

Self-growing Photonic Composites with Programmable Colors and Mechanical Properties

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Article

Keywords: Self-growth, Photonic composites, Self-healing, Flexible, Patterns

Posted Date: May 11th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1433654/v1>

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Version of Record: A version of this preprint was published at Nature Communications on December 19th, 2022. See the published version at <https://doi.org/10.1038/s41467-022-35555-0>.

Abstract

Many organisms produce stunning optical displays based on structural color instead of pigmentation. This structural or photonic color is achieved through the interaction of light with intricate micro-/nano-structures, which are “grown” from strong, sustainable biological materials such as chitin, keratin, and cellulose. In contrast, current synthetic structural colored materials are usually brittle, inert, and produced via energy-intensive processes, posing significant challenges to their practical uses. Inspired by the brilliantly colored peacock feathers which selectively grow keratin-based photonic structures with different photonic bandgaps, we develop a self-growing photonic crystal system in which the photonic bandgaps and hence the coloration can be easily tuned. This is achieved via the selective growth of the polymer matrix with polymerizable compounds as feeding materials in a silica nanosphere-polymer composite system, thus effectively modulating the photonic bandgaps without compromising nanostructural order. Such strategy not only allows the material system to continuously vary its colors and patterns in an on-demand manner, but also endows it with many appealing properties including flexibility, toughness, self-healing ability, and reshaping capability. As this novel self-growing method is simple, inexpensive, versatile, and scalable, we foresee its significant potential in meeting many emerging requirements for various applications of structural color materials.

Introduction

Structural coloration, which was first observed by Robert Hooke and Isaac Newton on peacock’s feathers more than 350 years ago, constitutes a class of fundamentally different mechanisms to generate color in contrast to chemical or pigment-based coloration¹⁻³. Here the colors are produced by the microscopical structures or surfaces fine enough to interfere with light and thus show appealing features such as brilliant, stable, and non-toxic⁴. This phenomenon has initiated the field of artificial structural color materials and inspired many applications in optoelectronics⁵, anti-counterfeiting⁶, sensors⁷, etc. Essential to these applications is the fabrication of various sophisticated periodic photonic nanostructures⁸⁻¹¹. To this end, both top-down and bottom-up technologies have been developed^{12,13}. The former mainly depend on microfabrication processes¹⁴ that often suffer from high processing cost and low production efficiency, which hinders their scalable manufacture of structural color products. In contrast, bottom-up methods in which ordered nanostructures are made through the self-assembly of nano-/microscopic building blocks are simple, cheap, and scalable¹⁵. In self-assembly methods, building blocks with uniform sizes are required for achieving ordered nanostructures, which leads to single bandgaps and hence monochrome or iridescence¹⁶. To achieve multicolored images, several methods are developed recently, including confinement deposition¹⁷, regioselective removal¹⁸, post-modification of inverse opal¹⁹, etc. These methods involve elaborate fabrication techniques requiring superb synthetic skills and the obtained images are either ephemeral, low-resolution, or relatively dull. Moreover, artificial structural color materials are often fragile and not reprocessable^{20,21}, in stark contrast to their glorious, durable, and lightweight natural counterparts. Therefore, it is highly desirable to develop facile approaches for fabricating bright, robust, and adaptive structure color images.

The intricate microstructures for structural colors of living creatures are produced via a natural growing process^{22–25}. Take the brilliantly colored eye pattern of the peacock's tail as an example (Fig. 1a). The barbules within this coloration pattern contain two-dimensional (2D) photonic crystals made up of melanin rods and air holes embedded in a keratin matrix^{26,27}. By controlling the growth of keratin during feather development, peacocks can vary the spacing between adjacent melanin rods, which effectively adjust the lattice constant to modulate the photonic bandgaps for producing diversified colors (Fig. 1b **and Figure S1**). Such a sustainable approach not only allows living organisms to continuously and precisely evolve their colors and patterns on original coats, rather than to generate new substrates with a set of components with different sizes, but also mechanically robust matrices, implying a fundamentally new, efficient, sustainable method to synthesize or mediate structural color figures.

Inspired by the structural designs of peacock's tail feathers, here we report a growing strategy for fabricating photonic crystal composites with controlled structural coloration, patterning capability, and versatile mechanical properties. As shown in Fig. 1c, this novel material system is composed of SiO₂ nanospheres embedded in a “living” polymer matrix, which can undergo spatial-selective growth by introducing “nutrients” in the external environment. The growth-induced expansion of the lattice parameters allows the system to precisely and continuously vary its photonic bandgaps and thus color in an on-demand manner. More specifically, the growth is achieved via homogeneously swelling the crosslinked polymer matrices using a nutrient solution consisting of monomer, crosslinker, photoinitiator, and catalyst simultaneously, followed by light-induced polymerization. A new-old double network structure forms, in which the original network is stretched. Note that the stretched conformation would restrict the uptake of more nutrient solution for further growth. The catalyst in the nutrient solution is thus designed to remove such restriction by inducing chain exchange between new and old networks to homogenize the matrices, allowing the system to further grow. Under this growing mechanism, we can continuously change the photonic bandgap and composition of systems for modulating their colors and mechanical properties. Because of the spatial selectivity of the photopolymerization, it is facile to generate multicolor images.

