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Citation	Zhu, Qingdi, Vliet, Krystyn, Holten#Andersen, Niels and Miserez, Ali. 2019. "A Double#Layer Mechanochromic Hydrogel with Multidirectional Force Sensing and Encryption Capability." <i>Advanced Functional Materials</i> , 29 (14).
As Published	http://dx.doi.org/10.1002/adfm.201808191
Publisher	Wiley
Version	Author's final manuscript
Citable link	https://hdl.handle.net/1721.1/140978
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A Double-Layer Mechanochromic Hydrogel with Multi-Directional Force Sensing and Encryption Capability

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Abstract

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, we present a distinct concept and simple fabrication strategy to produce luminescent mechanochromic hydrogels based on a double-layer design. The two layers contain different

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version of Record](#). Please cite this article as [doi: 10.1002/adfm.201808191](https://doi.org/10.1002/adfm.201808191).

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luminescent species –carbon dots (CDs) and lanthanide (Ln) 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. We finally demonstrate proof-of-concept applications of our mechanochromic hydrogel for pressure and contact force sensors as well as for encryption devices.

Main Text

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 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 pre-fabrication of nanoparticles or nano-templates.^[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 pre-cracked 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 response to uniaxial strain (in the direction perpendicular to the planes of the micro-cracks), 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.^[15] Under UV excitation, CDs exhibit blue emission while Ln ions (Eu^{3+} and Tb^{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 (**Fig. 1a**). We separate CDs and Ln ions into two layers, with the CD-incorporated hydrogel as the top UV absorption and modulation layer. 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 to 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 non-luminescent UV absorber into the top layer. Moreover, our mechanochromic hydrogels are able to response from 0 to 300%

uniaxial strain, a wider range than previously reported for silicone based devices, and can be used to visualize two-dimensional 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.

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

$$T = e^{-2.3kcx} \quad \text{Eq.1}$$

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:

$$T = e^{-2.3kcx_0(1+\varepsilon)^{-\nu}} \quad \text{Eq.2}$$

where x_0 is the initial film thickness, ε is the uniaxial strain and ν is the Poisson's ratio which is 0.5 for incompressible elastomers.^[16]

