Cholesteric cellulose liquid crystal ink for three-dimensional structural coloration

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Color reproduction is an important aspect of three-dimensional (3D) printing in terms of creating a colored visual appearance with high fidelity and stability. To this end, structural color is an ideal coloring mechanism, which processes unique nonfading ability and tunable optical features. In this study, we propose a printable structural color ink composed of cholesteric cellulose liquid crystals together with gelatin and a thermal-responsive hydrogel. The ink maintains a cholesteric liquid crystalline state that gives rise to the structural color, and the rheology properties of the ink are optimized by gelatin, which allows the ink to flow during printing and form self-supporting structures after printing. The incorporation of the hydrogel further enables shape maintenance of the ink after printing via in situ ultraviolet-crosslinking. Based on this, we print a series of graphics and 3D objects with angle-independent color appearances and demonstrate the versatility of the printing system in different substrates. Moreover, the printed objects possess dual thermal responsiveness, which results in visible color changes around body temperature. These performances, together with the biocompatibility of the constituents, indicate that the present ink represents a leap forward to the next-generation 3D printing and would unlock a wide range of real-life applications.

Significance

We propose a printable structural color ink composed of cholesteric cellulose liquid crystals together with gelatin and a thermal-responsive hydrogel. The ink is endowed with vivid structural colors and printability due to its constituents. Based on this, we print a series of graphics and three-dimensional (3D) objects with vivid color appearances. Moreover, the printed objects possess dual thermal responsiveness, which results in visible color change around body temperature. These performances, together with the biocompatibility of the constituents, indicate that the present ink represents a leap forward to the next-generation 3D printing and would unlock a wide range of real-life applications.

Three-dimensional (3D) printing is a revolutionary technique that utilizes computational control to process feedstocks into materials with sophisticated architectures. It is applicable to a wide range of products, thus promoting the interactions and collaborative development of science, engineering, and high-tech industry (1–10). The properties of the feedstocks are crucial for 3D printing in terms of processability, shape maintenance, and functionality. There are currently a wide variety of materials compatible with 3D printing, including powdery metals, ceramics, polymers, carbon materials, as well as composite materials such as biohybrid hydrogels (11–13). Particularly, color reproduction is a significant aspect of 3D printing since a colored appearance of the printed objects would be most favorable for real-world applications such as ornaments, graphic labeling, information coding, etc. (14–17). However, the current feedstocks are mostly colored by doping with dyes or pigments, whose long-term color fidelity and stability remain an open question. The interactions between the pigments and the feedstock could result in changes in the rheology behaviors, which might add a type of unpredictability to the printing process (18, 19). By contrast, structural coloration is a nature-inspired phenomenon that produces colors through interactions between light and intrinsic nanostructures. Owing to its unique optical features including color purity, brightness, and the ability of being free from photochemical degradation, structural color materials have been extensively employed in many fields including display, sensing, anti-counterfeiting, actuators, etc. (20–22). Nevertheless, creating genuine 3D structural color objects has so far been challenging since the corresponding feedstocks remain to be explored. Therefore, the development of a general structural color feedstock is highly anticipated for the direct printing of 3D materials with macroscopic shapes and high-fidelity color appearances.

Here, we propose a cholesteric cellulose liquid crystal ink for printing 3D structural colored objects, as shown in Fig. 1. Cholesteric liquid crystal (CLC) is a distinct form of material with a periodic arrangement of twisted layers composed of rod-like nanoparticles or molecules, referred to as mesogens, aligning in parallel (23). As an ideal candidate for mesogens, hydroxypropyl cellulose (HPC) is a long-chain cellulose derivative molecule with abundant resources and good biocompatibility (24–26). HPC in solution could self-assemble into CLC within a specific concentration range and show vibrant and metallic structural colors (27–29). To further make HPC printable, we incorporate two other ingredients, gelatin and poly(acrylamide-co-acrylic acid) (PACA), to prepare a composite HPC-gelatin-PACA (HGP) ink. Gelatin provides appropriate rheology properties during printing, and PACA enables postprinting shape maintenance via in situ ultraviolet (UV)-crosslinking. With that, the ink could be formulated...
into 3D customized objects on arbitrary substrates, both showing vivid and angle-independent structural colors. Due to the synergic thermo-responsiveness of both HPC and PACA, the resultant macroscopic 3D objects show color tunability under the control of environmental temperature. Moreover, as a feedstock consisting primarily of cellulose derivatives and gelatin, the composite HGP ink provides an environmentally friendly alternative to current colored inks. These results indicate that the composite cholesteric cellulose liquid crystal ink would shed light on sustainable 3D printing and intelligent photonic materials in many application scenarios.

