A Double-Layer Mechanochromic Hydrogel with Multidirectional Force Sensing and Encryption Capability

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Hydrogel-based soft mechanochromic materials that display colorimetric changes upon mechanical stimuli have attracted wide interest in sensors and display device applications. A common strategy to produce mechanochromic hydrogels is through photonic structures, in which mechanochromism is obtained by strain-dependent diffraction of light. Here, a distinct concept and simple fabrication strategy is presented to produce luminescent mechanochromic hydrogels based on a double-layer design. The two layers contain different luminescent species—carbon dots and lanthanide ions—with overlapped excitation spectra and distinct emission spectra. The mechanochromism is rendered by strain-dependent transmittance of the top-layer, which regulates light emission from the bottom-layer to control the overall hydrogel luminescence. An analytical model is developed to predict the initial luminescence color and color changes as a function of uniaxial strain. Finally, this study demonstrates proof-of-concept applications of the mechanochromic hydrogel for pressure and contact force sensors as well as for encryption devices.

1. Introduction

Mechanochromic materials change their optical appearance (transparency, color, luminescence intensity) in response to external mechanical stimuli.[1] These optical characteristics make these materials promising candidates for a range of applications such as strain sensors,[2] materials failure indicators,[3] encryption devices,[4,5] or smart windows.[6] Hydrogel-based materials have in particular emerged as materials of choice for the fabrication of mechanochromic devices owing to their widely tunable mechanical properties,[7] intrinsic optical transparency,[8] and water compatibility.[9] The design of most current mechanochromic hydrogels is based on the photonic effect, i.e., the creation of an optical bandgap through the assembly of periodic nanostructures within the hydrogel.[10] These photonic hydrogels undergo structural color change upon mechanical deformation via shifts of Bragg diffraction peaks and optical bandgap, thus finding applications in display and mechanical sensing.[11,12] However, the fabrication of photonic gels requires the precise assembly of nanostructures in the gel, a process which usually involves prefabrication of nanoparticles or nanotemplates.[11,13] Moreover, the structural color of photonic gels depends on the light incident angle and the gels must also be free of structural flaws to be fully efficient, limitations which can restrict their practical use.[14] Therefore, it remains challenging to fabricate mechanochromic hydrogels with facile methods and with stable, tunable, and predictable mechanochromism.

In a recent report, Zeng et al.[5] introduced a method to fabricate mechanochromic devices on silicone substrates based on the modulation of transmittance of light through a precracked opaque layer. When the device was stretched, the increase in crack area promoted better light penetration to the bottom fluorescence layer and rendered mechanochromism. Nevertheless, these devices could only respond to uniaxial strain (in the direction perpendicular to the microcracks), and the response range was limited to 0–40% of strain, both of which would limit their applications in strain sensing and mapping. We recently...
reported on how to combine lanthanide (Ln) ions and carbon nanodots (CDs) to produce hydrogels with tunable luminescent color, including white luminescence.\textsuperscript{[15]} Under UV excitation, CDs exhibit blue emission while Ln ions (Eu\textsuperscript{3+} and Tb\textsuperscript{3+}) coordinated by the ligand terpyridine display red or green emission, spectrally far from the excitation wavelength due the energy transfer from the terpyridine “antenna” molecules. As a result, CDs- and Ln-containing hydrogels display a small emission overlap. Exploiting these distinct spectral features, we herein present a new and simple strategy to fabricate mechanochromic hydrogels based on a double-layer design (Figure 1a).

We separate CDs and Ln ions into two layers, with the CD-incorporated hydrogel as the top UV absorption and modulation layer (Figure 1b). When an external strain is applied to the double-layered hydrogel, the thickness of this top CD-layer decreases due to the Poisson’s effect, resulting in an increase in light transmittance and subsequently in enhanced emission from the bottom Ln-layer, thereby providing mechanochromic characteristics. We show that this mechanochromism can be easily tuned by changing the CD concentration or by adding a nonluminescent UV absorber into the top-layer. Moreover, our mechanochromic hydrogels are able to respond from 0% to 300% uniaxial strain, a wider range than previously reported for silicone-based devices, and can be used to visualize 2D as well as contact pressure strain fields. We also develop a simple analytical model to predict the mechanochromism of the hydrogel as a function of the uniaxial strain, which makes it possible to design hydrogels with programmed mechanochromism.
Finally, we demonstrate three proof-of-concept applications of our double-layer mechanochromic hydrogel: i) a bulging pressure sensor; ii) a contact force sensor; and iii) stretching/pressing encryption devices.