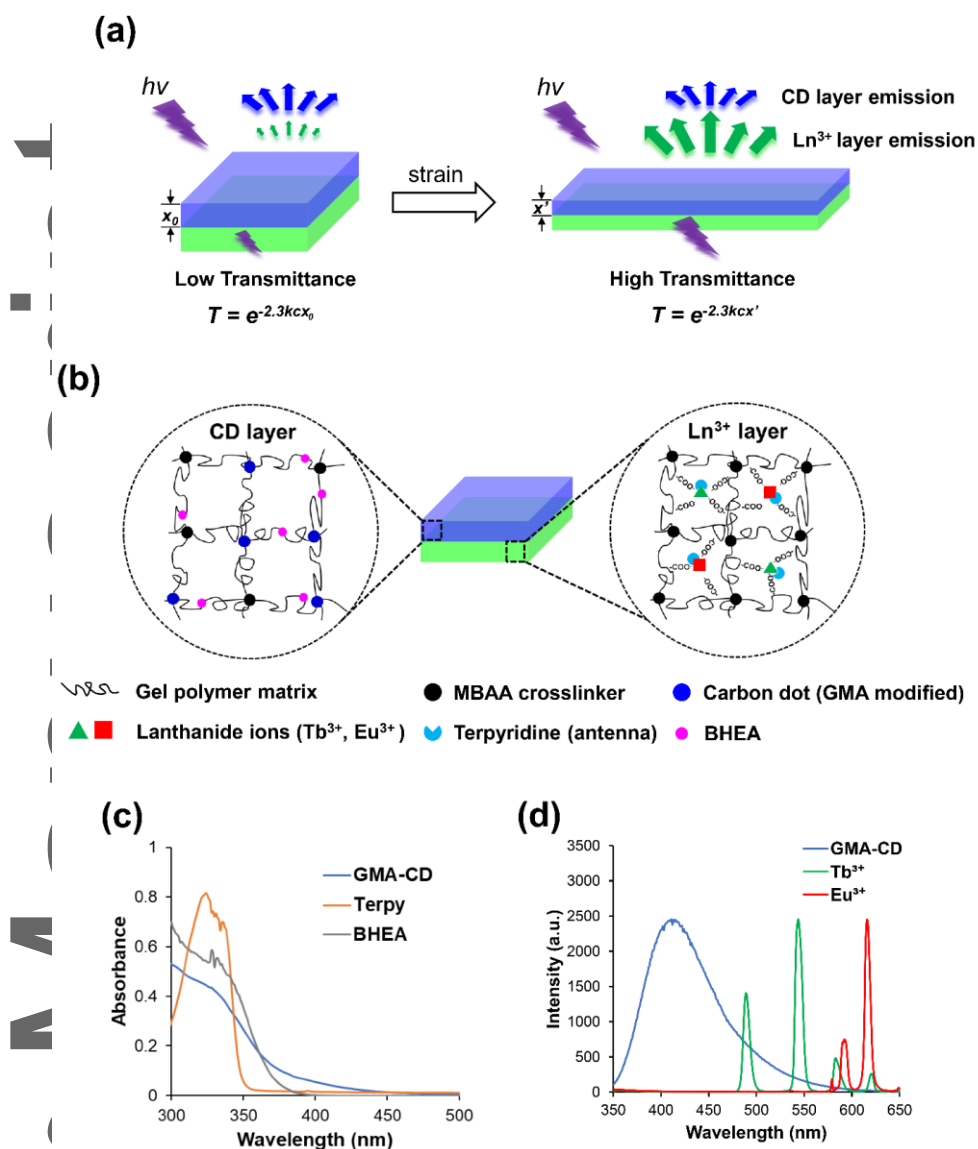


Figure 1. Design of mechanochromic hydrogel. (a) Design principle of double-layer mechanochromic materials based on the strain-transmittance relationship. (b) Schematic diagram showing the chemical components in the double-layer hydrogel. (c) Absorption spectra of GMA-CD, terpyridine (Terpy), and BHEA. (d) Emission spectra of luminescence species (GMA-CD, Tb³⁺ and Eu³⁺) used in the double-layer mechanochromic hydrogel.

The concept of our double-layer mechanochromic hydrogel is depicted in **Fig. 1a**. CDs were covalently incorporated into the top-layer polyacrylamide gel with or without a non-luminescent UV absorber, 2-(4-benzoyl-3-hydroxyphenoxy)ethyl acrylate (BHEA), which served as a blue emission and UV-absorbing layer (**Fig. 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 (**Fig. 1b**). Mechanical tests (**Figs. S1-3**, Supporting Information) showed that both gels were elastic with almost no hysteresis while the double layer gel exhibits very small hysteresis. Thus, the aforementioned strain-transmittance relationship (Eq. 2) is considered a good approximation for this material. As CD and terpyridine all have strong absorbance in the UV range (**Fig. 1c**), distinct luminescence emissions from CDs and Ln ions (**Fig. 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 (**Figs. 1c,d**), the luminescence emission from the bottom-layer could transmit through the top-layer gel without any loss due to re-absorption. 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 minimized the influence of the light path length of the bottom-layer luminescence (**Figs. S4a-b**, Supporting Information). Here the terpyridine-incorporated bottom gel layer had an absorbance of ~2.3, resulting in a negligible

luminescence loss of *ca.*7% due to the light path reduction at a uniaxial strain of 300% in a single layer scheme (**Fig. S4c**, Supporting Information).

Based on Eq. 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 to 10 mg/ml) and Tb^{3+} in the bottom-layer showed a distinct color change at 300% strain only when the CD concentration is 4 mg/ml (**Fig. 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), the low initial absorbance resulted in a small fold change of transmittance under strain and high initial r value (**Figs. S5c-d**, Supporting Information) (green luminescence dominates). Therefore, D was small and the color always remained in the green region with insignificant color change (**Figs. S6a and S6c**, Supporting Information). On the contrary, at high CD concentrations (> 4 mg/ml) the higher initial absorbance yielded a small initial r value (**Fig. S5d**, Supporting Information) (blue luminescence dominates), which cannot be compensated by the larger fold change of transmittance (**Fig. S5c**, Supporting Information) as well as the larger D (**Fig. S6c**, Supporting Information), causing the overall color to remain in the blue region (**Fig. S6a**, Supporting Information). At the intermediate CD concentration of 4 mg/ml, 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 (**Figs. S6a and S6c**, Supporting Information).