Results

System and synthesis

Acrylate-based polymers were selected as the growing matrices because of their widespread usage in various applications. The initial photonic crystal films were made from SiO₂ nanospheres (**Figures S2 & S3**) and poly(ethylene glycol) diacrylate (PEGDA). Briefly, the suspending solutions of SiO₂ nanoparticles and PEGDA in ethanol were allowed to evaporate to induce the self-assembly of SiO₂ into colloidal crystals, followed by curing under UV irradiation (**Scheme S1**) in homemade containers. After annealing, vivid films were obtained. The formation mechanism and driving force of SiO₂ forming an ordered structure were polymerization-induced colloidal assembly which had been carried out by Ge et al²⁸. Scanning electron microscopy (SEM) study illustrates that the samples consisted of both ordered and

disordered domains (**Figure S4**). In the ordered domain, SiO₂ nanoparticles arranged into ordered structures with uniform photonic bandgaps. Due to such a short-range ordered structure, the obtained structural color is angle-independent (**Figure S5**)²⁹. The wavelength (λ) of the reflected light to this class of structural color films could be estimated by the Bragg's diffraction Eq. 3⁰:

$$m\lambda = 2dn_{eff} \quad (1),$$

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where d refers to the interplanar spacing of the photonic crystal lattice, n_{eff} indicates the mean refractive index of the composites, and m is the order of reflection ($m = 1, 2, \dots$). In our design, d could be modified by allowing the polymer matrices to grow.

The mixture of an acrylate monomer, 1,6-hexanediol diacrylate (HDDA, crosslinker), 2-hydroxy-2-methylpropiophenone (photoinitiator), and benzenesulfonic acid (BZSA, transesterification catalyst) was used as the nutrient solution. Here, three kinds of monomers were employed, including 4-hydroxybutyl acrylate (HBA), PEGDA, and 2-hydroxyethyl methacrylate (HEMA). HBA is a commonly used elastomer precursor, while PEGDA is the compound used to prepare the initiated sample and therefore would not vary the composition of the sample matrices during growth; compared to HBA and PEGDA, HEMA could form rigid polymer main chains and thus provided an approach to tune material mechanical properties. The nutrient solution containing HBA, PEGDA, or HEMA used for growth was defined as nutrient solution *B*, *EG*, or *M*, respectively. For growth, as-prepared purple films (typical mass percentage of the polymer matrix: 40 wt%) were selected as the initial samples. They were first immersed in a nutrient solution for swelling. During swelling, the samples increase in size and change their colors (Fig. 2a). The samples could swell the tested nutrient solutions with equilibrium swelling ratios of 9.1 wt% (*B*), 6.2 wt% (*EG*), and 7.1 wt% (*M*), respectively (**Figure S6**). The relatively low swelling ratios were attributed to the low polymer fraction in the photonic crystal films and their rigid nature. Despite low swelling ratios, obvious color changes were observed. The colors were unstable and would turn back to purple again if the samples were washed to remove the entrapped nutrient solution. Besides, the swelling significantly weakened the Young's modulus of the samples (**Figure S7**). By contrast, the samples that were subsequently irradiated by UV light (365 nm, 10 mW·cm⁻²) to trigger photopolymerization preserved their after-swelling weights and colors, as well as became tougher (Fig. 2a and **Figure S8**). The photopolymerization reaction was exothermic, which could heat the systems to 47.1°C in 50 s (**Figure S9**). Such thermal effects could trigger transesterification reactions to release any polymerization-induced mechanical tension in such dynamic networks³¹. The grown samples could swell nutrients again for further growing cycles (Fig. 2b). To illustrate the role of this homogeneous step in growth, a control sample without transesterification catalyst was treated under the same process aforementioned, and as expected, this catalyst-free sample was nearly non-swellable to the nutrient solution after the first growing cycle. We denoted the initial

sample as EG_n where n is the mass percentage of the polymer matrix, while the grown samples as $EG_n - B/EB/M_m$, where m is the increased mass of corresponding polymer matrices compared to the entire original sample. For example, specimen $EG_{40} - B_{9.7}$ was the grown sample of EG_{40} obtained from nutrient B with a net increase of 9.7 wt% compared to initiated weight (total polymer fraction: $(40 + 9.7)/(100 + 9.7)$ wt%). All the specimens, including both initiated and grown ones, were self-standing and macroscopically uniform.

Optical property

The homogeneous growth allowed for flexible modulation of sample colors in the full visible light spectrum from purple to red (Fig. 2c). During growth, SiO_2 colloidal nanoparticles maintained their ordered arrangement in the polymer matrix but showed increasing interplanar lattices, as evidenced by the gradual change of the double interplanar spacing $2d$ from 313 to 473 nm collected from the SEM images (Fig. 2d). UV-Visible reflection spectroscopy was employed to characterize the optical properties of different grown samples (Fig. 2e). With the increase in polymer matrices (then lattice distances), the reflection peak (λ) shifts from 481 to 690 nm. These reflection peaks were surprisingly intensive and narrow, implying a highly ordered arrangement of SiO_2 colloid crystals. In our self-growing photonic composites, the changes in both double interplanar spacing $2d$ and reflection peaks (the colors) were predictable. For a photonic composite with a homogeneous ordered structure, the double interplanar spacing $2d$ was proportional to the cube root of the volume fraction of SiO_2 nanoparticles ($1/\sqrt[3]{1 - \varnothing}$, where \varnothing is the volume fraction of the polymer matrix). By using the experimental data obtained from the initial photonic composite to establish the linear relationship (See section 9 in supplementary information for calculation detail, **Table S1**), we found that the theoretic curve compared well with the experimental $2d$ values (Fig. 2f), suggesting that the $2d$ could be precisely controlled by growth. Furthermore, in our system, the monomer showed a similar refractive index n with that of SiO_2 (SiO_2 : 1.45; monomer: 1.457 at 20°C), and therefore, the n_{eff} could be considered as a constant during growth. It indicated a linear relationship between λ and $2d$ based on equation #1. When we plotted the experimental λ to $2d$, they all well fit with the theoretic curve (obtained from equation #1 with a n_{eff} of 1.453, Fig. 2g). All these results indicated that the optical properties of photonic crystal films could be precisely post-modulated by growth.