2. Results and Discussion

2.1. Design Principle for the Double-Layer Mechanochromic Hydrogel

The classic Lambert–Beer law defines the light transmittance (T) through a translucent material as

\[ T = e^{-kcx} \]  

(1)

where \( k \) is the molar absorptivity, \( c \) is the concentration of the light-absorbing material, \( x \) is the film thickness (optical path), and \( A = kcx \) is the absorbance. For a translucent and stretchable film, a uniaxial stretch in the longitudinal direction reduces the film thickness and increases the transmittance based on Poisson’s effect. For an incompressible elastic material, the concentration of the absorber is not affected by the elastic strain and the strain-induced transmittance change is only determined by the strain-dependent thickness change. The change of transmittance of an elastomeric film during a uniaxial strain can therefore be expressed as

\[ T = e^{-2.3 kcx_0 (1 + \varepsilon)} \]  

(2)

where \( x_0 \) is the initial film thickness, \( \varepsilon \) is the uniaxial strain, and \( \nu \) is the Poisson’s ratio which is 0.5 for incompressible elastomers. [16]

The concept of our double-layer mechanochromic hydrogel is depicted in Figure 1a. CDs were covalently incorporated into the top-layer polyacrylamide gel with or without a nonluminescent UV absorber, 2-(4-benzoyl-3-hydroxyphenoxy)ethyl acrylate (BHEA), which served as a blue emission, and UV-absorbing layer (Figure 1b). The bottom-layer polyacrylamide-co-polyacrylic acid gel was doped with Ln ions through coordination with carboxyl groups. Terpyridine “antenna” were also added to enhance Ln ion luminescence through energy transfer (Figure 1b). Mechanical tests (Figures S1–S3, Supporting Information) showed that both gels were elastic with almost no hysteresis while the double-layer gel exhibited very small hysteresis. Thus, the aforementioned strain-transmittance relationship (Equation (2)) is considered a good approximation for this material. As CD and terpyridine all have strong absorbance in the UV range (Figure 1c), distinct luminescence emissions from CDs and Ln ions (Figure 1d) were obtained with single-wavelength UV excitation. [15] When the UV light passed through the top-layer, it was partially absorbed by CDs and blue fluorescence was emitted. Simultaneously, the light transmitted through the top-layer was absorbed by the bottom-layer, where terpyridine allowed for energy transfer to the Ln ions, resulting in green or red luminescence emission. As the Ln ion emission spectra do not overlap with the absorption spectrum of CDs or BHEA (Figure 1c,d), the luminescence emission from the bottom-layer could transmit through the top-layer gel without any loss due to reabsorption. As a result, the overall emission spectrum represented the combined contribution of both CDs and Ln ions. When a uniaxial strain was applied, transmittance of light into the bottom-layer increased, resulting in enhanced emission from the Ln ions. A mechanochromic effect was thus expected as the strain increased owing to changes of the combined contribution of CDs and Ln ions luminescence spectra. We note that the uniaxial strain also decreased the bottom-layer thickness, which could reduce the amount of luminescence species in the light path and potentially decrease the intensity from the bottom-layer. One strategy to alleviate this drawback is to use a bottom-layer gel with a high absorbance (low internal transmittance) to induce an “inner filter” effect, [17] which minimizes the influence of the light path length of the bottom-layer luminescence (Figure S4a,b, Supporting Information). Here the terpyridine-incorporated bottom gel layer had an absorbance of ~2.3, resulting in a negligible luminescence loss of ~7% due to the light path reduction at a uniaxial strain of 300% in a single layer scheme (Figure S4c, Supporting Information).