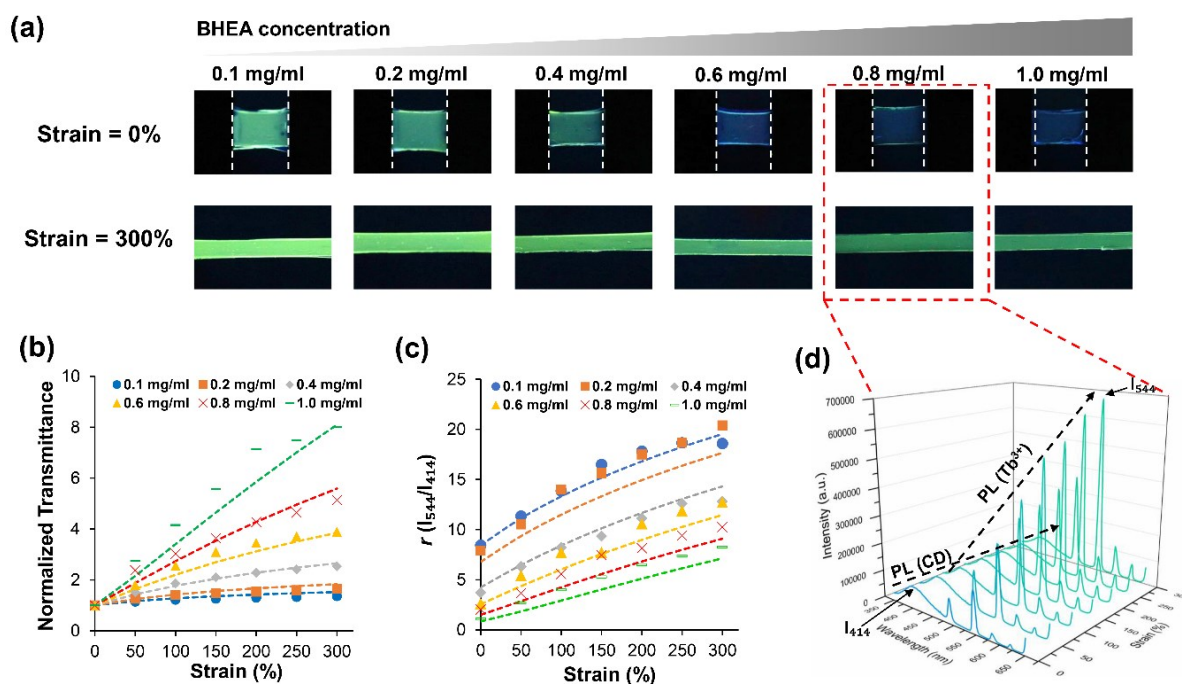


Figure 2. Tuning the mechanochromism of the double-layer gels by varying BHEA concentration. (a) Photographs showing the mechanochromic change of the double-layer hydrogel with different top-layer BHEA concentrations and a fixed CD concentration of 1 mg/ml after it was applied with 300% uniaxial strain. White dashed lines represent the position of the clamps on the micro-tensile testing machine. (b) Change of luminescence spectrum vs. uniaxial strain for the double-layer gel with 0.8 mg/ml BHEA and 1 mg/ml CD in the top-layer. (c) Change of normalized transmittance for the CD-BHEA gel vs. uniaxial strain. (d) Evolution of r value for the double-layer gel with CD-BHEA as the top-layer gel. Dashed lines in (b) and (c) represent results from the analytical modelling.

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 cross-linkable UV absorber BHEA along with CDs.^[18] Adding BHEA not only increased the initial absorbance but also decreased the initial CD emission due to the “inner filter” effect (Fig. 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) 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 (**Fig. 2**). At BHEA concentration of 0.6 mg/ml 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 BHEA (**Fig. 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 (**Fig. 2b**), which in turn enhanced the bottom-layer Tb^{3+} -centered luminescence, and (ii) the weaker initial CD emission intensity (**Fig. S9b**, Supporting Information). These combined effects resulted in a more pronounced variation of r with strain (**Fig. 2c** and **Fig. 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 **Figs. 2b-c**, **Figs. S5c-d**, **S9** and **S11**, 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.