Mechanical properties

Growth allowed the samples to vary their compositions for modulating their mechanical properties. Two kinds of approaches could be applied, including changing the monomer types or the crosslinker concentration in the nutrient solution. For example, in the case of using crosslinker-free nutrient solutions, the sample would maintain its modulus when grown from nutrient EG but become softer or stiffer from nutrient B or M , respectively (Figs. 3a). On the other hand, increasing crosslinker concentration in the nutrient solution stiffens the samples regardless the monomer types (Figs. 3b).

Besides stiffness modulation, growth also significantly toughened the photonic composite structure. The as-prepared initial samples were brittle and would fracture upon bending (Fig. 3c). Such brittle samples could grow to be fully flexible by adding agents that could soften the matrices in the nutrient. In the current system, the composites were stiffened by both the highly crosslinking structure of polymer matrices and the covalent connection between SiO₂ nanoparticles and polymer chains of matrices (**Figure S10&S11**, FTIR results indicated the existing of the transesterification between the ester polymer and the hydroxyl on the surface of SiO₂ nanoparticles during the preparation of the initiated samples). Since both linkages were ester-based bonding, alcohol that could hydrolyze the ester connection was selected as the additive (Fig. 3d). As expected, the grown sample obtained from an alcohol-contained nutrient was very flexible. More than bending, the flexible grown sample can be rolled up, twisted, or folded (Fig. 3e) and shows fair elasticity. The sample became more stretchable without a tradeoff in strength (Fig. 3f). Here, the alcohol could either be used as an additive in normal nutrient solutions or an independent agent (a nutrient consisting of only alcohol) to make the sample flexible (**Figure S12**). The transesterification-based softening mechanism was confirmed by using a SiO₂-free PEGDA film in which the contribution of SiO₂ nanoparticles to material mechanical properties was absent. The film was grown in alcohol-free and alcohol-containing *EG*, respectively. The grown sample made from an alcohol-containing nutrient shows a nearly 50% increase in flexibility compared to the grown sample prepared by alcohol-free *EG* (**Figure S13**). To further prove the mechanism, hydroxyl-free agents like tetrahydrofuran were employed as the additive, and none of them could make the sample flexible (**Figure S14**). Traditional photonic crystal-based structural color materials are normally brittle and improving their mechanical properties thus constitutes one of the most critical aspects of current research^{32,33}. Two strategies, i.e. softening photonic crystal materials by the use of flexibilizers or increasing polymer fractions³⁴ and fabricating full organic-based inverse opal structures³⁵, had been developed. In the former, increasing polymer/flexibilizer fraction would disturb the self-assembly of particles and thus destroy the ordered crystal microstructure. The materials with inverse opal structures show excellent flexibility, but their preparation normally required HF-based etching treatment and the materials display milky appearance and low color saturation due to the higher light scattering in inverse opal³⁶. In contrast, the growth method allowed for post-modulation of the composition without compromising the ordered microstructure, implying a more efficient method to get mechanically robust photonic crystal materials.

Reshape

The alcohol-based transesterification reactions were reversible and the broken ester linkages could reform by removal of the absorbed alcohol (Fig. 3d). To elucidate this idea, the softened PEGDA film made from the alcohol-containing nutrient was annealed at 70°C for 4 h to remove the alcohol moieties. The grown sample became stiffer and showed a modulus similar to that of the grown sample directly obtained from the alcohol-free nutrient (**Figure S13**). Such reversible softening-stiffening process allowed for multiple-time reshaping of the samples. As shown in Fig. 3g, a rigid flat film was first softened by growth with alcohol and then deformed, followed by annealing treatment (to remove the alcohol moieties) to fix the obtained structures. The reshaping could be repeated to achieve different forms. Interestingly, the

deformed sample maintained its new shape when it was turned into an elastic state. Compared to this processability, traditional structural color materials are either rigid (photonic crystal composite, would fracture) or elastic (inverse opal material, turn back to original shape), and do not show such reshaping capability.

Spatial-selective growth and multicolor patterning

Another significant advantage of this photonic composite system is its spatially selective growth capability by using patterned photoirradiation (Fig. 4a). As shown by the surface profile, the irradiated region grew up with a sharp boundary. A height drop of 9.5 μm (yellow-orange change) occurred in 1 μm distance (aspect ratio: 9.5). Consequently, the grown region showed a significantly different structural color from the unirradiated region. Note that the modulation could be achieved without the removal of the unreacted nutrient solution. In a previous study³¹, we have proved that region-selective conversion of the monomer and crosslinker into polymer matrices by photopolymerization would induce a concentration gradient of the monomer and crosslinker. Such gradient would drive the nutrient to transport from unirradiated region to irradiated one, leading to the formation of convex surface textures at the irradiated region. The same mechanism was expected here. After growth, the residual nutrient entrapped in the composite was still active and could be transported to new irradiated regions for creating other surface textures and colors. The structure of the grown region was further probed by SEM. In the cross-section image of a grown sample, a sharp boundary was also observed. In the grown region, SiO_2 nanoparticles distribute orderly as those in the unirradiated region but show a larger interplanar lattice, implying homogeneous expansion of the polymer matrices.