Results

In a typical experiment, the composite HGP ink is first prepared by mixing HPC (35–50 wt%), gelatin (10 wt%), and a pregel solution of PACA (8 wt%) using a planetary centrifugal mixer. After centrifugation to remove the bubbles and refrigeration to physically crosslink gelatin, the HGP ink is prepared, as shown in Fig. 2A. HPCs are long-chain, water-soluble cellulose derivatives possessing large numbers of hydroxyl groups in the side chains. In an HPC solution, the abundant hydrogen bonds between HPC and water molecules and the interactions between HPC molecules lead to the self-organization of HPCs to form CLCs (SI Appendix, Fig. S1). CLCs could be regarded as a typical type of 1D photonic crystal with the unique optical property of photonic bandgap. The light irradiating into CLCs could be selectively reflected, and the reflected light wavelength depends on the helical pitch ($\rho$) of CLCs, which refers to the physical distance of a 360° rotation of the twisted HPC molecule layers (SI Appendix, Fig. S1). Generally, $\rho$ can be modulated by many factors such as water content, environmental temperature, and external mechanical force. When $\rho$ is in the length scale comparable to the visible light spectrum, the reflection peak would be in the visible range, resulting in vivid metallic structural colors. Here, we find that when incorporated with gelatin and PACA monomers, the HGP mixture is found to retain the cholesteric mesophase, and the characteristic helical structure of the HGP mixture is confirmed by a scanning electron microscope (SEM), as shown in Fig. 2B. However, the HGP mixture does not show any color. We figure this out by measuring the reflection spectrum of the HGP mixture, which turns out to have a narrow peak, yet in the near-infrared (NIR) range (Fig. 2C).

Since PACA exists in the HGP mixture in the forms of uncrosslinked monomers, the HGP mixture can be chemically crosslinked by UV light to form an HGP hydrogel. Strikingly, after photo-crosslinking, the HGP mixture exhibits green color, as shown in Fig. 2D. We find that the HGP hydrogel still retains a helical structure, while it is more structurally confined by a polymer network (Fig. 2F). The reflection spectrum shows a significant blue shift to ~310 nm comparing that of the HCP before crosslinking (Fig. 2A). These results suggest that after photopolymerization, the pitch of the CLC is reduced due to the compression of the crosslinked polymer network. Therefore, the photo-crosslinking process not only helps to maintain the CLC nanostructure but also allows for coloration of the HGP mixture. It is also worth mentioning that carbon nanotube (CNT) is further included in the HGP mixture as a broadband light absorber to enhance the color saturation of the crosslinked HGP hydrogel (SI Appendix, Fig. S2) (28, 30).

Based on this phenomenon, we prepare a series of CNT-doped HGP mixtures as inks, and the water content of the inks is optimized around 35–45% to generate structural colors after photo-crosslinking. Notably, pure HPC solutions within this water content range could also exhibit structural colors. We therefore make a comparison of their visual colors, as shown in Fig. 3A. We find that with the increase of water content, the visual color of the three groups of samples gradually red-shift. Specifically, pure HPC solutions change from blue to red, HGP mixtures change from deep red to black (NIR), and HGP hydrogels change from purple to deep red. By measuring the reflection spectra, we find that when the water content is in the range of 35–49%, the reflection peak position of the photo-crosslinked HGP hydrogels is similar to that of the corresponding pure HPC solutions, yet with a broader overall variation range (Fig. 3B and C and SI Appendix, Fig. S3). By contrast, the peak value of the HGP ink before crosslinking is significantly larger than the other two. Compared with the corresponding pure HPC solution with the same water content, the longer reflection peak wavelength of the HGP mixture is attributed to the larger pitch due to the lower HCP content. After photopolymerization, the pitch is reduced, and such that the HGP hydrogel has a similar color to the pure HPC solution. However, the HGP hydrogel overall has a larger color.

![Schematic illustration of the cholesteric cellulose liquid crystal inks for 3D structural coloration. The ink (named as HGP) is composed of HPC, gelatin, and PACA hydrogel and could be printed into 3D customized objects with dynamic thermal responsive color variation. Here, we use a rod to represent the long-chain HPC molecule.](image-url)
variation range owing to the different compression degrees as to different water content.