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 (Fig. 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 that a correlation between the color coordinate and r can be obtained with a three-parameter fitting function ($R^2 > 0.99$) (Figs. 3a-b and Fig. S12; detailed derivation described in Supporting Information). For example, the x coordinate can be expressed as:

$$x = \frac{r + \alpha_x}{\beta_x r + \gamma_x} \quad \text{Eq. 3}$$

where α_x , β_x and γ_x are non-empirical fitting constants that are related to the tri-stimulus values in the CIE 1931 color system. The prediction of color change was thus achieved as a function of r (Figs. 3c-d and Figs. S13-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.

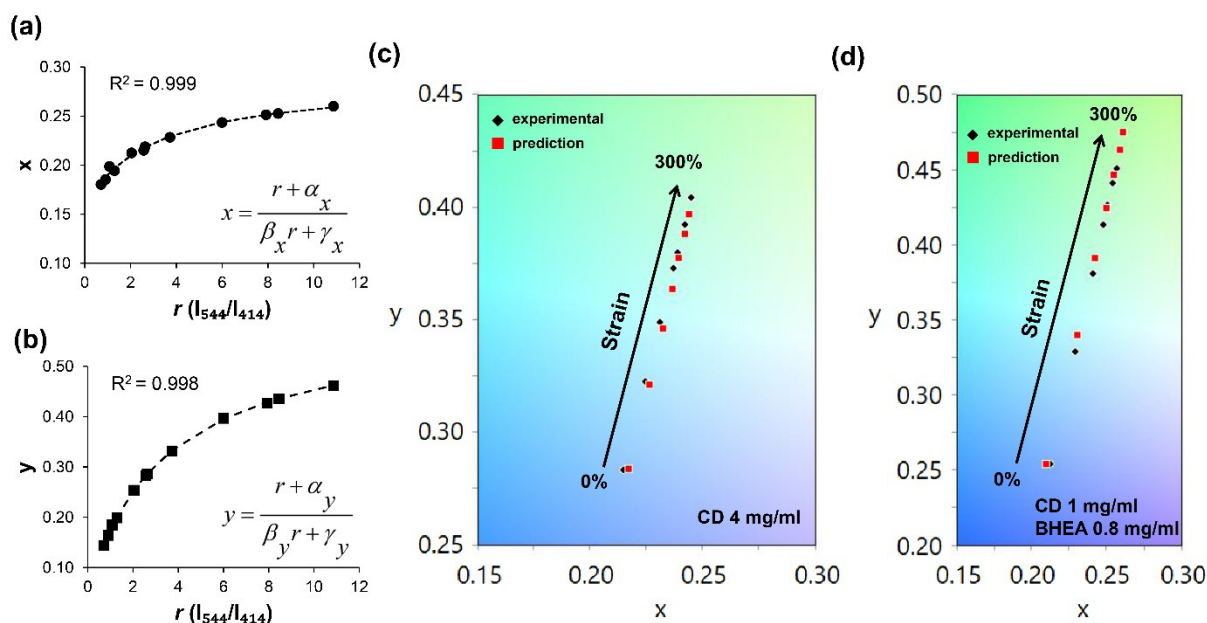


Figure 3. Prediction of the hydrogel mechanochromism. (a-b) Fitting the r value to the x (a) and y (b) coordinates on the color chart based on a proposed model function. A three-parameter (α , β , γ) fitting was obtained with $R^2 > 99\%$. **(c-d)** Comparison of the experimental (black diamond) with the predicted (red square) mechanochromism on the color chart for the double-layer hydrogel with 4 mg/ml CD (c) or 1 mg/ml CD and 0.8 mg/ml BHEA (d) in the top-layer and Tb^{3+} in the bottom-layer.

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 **Fig. 4a** and the measurement setup schematically illustrated in **Fig. 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 equibiaxial strain^[2, 20]– 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

Eu³⁺-gel in the bottom-layer were tested. The hydrogel bulged normal to the device (**Fig. 4c**) and a prominent color shift from blue-to-green (with Tb³⁺ gel) or blue-to-red (with Eu³⁺ gel) was observed in the center of the gel (**Supporting Videos S1 and S2**). 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 (**Figs. 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 Tb³⁺) and subsequently by converting the transmittance to the thickness and the out-of-plane strain (**Fig. 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 *ca.* 52%. Therefore, our hydrogel could not only be used as a bulging pressure sensor, but also potentially to map plane-strain fields.

