydrogen bonding. Low-magnification images reveal that both PNIPAm-*co*-AAc-PCs and the amination-BWs consist of scales that have parallel ridges (Figure S3 of the Supporting Information). The smooth surface of PNIPAm-*co*-AAc-PCs

demonstrates the homogeneous polymerization of PNIPAm-*co*-AAc on BWs.[14] Specifically, the polymerization can be deduced by the change on the width of the ridge, which ascends from 105 nm in amination-BW (Figure 2a) to 120 nm in PNIPAm-
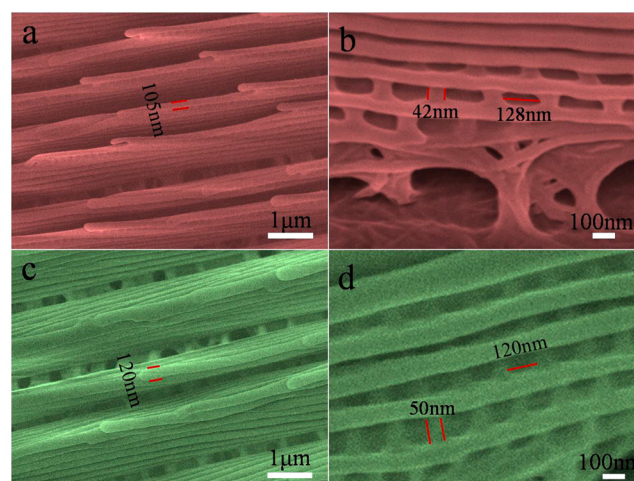

Figure 2. SEM micrographs of (a, b) amination-butterfly wing and (c, d) PNIPAm-*co*-AAc-PC.

co-AAc-PCs (Figure 2c). The same result also can be obtained by an increase of 8 nm in the width of a microrib and an equal decrease of rib-gap, as evidenced by Figure 2b and d. Thus, it is obvious that PNIPAm-*co*-AAc-PCs inherited the intricate and highly interconnected hierarchical structure of the original BWs in our fabrication.

The thermogravimetric analysis (TGA) technology is usually used to differentiate the thermostability and components of materials. In our study (Figure 3), the nearly same TGA curves of amination-BW and PNIPAm-*co*-AAc-PC indicate that they share a common substrate of the wing scales. On the other hand, the difference of the last transition temperature (490 °C for the former, the decomposition of chitin/chitosan; while 530 °C for the latter, the decomposition of complex) reveals that they are not identical components. Besides, when the temperature reaches 600 °C, the residue of the biotemplate is
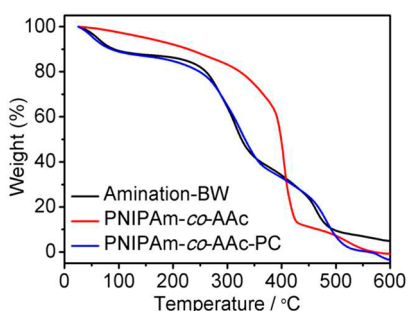
Figure 3. TGA curves of different samples.

about 8 wt %, while PNIPAm-*co*-AAc-PC is completely exhausted. Therefore, according to the TGA results, we can confirm that PNIPAm-*co*-AAc layers have been coated on the hierarchical photonic structures of the biotemplate successfully.

As an effective method to detect the composition of materials, Fourier transform infrared (FTIR) spectroscopy was used to investigate whether there is an interaction between amination-BW and PNIPAm-*co*-AAc. As shown in Figure 4a,
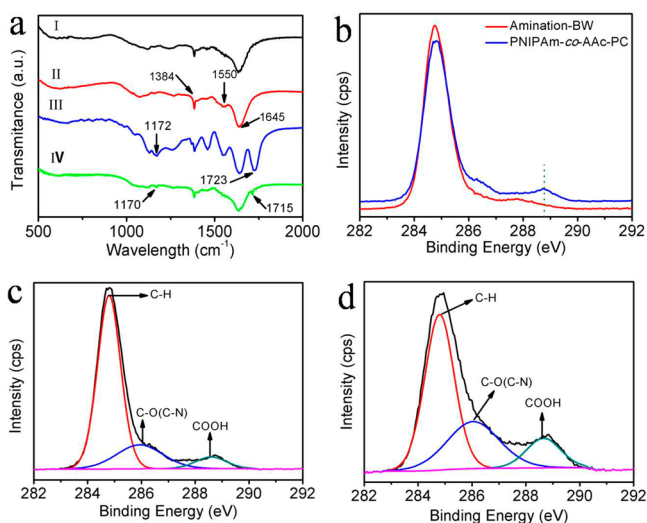