We next investigate the printability of the HGP photonic ink. Compared to an HPC-PACA (HP) mixture with the same water content but without gelatin, the incorporation of gelatin could endow the HGP ink with a certain degree of rigidity. We test this hypothesis by placing a sample of HGP ink and HP mixture upside down for 72 h. We find that, although being viscous, the HP mixture flows downward. By contrast, the HGP ink could avoid flowing under its own weight (SI Appendix, Fig. S4). This could be attributed to the introduction of gelatin, which increases the elastic contribution of the material system (31) and gives the HGP ink a certain stiffness that allows self-supporting and shape retention. We then compare the printability between the HP mixture and the HGP ink through a simple extrusion experiment. HGP and HP samples with the same crosslinking-resultant colors are prepared. As shown in SI Appendix, Fig. S5, with in situ UV-crosslinking process, the HP mixture extruded through a metal needle tip exhibits a drop-like shape while the HGP ink could be successfully extruded to form a fiber. Layer-stacked scaffolds are constructed from both samples. The HGP-derived scaffold has better structural stability, as the connection points are well defined and mutually supported without any fusion caused by flow, as is the case of the HP-derived one (Fig. 4A). These results demonstrate the role of gelatin in enhancing the printability of the HGP ink.

We conduct a series of rheological tests to further elaborate on the above observations. We prepare two groups of samples, the HGP group and the HP group; each group includes three samples with water concentrations of 42, 40, and 38 wt%, respectively. As previously reported, an aqueous HPC solution exhibits non-Newtontian, shear-thinning behavior even at low shear rates (32, 33). We perform shear-viscosity tests and find that such shear-thinning behavior exists in all HP and HGP samples, as manifested by the decrease of viscosity with the increase of shear rate (Fig. 4B). Amplitude sweep tests are then performed on HP and HGP samples, as shown in Fig. 4C. In the HP group, the storage modulus $G''$ decreases with the increase of the water content, while an opposite trend is found in the HGP group. This suggests that in the HP group, $G''$ is dominated by the HPC content, and an increased amount of water results in the expansion of the cholesteric liquid crystalline structure, which is consistent with the change of the $p$ (and thus the redshift of the color shown in Fig. 3A). In the HGP group, however, gelatin comes into play. Thus, more water available to gelatin results in an increase of $G'$. These results support the fact that the presence of gelatin increases the elastic contribution of the HGP ink.

We then perform frequency sweep tests to study the time-dependent behavior of both HGP and HP samples as the angular frequency falls from $10^2$ to $10^{-2}$ rad s$^{-1}$. As shown in Fig. 4D, the ratio of viscous modulus $G''/G'$ is expressed as the loss factor $\tan \delta (G''/G)$, is plotted as a function of the angular frequency. When $\tan \delta > 1$, the sample behaves as a viscoelastic liquid; when $\tan \delta < 1$, it is a viscoelastic solid; the black dashed line represents the gel-transition point when $\tan \delta = 1$. We find that the HP mixture exhibits a typical viscoelastic liquid behavior over all test frequencies, presented as an obvious fluidity regardless of the water content. In contrast, as the test frequency reduces, the HGP ink gradually converts from an initial liquid state (under high frequency) to the state of viscoelastic solid. The angular frequency at which the gel transition occurs ranges from 0.4 to 1 rad s$^{-1}$. This indicates that as the angular frequency increases and exceeds the transition point, the HGP ink can change from a gel state where it is at rest to a liquid-like state, which facilitates physical processing such as being extruded through a nozzle. When the shear is removed, the elastic contribution dominates the viscous contribution, and thus the material solidifies again, which allows it to maintain its prescribed shape. The rheological features make the HGP ink ideal for printing since it could flow during printing and form self-supporting structures after printing.

The above optical and rheological properties ensure that the presented HGP ink could be processed by direct printing. Therefore, we construct a 3D printing setup consisting of a displacement-driven 3D printer, a UV light source, and peristaltic pumps, as shown in SI Appendix, Fig. S6. The HGP inks are loaded in syringes and pumped to the nozzle and are then printed onto a glass slide substrate with desired patterns driven by the displacement platform. Meanwhile, the printed HGP
Ink is crosslinked by UV light in situ and maintains a gel-like state. The printed filaments are 0.5 mm in diameter. There is no obvious correlation between the filament thickness and the optical properties, which depends mainly on the HPC concentrations. We explore the macroscopic responsiveness feature of the printed 3D objects. Notably, both HPC and the PACA hydrogel scaffold have brilliant thermal responsiveness. The helical pitch of HPC could be modulated by environmental temperature that causes the variation of intermolecular interactions. PACA hydrogel responds to temperature by volume change.