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 (**Figs. 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 Tb³⁺- or Eu³⁺-gel in the bottom-layer were tested and luminescence spectra were acquired with 1 N increments of external force. As shown in **Fig. 4h**, a color shift from blue to green (with the Tb³⁺-gel) or blue to red (with the Eu³⁺-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 (**Figs. 4i-j**). Moreover, the force-color

relationship can be converted into pressure-color relation, potentially making our hydrogel a touch pressure sensor (Figs. 4i -j).

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 Tb³⁺ 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 (Fig. 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 that rendered an initial UV (330 nm) transmittance of *ca.* 0.02%. Upon stretching the gel to 4 times its original width, the UV transmittance of the film rose to *ca.* 10%, high enough to excite the bottom Tb³⁺-gel pattern and to display the luminescent “SMART” logo (Fig. 5a). Therefore, the design could be used as a material-based communication encryption device with concealed information revealed only by external stretching under UV light.

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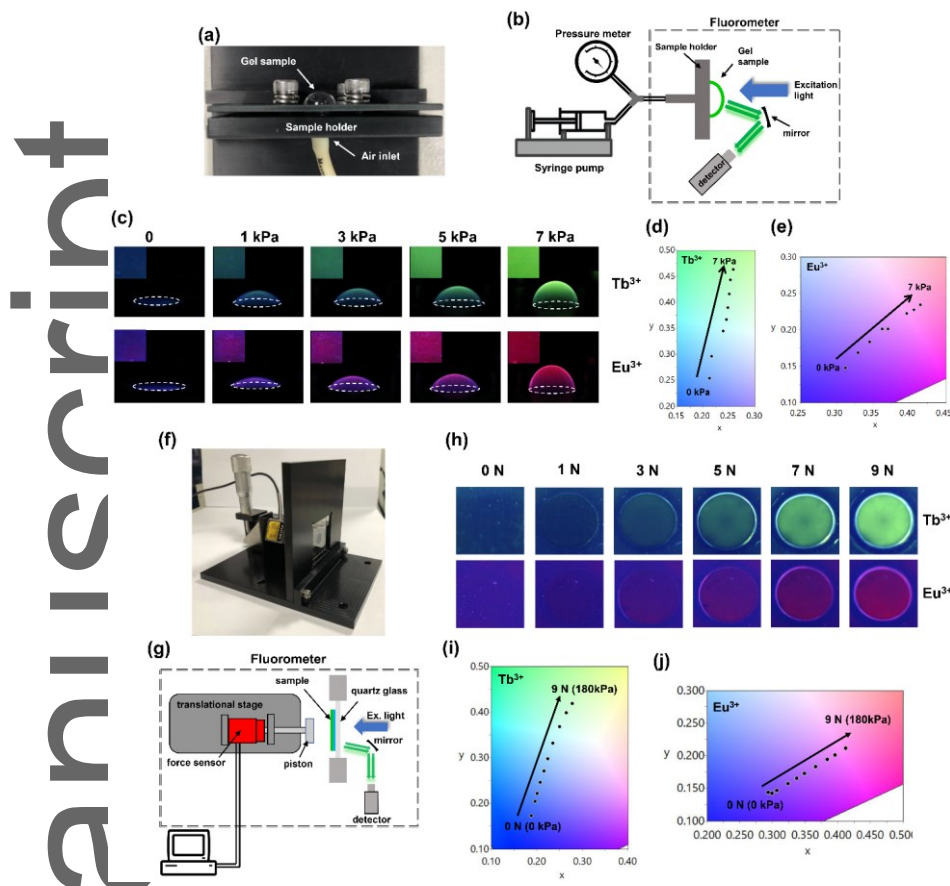