Localized growth of photonic crystal films indicated a novel approach for chromatic patterning. We fabricated a “Sichuan facebook” using a EG_{48} substrate with single blue color to demonstrate the flexibility of this approach. As shown in Fig. 4b, the profile of the “Sichuan facebook” was outlined on the substrate swollen with nutrient EG after simple irradiation through a mask. Without any additional treatment, further selective irradiations through the masks could induce the formation of new structural colors and a clear multicolor image was created. This growth-based patterning approach differed from the reported methods based on either complicated instruments^{37,38} or sophisticated skills. Here the structural color was patterned by user-friendly photo-lithography to directly achieve complicated, high-resolution images. The obtained pictures were not only stable but also always permitted further modification, due to the “living” growing mechanism, implying a more facile and effective direction for batch manufactures.

Self-healing

The self-healing of mechanical damages on structure colored materials was extremely challenging because of their rigid nature^{39,40}. Since growth allowed for selective formation of new matrices in the irradiated region, it opened up a novel approach for our composite photonic system to restore the

damage. To demonstrate this self-healing capability, a photonic crystal structural color film was first scratched on its surface. Although the polymer matrix itself is self-healable at high temperatures due to the transesterification-based chain exchange reaction⁴¹, the scratch did not effectively repair upon heating treatment (**Figure S15**). In contrast, when we selectively induced growth on the damaged region by light irradiation, the scratch was completely repaired, and an intact photonic crystal film was achieved (Fig. 4c). The healed film maintained its vivid structural color through the whole body (color in the healed region might slightly shift due to the change in the photonic bandgap, **Figure S16**). This growth-based self-healing method differed from traditional intrinsic and extrinsic self-healing strategies. In the intrinsic self-healing, no new matrix would form and the polymer chains should be mobile enough to undergo reconfiguration^{42,43}. It is difficult for a rigid substrate to self-heal through this mechanism. Extrinsic self-healing strategy allows for the formation of new matrices but no ordered structure forms in the healed matrices⁴⁴. Moreover, an interface between original and healed matrices often appears, which is unfavorable for the recovery of the mechanical properties. Here, our method combined the merits of both intrinsic and extrinsic strategies, and the healed sample completely restored its color and mechanical properties. The healed region exhibits comparable mechanical strength as the original sample (the self-healing efficiency: 80.1%, evaluated by the work, Fig. 4d), therefore, when stretched, the sample may even break at the intact region, rather than the healed one. By contrast, the scratched sample without self-healing was easily broken (8.8%).

Discussion

Inspired by the forming process of peacock's tail feathers, we have proposed a fundamentally new strategy for fabricating photonic crystal structural color composites. This strategy involves the uniform expanding of the polymer matrices of the structural color composites by allowing the matrices to grow, in which the finely ordered microstructure is maintained. By varying the component in the nutrient used for the growth and the growing cycles, the samples can be selectively changed their sizes, color, and mechanical properties. Under this mechanism, the obtained materials not only show good flexibility, toughness, and self-healing/reshaping ability but also permit the fabrication of complicated, high-resolution patterns. Since this facile method can be applied to commonly used polymer systems and results in excellent performances, we foresee its great application potential in meeting many emerging challenges of structural color materials and broadening their commercial values.

Methods

Materials 4-Hydroxybutyl acrylate (HBA, refractive index n (20°C): 1.452), poly(ethylene glycol) diacrylate (PEGDA) (average $M_n = 250 \text{ g}\cdot\text{mol}^{-1}$, n (20°C): 1.457), ammonia (28 vol%), 2-hydroxy-2-methylpropiophenone (photoinitiator), 1,6-hexanediol diacrylate (HDDA), and benzenesulfonic acid (BZSA, transesterification catalyst) were purchased from Aladdin Co. (Shanghai, China).

Tetraethylorthosilicate (TEOS, 99.5%), 2-hydroxyethyl methacrylate (HEMA, 99%, n (20°C): 1.441), tetrahydrofuran (THF, 99.8%, anhydrous), and ethanol (AR, $\geq 99.8\%$) were purchased from J&K (Beijing,

China) and Aladdin Reagent Co. (Shanghai, China). Ethyl decanoate (98%) was brought from Tansoole (Beijing, China). All reagents and solvents were used without further purification. Ultrapure water (18.25 M Ω ·cm, 25°C) was used.

Synthesis of SiO₂ nanoparticles. SiO₂ nanoparticles were prepared via a modified *Stöber* method involving the hydrolysis and condensation of TEOS in ethanol in the presence of ammonia (catalyst)⁴⁵. Briefly, the mixture of 100 mL ethanol and 15 mL ammonia in a 250 mL flask containing was heated to 60°C under a stirring condition, followed by adding 6 mL TEOS. The mixture was stirred at 60°C for 8 h. Excess ammonia and unreacted reagents in the matrix were removed by washing with ethanol and the product was collected by high-speed centrifugation (a rate of 9000 r·min⁻¹ for 5 minutes). The total washing times should not be less than 6.