**Fig. 3.** The photonic properties of the HGP inks with different visual color exhibition. (A) Photographs of three groups of HPC samples (i.e., pure HPC solutions, HGP inks, and photo-crosslinked HGP hydrogels); each group contains six samples with varying water content. (B) Reflection spectra of photo-crosslinked HGP hydrogels with different water contents. The numbers are the corresponding water content expressed in percentage. (C) Reflection peak value of the three groups of HPC examples as a function of the concentration of water.

**Fig. 4.** Study of the printability through extrusion experiments and rheological tests. (A) Optical images of filament stacking of (i) HP and (ii) HGP. (B) Shear viscosity profiles as the shear rate is ramped from 0.01 to 100 s⁻¹. Hollow points: HGP group. Solid points: HP group. (C) Rheological amplitude sweep profiles with the applied strain increasing from 0.01 to 1000%. G' is plotted at a constant angular frequency of 10 rad s⁻¹. (D) Rheological frequency sweep profiles with the angular frequency decreasing from 100 to 0.01 rad s⁻¹. tan δ is plotted at a constant applied strain of 0.1%. (Scale bar: 1 mm.)
change due to the formation/breakage of the hydrogen bonds between the copolymer segments. The structural contraction or relaxation of HPC and PACA has the same trend with temperature, which should lead to volume expansion and redshift of the color of the printed objects under heating. This allows us to control the macroscopic visual appearance of the 3D printed objects by tuning the environmental temperature, as shown in Fig. 5A and B. The corresponding reflection spectra of the object are shown in SI Appendix, Fig. S7, with a fixed measuring spot. Although the temperature response range of HGP is relatively narrow compared to the HP system, it can achieve a significant visual variation from green to red in the range of 20–40 °C, which is close to body temperature (Fig. 5C). Cyclic tests are performed to prove the reversibility of the thermal responsiveness. As shown in Fig. 5D, after repeated heating and cooling, the printed object still shows precise reflection wavelength variation, indicating that it could be used as thermal sensors. Finally, due to the biocompatible and edible features of the main constituents, HPC and gelatin, these 3D responsive structural color objects are expected to be applied in actual life.

We then prepare a series of HGP inks with different water content. With the aid of computer-controlled programs, we achieve complex graphics with vivid structural colors, including hexagram, heart-like shape, zigzag pattern, pentagram, and spiral line, as shown in Fig. 6A. The visual colors of these graphics depend on the water contents of the HGP inks. The postprinting gel-transition of the HGP inks allows for the accumulative buildup of multiple layers. Moreover, with the combination of in situ photo-crosslinking, the printed filaments can be structurally confined, to realize 3D structural color objects with complex structures (Fig. 6B and C). Moreover, when coupling multiple HGP ink-loaded syringes onto the 3D printer, graphics and 3D objects with multi colors and high shape fidelity can be prepared via a multistep printing program (Fig. 6D and E). Of all the printed objects, the visual displays are not affected by viewing angles, which is called the angle-independent property (Fig. 6B, C, and E and SI Appendix, Fig. S8). This might be because the filaments extruded from the nozzle are cylindrical, which contain long-range disordered but short-range ordered CLC domains. Practically, the HGP-based 3D printing method is not limited by the substrate. Apart from the common glass slides, we prove that it is possible to print HGP objects on other surfaces, either soft or hard, such as a piece of tinfoil and a laboratory bench (SI Appendix, Fig. S9). These results demonstrate the versatility of the HGP-based structural color printing platform.

Discussion

In summary, we present a cholesteric liquid crystal cellulose ink based on HPC, gelatin, and PACA hydrogel (named as HGP) for 3D printing. The HPC cholesteric mesophase contributes to structural coloration and the incorporation of gelatin
improves the printability of the ink. Combined with in situ photo-crosslinking of the PACA polymer, the cholesteric mesophase can be retained in the gel state, resulting in vivid metallic structural colors of the HPG hydrogel. Due to the thermal responsiveness of both HPC and PACA polymer, these printed objects show visible color changes around body temperature. Moreover, we construct a 3D printing setup and fabricate a series of graphics and 3D photonic objects, even with multiple colors. These results indicate that the presented HGP ink unlocks a wide range of real-world applications. Since it is able to be processed as liquid at increased shear rates and relax back to a self-supporting gel state with the reduced shear, it is therefore versatile for large-scale production with well-established industrial processing techniques. The main constituents of the HGP ink are HPC and gelatin, which are edible, cost-effective, and biocompatible. Thus, further modifying the formulation of the ink is expected, such as replacing the responsive hydrogels with natural derived alternatives. Thereafter, this system can be extended to daily-life commodities including colorant-free decorations in food industry, drugs, and cosmetics, as well as wearable biosensors or customized bionic skins. Thus, we believe that this cholesteric liquid crystal ink can shed light on next-generation environmentally friendly 3D photonic printing.