Figure 4. (a) FTIR spectra of I, BW; II, amination-BW; III, PNIPAm-*co*-AAc; and IV, PNIPAm-*co*-AAc-PC. (b) C 1s XPS contrastive analysis of amination-BW and PNIPAm-*co*-AAc-PC. (c) C 1s peaks of PNIPAm-*co*-AAc-PC. (d) C 1s peaks of PNIPAm-*co*-AAc.

there is no significant difference between the absorption lines of BW and amination-BW, in addition to the slightly stronger peak of the latter, especially for the peak at 1550 cm^{-1} (amide II vibration, $-NH_2$ bonding in nonacetylated 2-aminoglucose primary amine; the enhancement represents a transformation of the chitin in BWs into chitosan that exposes more free $-NH_2$ functional groups).[14,23] The characteristic absorption peaks at 1645 and 1384 cm^{-1} are attributed to the $-C=O$ (amide I vibration) and $-N-H$ stretching or $-C-N$ bond stretching vibrations (amide III vibration),[23] respectively. Similarly, as a polymer containing amide groups, PNIPAm-*co*-AAc presents the same feature peaks between 1360 and 1650 cm^{-1}.[24] Compared with an absorption line at 1172 cm^{-1} for PNIPAm-*co*-AAc, a new absorption line at 1170 cm^{-1} is observed in PNIPAm-*co*-AAc-PC for the vibration of the isopropyl group, indicating that the PNIPAm-*co*-AAc grows on the surface of amination-BW.[24,25] The characteristic peaks at 1723 cm^{-1} in

PNIPAm-*co*-AAc and 1715 cm^{-1} in PNIPAm-*co*-AAc-PC demonstrate the existence of AAc in the copolymer,[24] as evidenced by Figure 4a III and IV.

To get more detailed insight into the composition of the different samples, X-ray photoelectron spectroscopy (XPS) analysis was performed on these materials. Typical peaks for C 1s, N 1s, and O 1s are observed for all the samples (Figure S4 of the Supporting Information). By comparing the C 1s spectra of amination-BW and PNIPAm-*co*-AAc-PC, the expected new peak for the carboxyl C (COOH) at 288.8 eV[14] (Figure 4b) in PNIPAm-*co*-AAc-PC suggests deposition of PNIPAm-*co*-AAc on the butterfly surface. This is further supported by the peak-differentation-imitating analysis of PNIPAm-*co*-AAc-PC (Figure 4c) and PNIPAm-*co*-AAc (Figure 4d), which indicates that they have similar binding energy values of 284.58 eV (aliphatic carbon, C−C, C−H),[26,27] 286.03 eV (C−O or C−N),[14,26] and 288.8 eV (COOH).[14]

The functionalities of their spectral properties with variation of temperature have been tested and are described in the following part. First, we investigate the different reflection spectra of BW, amination-BW, and the final PNIPAm-*co*-AAc-PC. As shown in Figure 5a, the BW exhibits the strongest
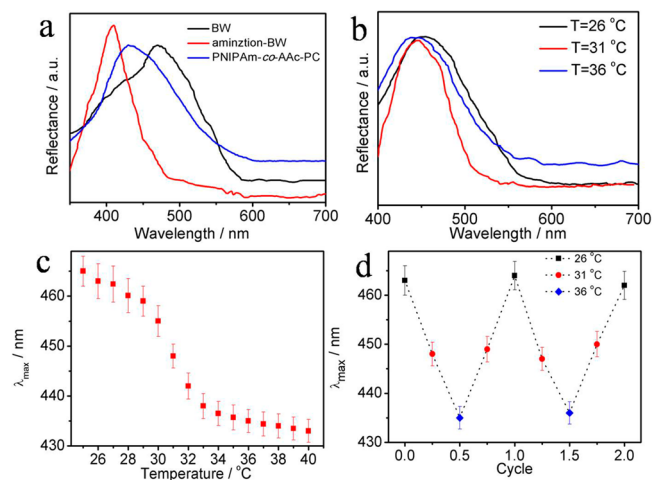