SiO₂/PEG precursors. Take *EG*₄₀ precursor as an example. Briefly, 60 μ L PEGDA containing photoinitiator (5 wt%) was added into 0.132 g SiO₂ ethanol suspensions (6 wt%). The solution was treated with vortex mixing and sonication, followed by annealing in an oven at 90°C for 2 h to allow for solvent evaporation. When the ethanol solvent was evaporated, a supersaturated acrylate solution of SiO₂ was obtained. The precursor solution was nearly transparent and kept in dark for 5 h before use. The same protocol was used to prepare the other precursor solutions with different ratios of SiO₂ nanoparticles and PEGDA²⁸.

Fabrication of photonic crystal films. For example, 50 μ L precursor solution was sandwiched between a glass slide (18 \times 18 mm) and a hydrophobic cover silicon wafer (18 \times 18 mm) (**Scheme S1**). The sample was irradiated by UV light (365 nm, 10 mW·cm⁻²) for 2 min. After illumination, a vivid film formed and it was peeled off from the substrate for further study. This method could be applied to prepare large-scale films and the thickness of the films was controlled by the amount of the precursor solution and the area of the substrate.

Data Availability

The authors declare that the main data supporting the findings of this study are available within the article and its Supplementary Information files. Extra data are available from the corresponding author upon reasonable request.

Declarations

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51973023 and 52003035), Sichuan Science and Technology Program (2021JDRC0014 and 2021JDRC0106) and China Postdoctoral Science Foundation (W03019023601004133). We also thank Ms. Songzi Xu and Junchang

Guo at University of Electronic Science and Technology of China for their help on experiments and discussion.

Author contributions

J.C. and J.X. conceived the concept. J.C. supervised the project. J.C. and J. X. designed the experiment. J.X., X.Y., and C.Z. conducted the experiments. J.X., J.C., and L.L. wrote the manuscript. All authors contributed to the analysis and discussion of the data.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at <https://xxxxxxx>.