2.2. Tuning the Mechanochromism of the Hydrogel

Based on Equation (2), the increase in top-layer transmittance with uniaxial strain is determined by the term \( kcx_0 \) (the initial absorbance of the top-layer hydrogel). Therefore, it is possible to tune the overall spectrum of the double-layer gel by simple variation of the CD and BHEA concentrations in the top-layer, thus rendering mechanochromism upon strain. Initial tests for double-layer hydrogels with varied top-layer CD concentrations (1–10 mg mL\(^{-1}\)) and Tb\(^{3+}\) in the bottom-layer showed a distinct color change at 300% strain only when the CD concentration is 4 mg mL\(^{-1}\) (Figure S5a, Supporting Information). Two arbitrary parameters were defined to more accurately evaluate the mechanochromism, namely, the color ratio \( r = I_{544}/I_{414} \) where \( I_{544} \) is the peak intensity of Tb\(^{3+}\)-centered luminescence (green emission) and \( I_{414} \) that of CD fluorescence (blue emission), and the mechanochromic shift (\( D \)) which is the distance between the data points on the color chart. At low CD concentrations (<4 mg mL\(^{-1}\)), the low initial absorbance resulted in a small fold change of transmittance under strain and high initial \( r \) value (Figure S5c,d, Supporting Information) (green luminescence dominates). Therefore, \( D \) was small and the color always remained in the green region with insignificant color change (Figure S6a,c, Supporting Information). On the contrary, at high CD concentrations (>4 mg mL\(^{-1}\)) the higher initial absorbance yielded a small initial \( r \) value (Figure S5d, Supporting Information) (blue luminescence dominates), which cannot be compensated by the larger fold change of transmittance (Figure S5c, Supporting Information) as well as the larger \( D \) (Figure S6c, Supporting Information), causing the overall color to remain in the blue region (Figure S6a, Supporting Information). At the intermediate CD concentration of 4 mg mL\(^{-1}\), the initial absorbance resulted in moderate initial \( r \) and fold transmittance change upon strain, allowing the Tb\(^{3+}\)-centered luminescence to gradually dominate with increasing strain to yield a prominent blue-to-green mechanochromism (Figure S6a,c, Supporting Information).
To further improve the sensitivity of the mechanochromism, we devised a strategy to increase the initial absorbance of the top-layer without significantly increasing its initial blue emission by introducing the crosslinkable UV absorber BHEA along with CDs. Adding BHEA not only increased the initial absorbance but also decreased the initial CD emission due to the “inner filter” effect (Figure S9b, Supporting Information), providing extra control over the sensitivity of the mechanochromism. Double-layer hydrogels were fabricated with various BHEA concentrations at a fixed CD concentration (1 mg mL\(^{-1}\)) in the top-layer gel (CD/BHEA gel).

Upon uniaxial strain, the bottom-layer Tb\(^{3+}\)-centered luminescence increased as the top CD layer fluorescence decreased, thereby expanding the overall spectral shift (Figure 2). At BHEA concentration of 0.6 mg mL\(^{-1}\) and above, a visible blue-to-green mechanochromic change was observed. Compared to the hydrogel containing only CDs in the top-layer, the incorporation of BHEA thus expanded the strain-dependent color shift and enhanced the mechanochromic sensitivity, as illustrated by \(D\) increasing from 0.054 (no BHEA) to 0.242 with 1 mg mL\(^{-1}\) BHEA (Figure S6d, Supporting Information). At high BHEA concentrations, the enhanced mechanochromic sensitivity can be attributed to: i) the enhancement in the strain-dependent fold increase of top-layer transmittance (Figure 2b), which in turn enhanced the bottom-layer Tb\(^{3+}\)-centered luminescence and ii) the weaker initial CD emission intensity (Figure S9b, Supporting Information). These combined effects resulted in a more pronounced variation of \(r\) with strain (Figure 2c and Figure S11b, Supporting Information). We note that the changes of both transmittance and \(r\), with or without BHEA in the top-layer, could be predicted based on the strain-transmission relation and the Lambert–Beer law (dashed line in Figure 2b,c and Figures S5c,d, S9, and S11 in the Supporting Information, the detailed derivations of the predictions are presented in the Supporting Information). Compared to photonic hydrogels, in which mechanochromism is tuned by changing hydrogel nanostructure[11,19], our double-layer mechanochromic hydrogel could be tuned by simply varying the concentration of CDs or BHEA in the top-layer, providing a facile and versatile method to fabricate functional mechanochromic hydrogels.