Figure 5. (a) Reflection spectra of natural butterfly wing, the amination-wing, and the final PNIPAm-*co*-AAc-PC sample. (b) Reflection spectra of PNIPAm-*co*-AAc-PC at different temperatures. (c) λ_{max} of PNIPAm-*co*-AAc-PC versus temperature. (d) Evaluating the reversibility of the temperature-dependent optical property at multiple cycles of the temperature value.

reflection around 470 nm, while the amination-BW shows a blue-shift reflection peak at 410 nm. When PNIPAm-*co*-AAc is coated on the amination-BW, correspondingly a red-shift reflection peak occurs for the PNIPAm-*co*-AAc-PC at 430 nm. The difference can be ascribed to the change in refractive indexes (n) of chitin (n = 1.56),[14,28] chitosan (n = 1.59),[29] PNIPAm (n = 1.495),[30] and AAc (n = 1.479).[31] Typically, the temperature-dependent optical property of PNIPAm-*co*-AAc-PC is shown in Figure 5b. Notably, the collapse transition of PNIPAm-*co*-AAc could be hindered if the pH for the copolymer is above pK_a of AAc (the pK_a of AAc is 4.25), which is a result of Coulombic repulsion between the deprotonated AAc.[12] Therefore, full thermoresponsive property can only be achieved when the pH is below 4.25. In our study, absorbance measurements were conducted in the pH = 3.0 solution (1 mM ionic strength adjusted with NaCl, as the local

Scheme 2. Mechanism for the Temperature Responsiveness of PNIPAm-*co*-AAc-PCs[a]
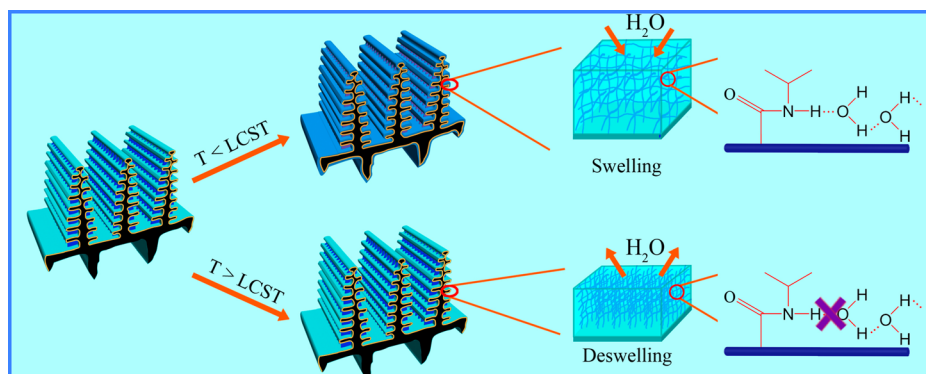
[a]The changing temperature results in the transformation of PC structures by the swelling/deswelling of the polymer with the enveloping/expelling of water molecules. The purple cross means an expel process of water molecules, as a few hydrophilically hydrated water molecules still interact with the amide groups in the collapsed state of the polymer.

ionic strength also has an effect on the response[32]). We get the information about λ_{max} dependence on temperature for PNIPAm-*co*-AAc-PC, and the experimental result is shown in Figure 5c. Apparently, the highest reflective peak exhibits a blue-shift with the increase of temperature, corresponding to the color change from bright blue ($\lambda_{max} = 463$ nm in 26 °C) to light blue ($\lambda_{max} = 435$ nm in 36 °C). It is well-known that as an extensively studied water-soluble thermoresponsive polymer, PNIPAm-*co*-AAc undergoes a coil (swollen) to a globule (collapsed) transition at 31 °C. During this transition process, the solvating water can be expelled;[12] accordingly in Figure 5c, a dramatic shift appears between 29 and 32 °C, which means a volume phase transition of PNIPAm-*co*-AAc occurring on the narrow range. To further investigate the durability of the obtained PNIPAm-*co*-AAc-PC, we had a test on the spectrum response of the sample in a changed temperature environment for a few cycles. Figure 5d shows the reversible change in λ_{max} of PNIPAm-*co*-AAc-PC as temperature varies, which indicates a satisfying durability of the PNIPAm-*co*-AAc-PC. This durability can be attributed to the physical volume change of the copolymer, which is more advantageous than the change caused by the chemical bond considering the reversibility.