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Figures

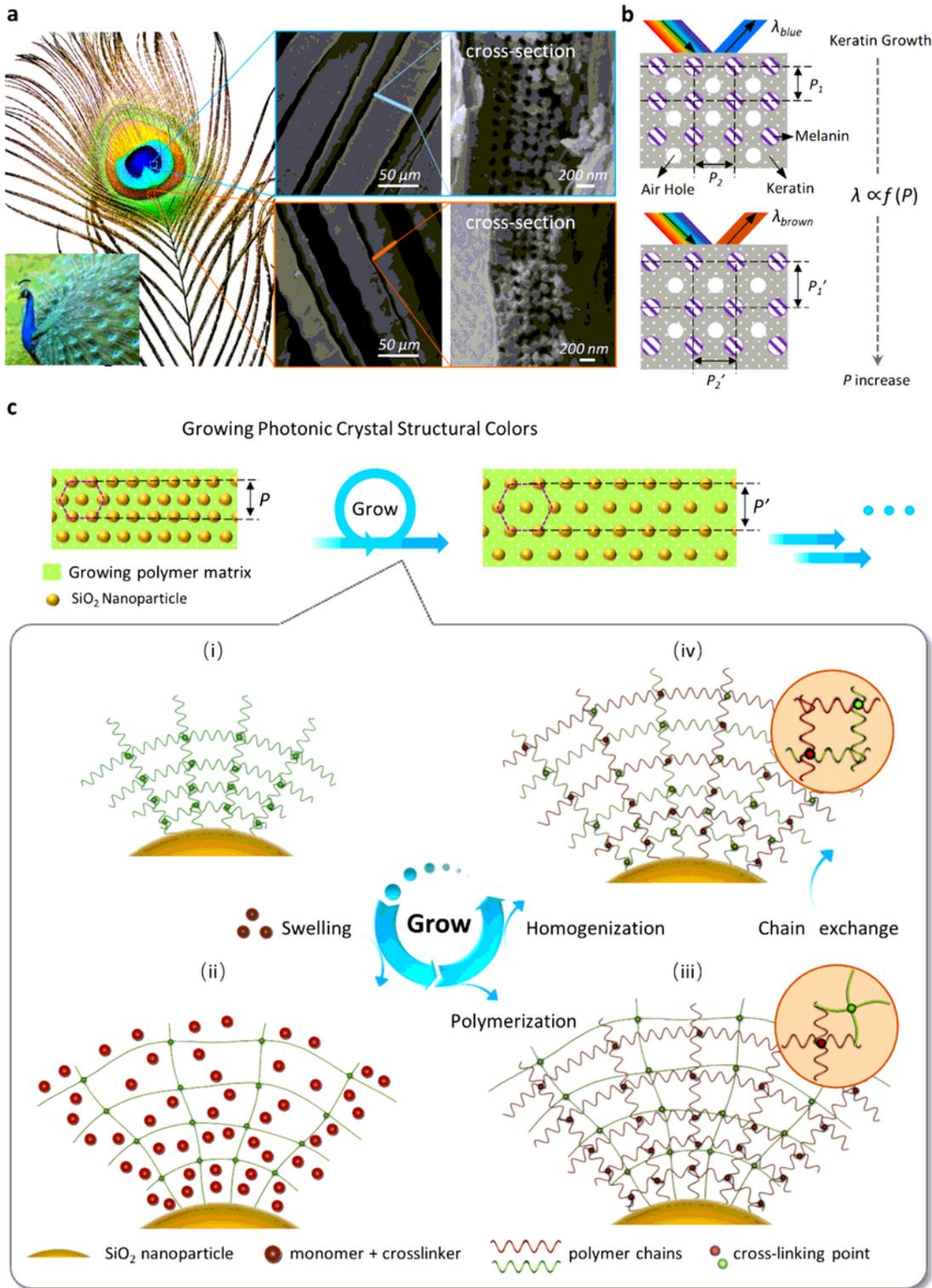


Figure 1

Growing photonic crystal structural color. (a) Images of a peacock and its tail feather. The SEM images show the blue (up) and brown (down) barbules and their transverse cross-section structures. (b) Schematic diagrams of the photonic crystal structure of the structural colors generated by a peacock.

Selective keratin growth leads to different structural colors and patterns. (c) Schematic diagram of the growth of a SiO_2 /polymer photonic crystal composite: the polymer matrix with a crosslinked structure (i) is swelled by a solution containing polymerizable compounds to change its size (ii); after polymerization, a new-old double network structure (iii) forms, in which the old network (green line) is stretched; a chain exchange-based homogenization process is triggered to get a uniform matrix with relaxed chain conformation (iv) which allows for further growing cycles.

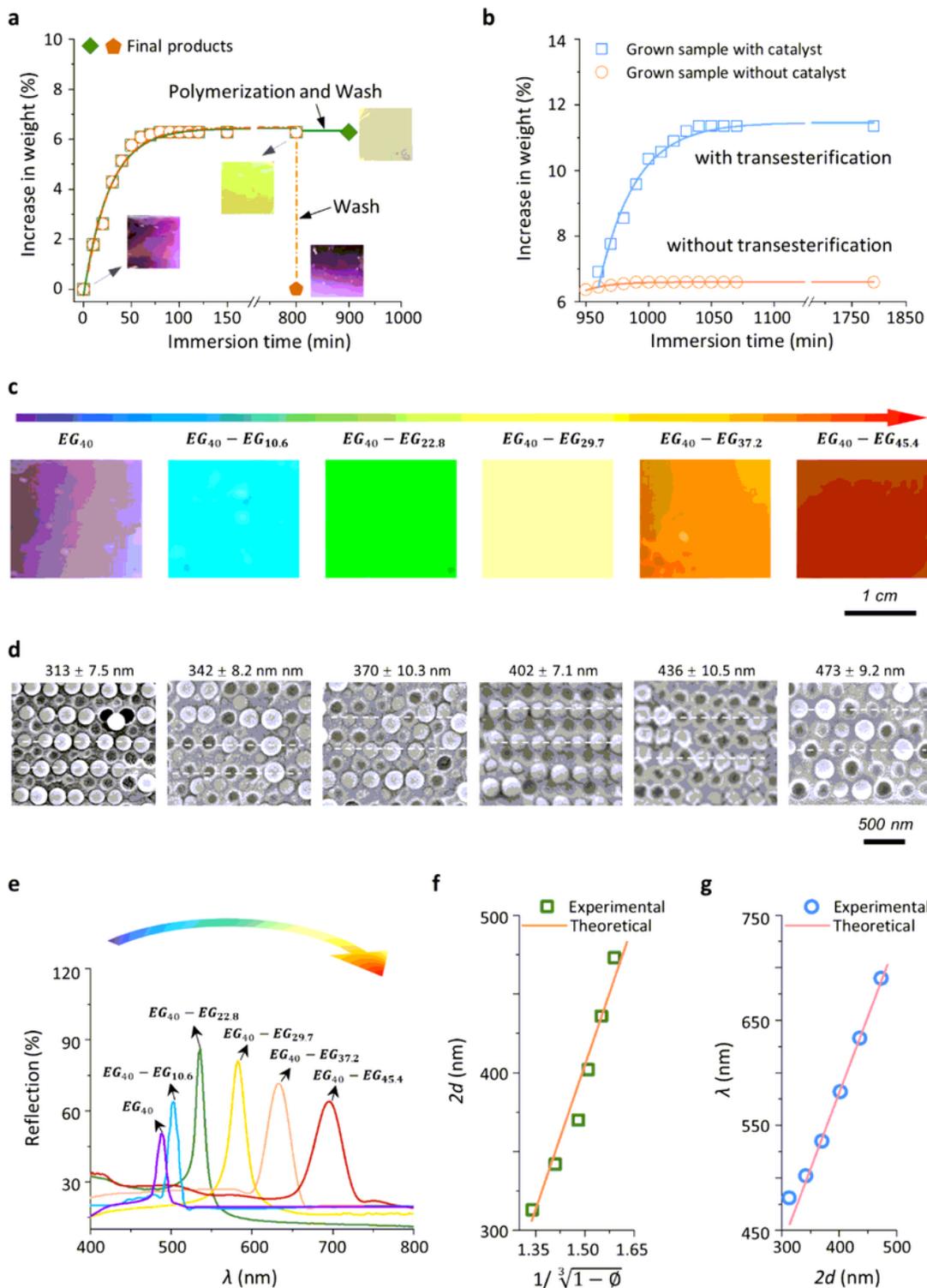


Figure 2

Optical properties of grown photonic crystal films. (a) Time-dependent weight of

immersed in nutrient *EG* (the mixture of monomer PEGDA, crosslinker, photoinitiator, and transesterification catalyst). Inserts are the digital photos of samples at different states. Ethanol/ CHCl_3 solution was used for washing. (b) Time-dependent weights of different grown samples immersed in a new nutrient *EG*. The catalyst-containing/free grown samples were obtained from nutrient *EG* with/without transesterification catalyst. Digital electronic photographs (c), cross-section SEM images (d), and UV-Visible spectra (e) of