2.3. Prediction of Mechanochromism under Uniaxial Strain

Ideally, mechanochromic materials should not only exhibit mechanochromic tunability but also include a strategy to design the material with a desired mechanochromism, i.e., programming the actual color coordinates as a function of deformation. The change of \(r\) values during uniaxial stretching could be predicted if the initial absorbance and \(r\) values are known (Figure S11, Supporting Information). Since \(r\) represents the
peak intensity ratio of Tb\(^{3+}\)-centered luminescence to that of CD fluorescence, it also reflects the green-to-blue color ratio. Thus, we postulated that \(r\) could be correlated with the actual color coordinates. Considering the relationship between color coordinates and the spectrum of the double-layer gel luminescence, using the measured \(r\) value and the corresponding color coordinates calculated from the spectrum, we established a correlation between the color coordinate and \(r\) with a three-parameter fitting function (\(R^2 > 0.99\)) (Figures 3a,b and Figure S12 in the Supporting Information; detailed derivation described in the Supporting Information). For example, the \(x\) coordinate can be expressed as

\[
x = \frac{r + \alpha_x}{\beta_x r + \gamma_x}
\]

where \(\alpha_x\), \(\beta_x\), and \(\gamma_x\) are nonempirical fitting constants that are related to the tristimulus values in the CIE 1931 color system. The prediction of color change was thus achieved as a function of \(r\) (Figures 3c,d and Figures S13 and S14, Supporting Information), making it possible to program the initial color, the mechanochromic sensitivity, as well as the color at a given strain as part of the double-hydrogel fabrication.

2.4. Double-layer Mechanochromic Hydrogel as a Bulging Pressure Sensor

As the mechanochromism of our hydrogel arises from a strain-induced thickness decrease, we hypothesized that the color shift would not be limited to uniaxial deformation but could also be achieved with more complex strain fields. For example, we designed an inflation device to demonstrate the application of our hydrogel as a bulging pressure sensor. The photograph of the device is shown in Figure 4a and the measurement setup is schematically illustrated in Figure 4b. The hydrogel was clamped between two aluminum plates with a circular hole of 10 mm in diameter at the center. The device was pressurized through a syringe pump to bulge the gel and the pressure was monitored in real time by a pressure meter. During the bulging process, the center of the specimen—which bear in-plane equi-biaxial strain—was aligned with the excitation light and its spectrum was acquired with a fluorometer. Double-layer hydrogels with CD/BHEA-gel in the top-layer and either Tb\(^{3+}\) or Eu\(^{3+}\)-gel in the bottom-layer were tested. The hydrogel bulged normal to the device (Figure 4c) and a prominent color shift from blue-to-green (with Tb\(^{3+}\) gel) or blue-to-red (with Eu\(^{3+}\) gel) was observed in the center of the gel (Videos S1 and S2, Supporting Information). Pressure as low as 1 kPa could be visualized with a resolvable color shift, and colorimetric detection of pressure up to 7 kPa could be achieved (Figure 4d,e). In addition, the local in-plane equi-biaxial strain in the center of the specimen could be estimated by inferring the transmittance of the gel from the \(I_{544}/I_{414}\) measurements (bottom gel with Tb\(^{3+}\) gel) or blue-to-red (with Eu\(^{3+}\) gel) was observed in the center of the gel (Videos S1 and S2, Supporting Information). Pressure as low as 1 kPa could be visualized with a resolvable color shift, and colorimetric detection of pressure up to 7 kPa could be achieved (Figure 4d,e). In addition, the local in-plane equi-biaxial strain in the center of the specimen could be estimated by inferring the transmittance of the gel from the \(I_{544}/I_{414}\) measurements (bottom gel with Tb\(^{3+}\) gel) and subsequently by converting the transmittance to the thickness and the out-of-plane strain (Figure S15, Supporting Information). For example, with a bulging pressure of 7 kPa, the in-plane equi-biaxial strain in the CD/BHEA/Tb gel was estimated to be \(\approx 52\%\). Therefore, our hydrogel could not only be used as a bulging pressure sensor but also potentially to map plane-strain fields.