According to our experimental results, we propose a mechanism for the optical variation of PNIPAm-*co*-AAc-PCs with different temperatures. For the hierarchical PCs, when the temperature is below the lower critical solution temperature (LCST) that corresponds to the volume phase transition temperature of PNIPAm-*co*-AAc, the macromolecules are enveloped by hydration shells, leading to the expansion of a polymer, which further results in an increasing thickness of the PC structures. Conversely, when the temperature is above the LCST of PNIPAm-*co*-AAc, the accompanying phase separation is caused by partial dehydration of the PNIPAm chains,[33] resulting in the collapse of the polymer volume and a decreasing thickness of the PC structure (hydrophobically hydrated water molecules, enveloping the *N*-isopropyl groups, are gradually expelling from the solvation layers of PNIPAm during phase separation), which is illustrated in Scheme 2. Furthermore, to validate theoretically the nature of the optical response of the final PNIPAm-*co*-AAc-PC and to confirm that it is due to the volume transition (swelling/deswelling behavior) of PNIPAm-*co*-AAc, we built a simple model to have a study. In the model, we took into account two factors for the optical variation of the hybrid: (1) thermal expansion that means the

relation between the increase of temperature and the *Morpho* nanostructure, and (2) thermo-optic effect, dn/dT, which means a rise in temperature T inducing change in the original BW refractive index n. As for factor 1, the increase in temperature (ΔT) of a sample leads to the thermal expansion of the sample (ΔL) described as the following equation.

$$\Delta L = L_o \alpha \Delta T$$

where α is the coefficient of linear thermal expansion and L_o is the initial length of the sample.[17] In our study, L_o is viewed as the space of lamellas and ridges in the wing scales. Generally, chitin/chitosan of the *Morpho* butterflies has a linear coefficient of thermal expansion of $(22-73) \times 10^{-6}$/°C,[34−37] resulting in space increases by $(330-1100) \times 10^{-6} L_o$ when we raise the temperature from 25 to 40 °C. Given that L_o of the wing scale is below 1 μm (Figures 1 and 2), the increase of ΔL is less than 1 nm, which almost has no influence on the optical response. Similarly, the thermo-optic coefficient (dn/dT) of BWs can be estimated as -32×10^{-6}/°C using an empirical linear relationship,[17,37] and so when we increase the temperature from 25 to 40 °C, the corresponding difference of n is -480×10^{-6}, which is negligible versus the original value of $n = 1.59$. Therefore, the reason for the temperature-responsive property of our PNIPAm-*co*-AAc-PC is the change of BW nanostructure induced by the volume change of PNIPAm-*co*-AAc and is not the thermal expansion or thermo-optic effect.

Usually, as the color of *Morpho* wing scales is related to refractive index and structural periodicity at the length scale of the wavelength of light used, people can change either of them to obtain a different reflectance spectrum. The foregoing discussion suggests that the spectral change caused by a thermally induced decrease in refractive index is negligible in our system. Therefore, the only way for preparing temperature-responsive PCs is to adjust the structural periodicity of *Morpho* BWs, which means changing the thickness of lamellae layers or the distance of ridges. Thus, our research offers valuable data support for the design of more stimuli-responsive functional materials with natural hierarchical structures. Also, our method, preparing tunable PCs with hierarchical structures based on the design of synergistic effect between smart polymers and biological substrate, provides a platform for the development of nanosmart biomaterials. Further coassembling biohierarchical structures with more functional polymer materials can be achieved from this platform.

CONCLUSIONS

In summary, we have demonstrated that the novel temperature-tunable PCs of hierarchical structures can be delicately fabricated by combining natural photonic crystals with a thermoresponsive polymer. The unique surface bonding and the polymerization route result in a homogeneously coating of PNIPAm-*co*-AAc on the hierarchical *Morpho* BW biotemplate. The fabricated PNIPAm-*co*-AAc-PC exhibits a reversible temperature response because of the variation of the nanostructure of PCs that is due to the changed volume of PNIPAm-*co*-AAc. Notably, PNIPAm-*co*-AAc-PC that presents synergistic effect between smart polymers and natural substrate is capable of converting thermal energy into characteristic optical signals. Thus, the coassembling method of smart polymers and biohierarchical structures supplies an effective route to obtain ideal stimuli-responsive materials of hierarchical photonic structures, which have great potential use in several fields such as sensor, biological detection, photonic switch, and so forth. Here, our work provides a novel idea and valuable data support for the artificial analogies of functional PCs. Future studies will focus on making the sample more visually distinct, and the photonic structures are worth being mimicked by synthetic photonic materials following a biomimetic approach.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional characterization details of SEM images and XPS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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