Materials and Methods

Materials. Hydroxypropyl cellulose (HPC, viscosity of 4.4 mPa \( \times \) s in 2 wt% aqueous solution at 20 °C) was purchased from Nippon Soda Co., Ltd. Gelatin, acrylamide (AAm), acrylic acid (AAC), N,N'-methylenebisacrylamide (Bis), and 2-hydroxy-2-methylpropiophenone (HMPP) are purchased from Sigma-Aldrich. Carbon nanotubes (CNTs, dispersed solution) are purchased from XF NANO Materials Tech Co., Ltd. Deionized water (resistivity higher than 18 MΩ cm) is acquired by a Milli-Q Plus 185 water purification system (Millipore).

Preparation of HGP and HP Feedstock. To generate the HGP ink, 8 wt% gelatin, 0.01 wt% CNTs, 4 wt% AAm (monomers), 4 wt% AAC (monomers), 0.4 wt% MBA (crosslinking agents), 1 wt% HMPP (photo-initiator), and a certain amount of HPC are mixed with water in a light-proof planetary centrifugal mixer (Shenke Instruments). The amount of HPC added depends on the water content required by the system. During this process, HPC should be added at regular intervals for homogeneous mixing, and the mixer should continue to work for more than a week after everything has been loaded. After extensive mixing, the sample is collected into 50 mL Falcon tubes and centrifuged to remove bubbles (H3-18K, Kecheng Instruments; 20 °C, 10,000 rpm, 30 min). Then the sample is stored at 4 °C for 3 d for the gelation of gelatin, away from light. Before use, the HGP ink should be taken out from the fridge and maintained at room temperature for 0.5 d, kept in the dark. For the HP mixture, the preparation procedure is the same as that for the HGP ink, except that the component of gelatin in the system is replaced by HPC.

Printing of 2D/3D HGP Objects. The 3D printing setup is composed of a displacement-driven 3D printer (FDM Desktop 3D Printer, Shenzhen Aurora Technology Co., Ltd.), a peristaltic pump (LSP01-2A, LongerPump), and a UV light source (S1000, OmniCure). All the 2D/3D models are based on computer-designed programs so that the 3D printer could recognize them. The HGP ink is collected in a 1 mL syringe coupling to the peristaltic pump. A polyethylene (PE) tube (BB31695-PE/3, Scientific Commodities, Inc.) with an inner diameter of 0.5 mm is used to transport the HGP ink. One end of the PE tube was attached to the needle of the syringe (inner diameter: 0.5 mm), and the other end, which served as the nozzle, was fixed to the displacement-driven platform. The pumping speed of the feedstocks is 3-5 mL/h, and the moving speed of the displacement-driven 3D printer is 12-20 mm/s. For the fabrication of the 2D patterns, as the HGP ink is pumped out of the nozzle, the displacement platform is engineered by a computer program to move synchronously so that the extruded filaments could form the desired 2D pattern on the glass slide substrates. These filaments are photo-crosslinked in situ by the UV light source fixed above to form stable photonic gels. The UV light source is fixed 5 cm above the nozzle with a power density of 3,000 mW/cm². For the fabrication of 3D objects, the displacement-driven platform not only moves in parallel, but also moves longitudinally under the control of the programs, so that the filaments could be stacked layer-by-layer. For the multicolored HGP objects, the HGP inks with different water contents are loaded into different syringes and extruded above to form stable photonic gels. The UV light source is fixed above to form stable photonic gels.
switched on/off to print different colored filaments, which are finally combined into multicolor products.

**Characterization.** The optical photographs of the printed objects are taken by a digital single-lens reflex camera (EOS R5, Canon) under white light without a polarizer. The characteristic reflection spectra are measured by a fiber-optic spectrometer (USB2000-FLG, Ocean Optics) equipped with an optical microscope (CX33, OLYMPUS). The rheologic tests are performed with a rheometer (Discovery HR 10, TA Instrument) with a gap size of 1 mm at 20 °C. The environmental temperature is measured by a thermo-hygrometer (F971, FLUKE). The SEM images are taken by an SEM (S-3000N, Hitachi) instrument.

**Data Availability.** All study data are included in the article and/or SI Appendix.

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