and its grown products. (f) Experimental and theoretical interplanar spacing $2d$ versus

of

and its grown products, where

is the volume fraction of the polymer matrix. The solid line is the theoretic curve. (g) The theoretical and experimental reflection wavelength λ versus interplanar spacing $2d$ of

and its grown products. The solid line represents a theoretical line obtained via equation #1, where a composite

of 1.453 (20°C) is used.

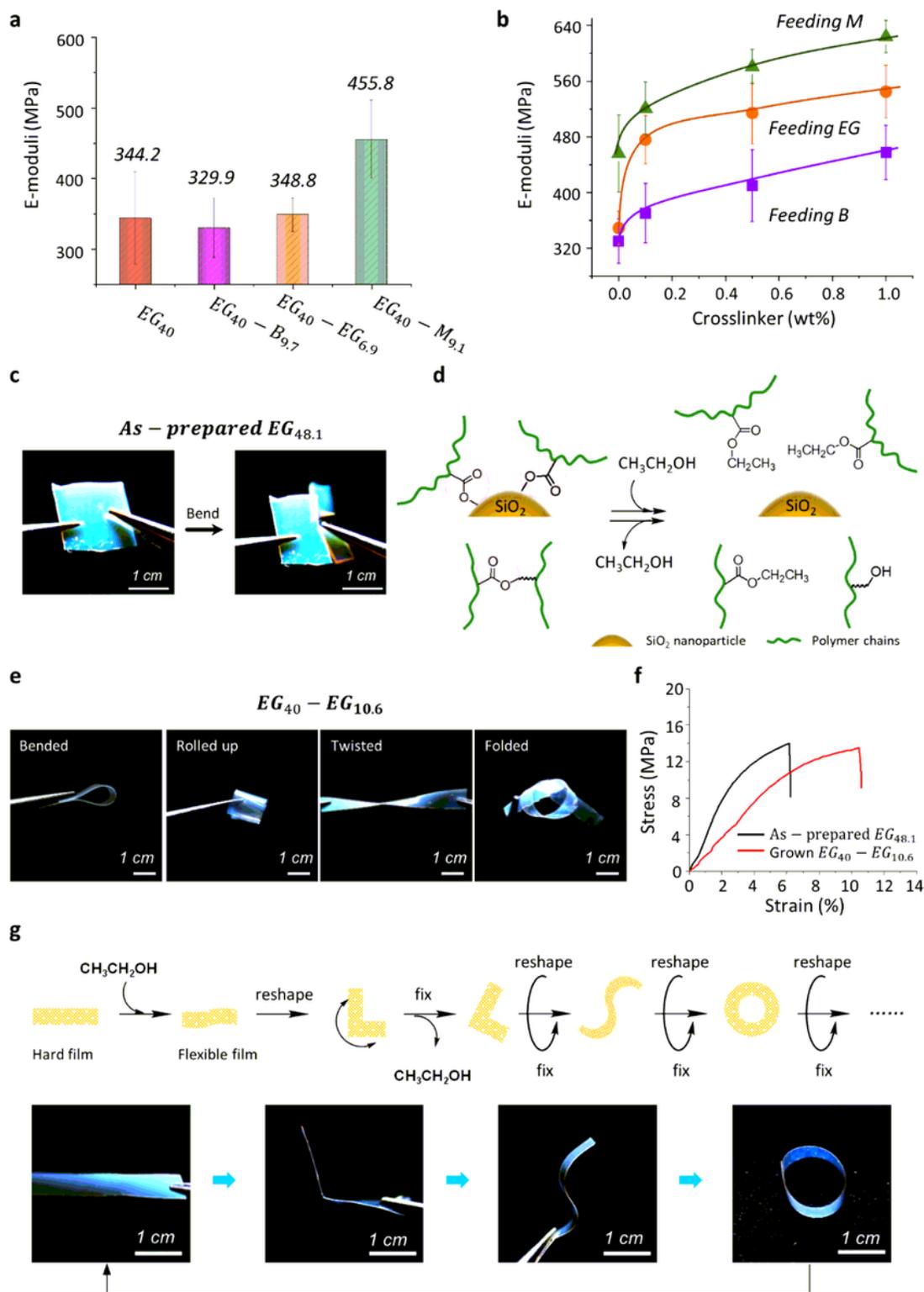


Figure 3

Mechanical property of grown photonic crystal films. (a) Elasticity moduli of

and its grown samples obtained from different crosslinker-free nutrients. (b) Elasticity moduli of

and

samples obtained from the nutrients with different crosslinker concentrations. The E-moduli in (a) and (b) were obtained from five independent measurements. (c) Digital photos of the fracture of an as-prepared

sample during bending. (d) Chemical mechanism of reversible softening: alcoholysis to dissociate the connecting structure (softening) and removal of the alcohol moieties to reform the connections (stiffening). (e) Digital photos of a flexible

sample (final *EG* fraction: 45.8%). (f) The strain-stress curves of

(as-prepared) and

(grown). The samples have similar compositions but the grown one shows a larger strain. (g) Reshaping mechanism (above) and the digital photos of a multiple-time reshaping sample. For reshaping, the sample was first softened by uptake of alcohol and deformed into a designed shape, followed by annealing treatment to remove the alcohol to fix the desired shape.