![Figure 3. Prediction of the hydrogel mechanochromism. a,b) Fitting the \(r\) value to the \(x\) a) and \(y\) b) coordinates on the color chart based on a proposed model function. A three-parameter (\(\alpha_x, \beta_x, \gamma_x\)) fitting was obtained with \(R^2 > 99\%\). c,d) Comparison of the experimental (black diamond) with the predicted (red square) mechanochromism on the color chart for the double-layer hydrogel with 4 mg mL\(^{-1}\) CD c) or 1 mg mL\(^{-1}\) CD and 0.8 mg mL\(^{-1}\) BHEA d) in the top-layer and Tb\(^{3+}\) in the bottom-layer.](image-url)
2.5. Double-layer Mechanochromic Hydrogel as a Contact Force Sensor

Another way to change the transmittance of an elastic material is through compressive loading. Therefore, our double-layer mechanochromic gels could in principle be used to monitor contact pressure. To apply our hydrogel for contact force sensing, a device was designed to allow simultaneous measurements of force and luminescence (Figure 4f,g). An aluminum piston connected to a force...
sensor was mounted onto a translation stage to allow contact of the hydrogel sample at defined forces, with the hydrogel fixed on a quartz window. Upon pressing, the exerted force and the luminescence spectra of the gel were simultaneously measured with a force sensor and a fluorometer. Double-layer hydrogels with CD/BHEA-gel in the top-layer and either Tb\(^{3+}\) or Eu\(^{3+}\)-gel in the bottom-layer were tested and luminescence spectra were acquired with 1 N increments of external force. As shown in Figure 4h, a color shift from blue to green (with the Tb\(^{3+}\)-gel) or blue to red (with the Eu\(^{3+}\)-gel) was observed at increasing external forces. Therefore, this mechanochromism can be used to visualize the magnitude of applied force ranging from 0 N for 9 N (Figure 4i,j). Moreover, the force–color relationship can be converted into pressure–color relation, potentially making our hydrogel a touch pressure sensor (Figure 4i,j).

2.6. Double-layer Mechanochromic Hydrogel as Encryption Devices

As a further proof-of concept, we designed encryption devices by encoding information into the bottom Ln-gel, which was subsequently uncovered by two different mechanical cues, namely, either stretching or pressing. For the stretching-based encryption device, a Tb\(^{3+}\) bottom-layer gel with a “SMART” logo was photo-patterned onto a polyacrylamide gel substrate and a layer of CD/BHEA-gel was placed over the logo (Figure S16a, Supporting Information). In order to obtain an invisible logo in the gel equilibrium state, the top-layer thickness was set at 1 mm with a CD and BHEA concentrations of 1 mg mL\(^{-1}\) that rendered an initial UV (330 nm) transmittance of \(\approx 0.02\%\). Upon stretching the gel to four times its original width, the UV transmittance of the top-layer, and a green “SMART” logo could be revealed from the blue background (Figure 5b and Video S3, Supporting Information). This enabled hidden information from the stamp to be revealed by application of pressure to the double-layer gel under UV light. We envision using this concept for anticounterfeiting applications as reported for other photonic elastomers.[4]

3. Conclusion

To sum up, we have reported a new strategy to fabricate luminescent and mechanochromic hydrogels based on a double-layer luminescent spectra design. Distinct from traditional mechanochromic photonic gels, which necessitate the prefabrication of well-ordered nanostructures or the preassembly of nanoparticles, this double-layer hydrogel requires simple fabrication procedures consisting mainly of casting. The key to achieve mechanochromism is to use CD and Ln ions as the luminescent species in the top- and bottom-layers of the gel, with the former acting not only as a blue fluorescence emitter but also as a UV absorber along with a nonluminescent absorber (BHEA). The thickness of the top-layer decreases by virtue of the Poisson’s effect, resulting in enhanced transmittance to the bottom-layer whose luminescence in turn increases. Because the relative increase of transmittance is determined by the initial absorbance of the top-layer, the mechanochromism can be tuned simply by changing the CD or BHEA concentration in the top-layer. We have also developed a model to predict the shift of the actual color coordinates during uniaxial stretching based on the initial concentration of UV absorber in the top-layer, thereby allowing programmable mechanochromic hydrogels. Toward practical applications, we have demonstrated the use of these mechanochromic hydrogels as bulging pressure and contact force sensors as well as material-based encryption devices that could be used for anticounterfeit applications or official document authentication. This double-layer concept should not be limited to hydrogels and could provide a new design strategy to guide the fabrication of mechanochromic devices with other stretchable materials.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
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Conflict of Interest

The authors declare no conflict of interest.

Keywords

double layer, encryption, lanthanides, luminescence, mechanochromic hydrogels

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