Figure 4. Application of mechanochromic hydrogel as pressure and force sensors. (a) Photograph and (b) schematic of the experimental setup for bulging pressure sensing. Top-layer CD concentration: 1 mg/ml; top-layer BHEA concentrations: 0.8 mg/ml (with Tb^{3+}) or 0.4 mg/ml (with Eu^{3+}). (c) Photographs of the mechanochromic hydrogel under different bulging pneumatic pressures. Insets: color in the center of the bulging gel. (d-e) Mechanochromism displayed as the correlation between color coordinates and bulging pressure for Tb^{3+} - (d) and Eu^{3+} - (e) bottom-layer gels. (f) Photograph and (g) schematic of the experimental setup for pressing force sensing. Top-layer CD concentration: 1 mg/ml; BHEA top-layer concentrations: 1 mg/ml (with Tb^{3+}) or 0.6 mg/ml (with Eu^{3+}). (h) Photographs of the mechanochromic hydrogel under different pressing forces. (i-j) Mechanochromism displayed as the correlation between color coordinates and pressing force for Tb^{3+} (i) and Eu^{3+} (j) bottom-layer gels.

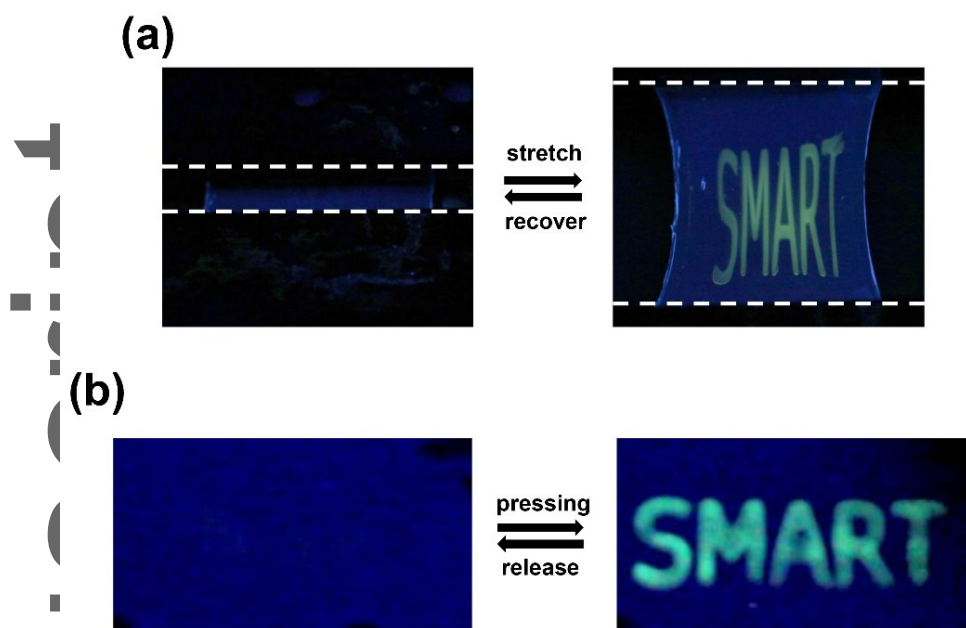


Figure 5. Application of mechanochromic double-layer hydrogel as encryption devices. (a) Photograph showing the concealed “SMART” logo revealed upon stretching a gel device in the vertical direction. **(b)** Photograph showing the concealed “SMART” logo revealed upon pressing a gel-containing device from the bottom. Schematics of device preparation are shown in **Fig. S16** in the Supporting Information.

In another design, we revealed the encoded information of the gel by compression. An encryption device prototype was fabricated (**Fig. S16b**, Supporting Information) by stacking the double-layer mechanochromic gel between a top quartz window and a bottom glass stamp patterned with the “SMART” logo. The mechanochromic gel consisted of a top-layer hydrogel with 1 mg/ml of both CDs and BHEA and a bottom-layer Tb^{3+} -hydrogel. By applying pressure to the top quartz window, the pattern of the hard stamp changed the local UV transmittance of the top-layer, and a green “SMART” logo could be revealed from the blue background (**Fig. 5b**, **Supporting Video S3**). 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 anti-counterfeiting applications as reported for other photonic elastomers^[4].

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 pre-fabrication of well-ordered nanostructures or the pre-assembly 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 non-luminescent 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. Towards 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 anti-counterfeit 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 in the online version of the manuscript.

Acknowledgements

This research was funded by a seed grant from the BioSystems and Micromechanics thrust of the Singapore-MIT Alliance for Research and Technology (BioSym-SMART). The authors thank Dr. Shahrouz Amini for his help in establishing mechanical testing and sensing devices and for insightful discussions. The authors also thank Dr. Lin Kan for help with MATLAB modeling.

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