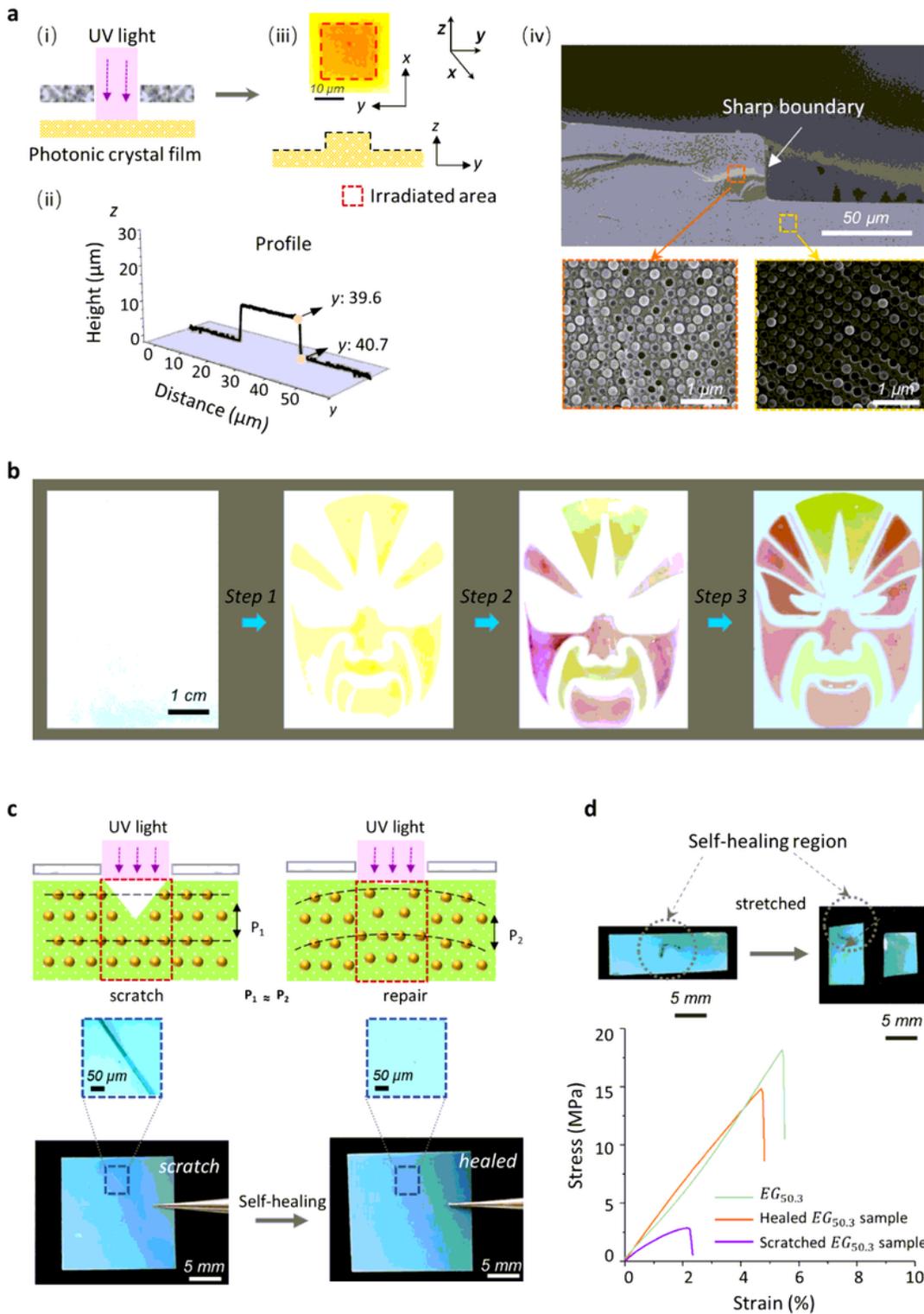


Figure 4

Spatial-selective growth of photonic crystal films. (a) Photo-induced selective growth. i. Schematic diagram of the light-induced growth process; ii. The profile of the grown sample; iii. Top view of a grown sample obtained from light-induced growth using a square photomask with $20 \times 20 \mu\text{m}^2$; iv. Transverse-section SEM image (top) of a grown sample and zoom in on the red and orange areas to obtain high

magnification SEM images (bottom). (b) Fabrication of multicolor “Sichuan facebook” from a substrate with single blue color.

was used as the starting substrate and the nutrient *EG* was used for growth. (c) Self-healing mechanism (above) and the digital photos of a self-healing

sample. For self-healing, the sample was first scratched using a sharp blade, followed by soaking in *EG* for 10 min and then UV irradiation at damage region (UV light intensity: $10 \text{ mW}\cdot\text{cm}^{-2}$, 2 min). The sample was further annealed at 70°C for 2 h before measurements. (d) Strain-stress curves of scratch samples before and after self-healing. Inserted (top) are digital photos of self-healed splines and stretched self-repairing spline. The black lines highlight the healed region.

Supplementary Files

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