

Double-Layer Hydrogels with Tunable Mechanofluorochromic Response for Smart Display

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Electronic Supplementary Information

Abstract Mechanofluorochromic materials that render sensitive fluorescence color/pattern change upon mechanical stimuli have drawn extensive attention. However, traditional mechanofluorochromism relies on the chemical transformations of mechanophores, but their types are quite few. It remains challenging to develop mechanofluorochromic materials with customized fluorescence color changing response. Herein, a generally applicable strategy is proposed to present a class of double-layer mechanofluorochromic hydrogels based on the facile integration of two different-colored fluorescent hydrogels. Due to the UV transmittance change of top layer under Poisson's effect, the emission intensity ratio of the upper and lower hydrogels exhibits a strain-dependent change, resulting in a force-triggered overlapping color variation. Both the UV transmittance of top layer and the fluorescence emission of bottom layer can be readily modulated to enrich the variety of mechanofluorochromism. Besides, the bottom layer is available to be printed by ion inks to fabricate patterned double-layer fluorescent hydrogel, holding great potential to design flexible mechanofluorochromic platforms for smart display and information encryption.

Keywords Mechanofluorochromism; Fluorescent hydrogel; Double layer; Smart display

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INTRODUCTION

Mechanosensitive systems are commonly found in living species, playing an important role in signal transduction to regulate life activities.^[1–5] For example, the body transparency of *Hippopodius* will change upon tactile stimulation, which is essentially caused by the contraction of radial muscles.^[6,7] Such phenomena are learned and exploited in the design of synthetic materials, and a myriad of mechanosensitive materials with custom properties have emerged in the past decades.^[8–12] Thereinto, mechanofluorochromic materials, capable of changing luminescence intensity/color in response to mechanical stimuli, have developed rapidly with wide applications in visual strain sensors,^[13–15] material failure indicators,^[16–18] smart display,^[19,20] information encryption,^[21–23] and so forth.

Currently, most reported mechanofluorochromic materials involve mechanophores, which possess mechanically labile molecular structure or conformation to exhibit force-

triggered fluorescent responses.^[24,25] Typical mechanophores include spiropyran,^[26,27] rhodamines,^[28,29] dioxetanes,^[30] ladderanes,^[31] rotaxanes,^[32] cyclophanes^[33] and others.^[34] However, the category of eligible mechanophores is finite, and the systems often lack adequate adjustability of mechanofluorochromism performances. Another general strategy has been proposed by introducing a nonluminous shielding layer that features force-sensitive cracks or wrinkles at micro-/nanoscale onto the luminous one.^[35–37] This strategy, despite being applicable to more general fluorophores, is limited by convenient and reliable techniques to fabricate micro-/nanostructured surfaces. To this end, Miserez and coworkers recently expanded this strategy by integrating two different-colored fluorescent materials together to produce double-layer mechanofluorochromic materials, which displayed a strain-dependent overlapping color change evoked by Poisson's effect.^[38] Despite research on this type of double-layer mechanofluorochromic materials is still at a premature stage, it is assumed to be prospective due to a wider choice of chromophores and easier preparation methods.

In recent years, fluorescent polymeric hydrogels have attracted great attention for their unique characteristics, and are considered as an ideal choice for the fabrication of mechanofluorochromic materials.^[39,40] For one thing, hydro-

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gel systems have a certain extent of openness, not only benefiting the modulation of optical properties, but resulting in good sensitivity and quick response to stimulus.^[41] For another, hydrogels have a soft and flexible nature, whose mechanical properties are tissue-like and widely tunable.^[42] Thus, the hydrogel-based mechanofluorochromic materials may adapt to various form of mechanical cues, and are expected to expand the field of applications (e.g., biomimetic skins).

Herein, we put forward an efficient way to construct double-layer mechanofluorochromic hydrogels. As illustrated in Scheme 1, red fluorescent hydrogel sodium alginate/poly(acrylamide/potassium 6-acrylamidopicolinate-Eu) (SPAA-Eu) were combined with blue fluorescent hydrogel sodium alginate/poly(acrylamide/4-(2-dimethylaminoethoxy)-*N*-allyl-1,8-naphthalimide) (SPAD) based on the interfacial hydrogen bonding between sodium alginate. As the top layer hydrogel, SPAD served as a luminescent source and gave out intense blue emission under illumination of 254 nm light. Meanwhile, it served as a UV absorber and suppressed the red emission from the bottom SPAA-Eu at unstretched state. When applying external force, the thickness of SPAD decreased with elongation, leading to an increase of UV transmittance as well as a decrease of blue emission intensity. Consequently, the red emission intensity was enhanced to give a significantly different overlapping color. Following a similar line, when pairing the top blue fluorescent hydrogel layer with bottom

green/yellow fluorescent hydrogel, mechanofluorochromic phenomena were also observed, indicating the generality of the proposed strategy. Furthermore, when patterned fluorescent hydrogel was employed as the bottom layer, meaningful fluorescent patterns will be gradually disclosed upon stretching, holding potential for applications such as smart display and information encryption.

EXPERIMENTAL

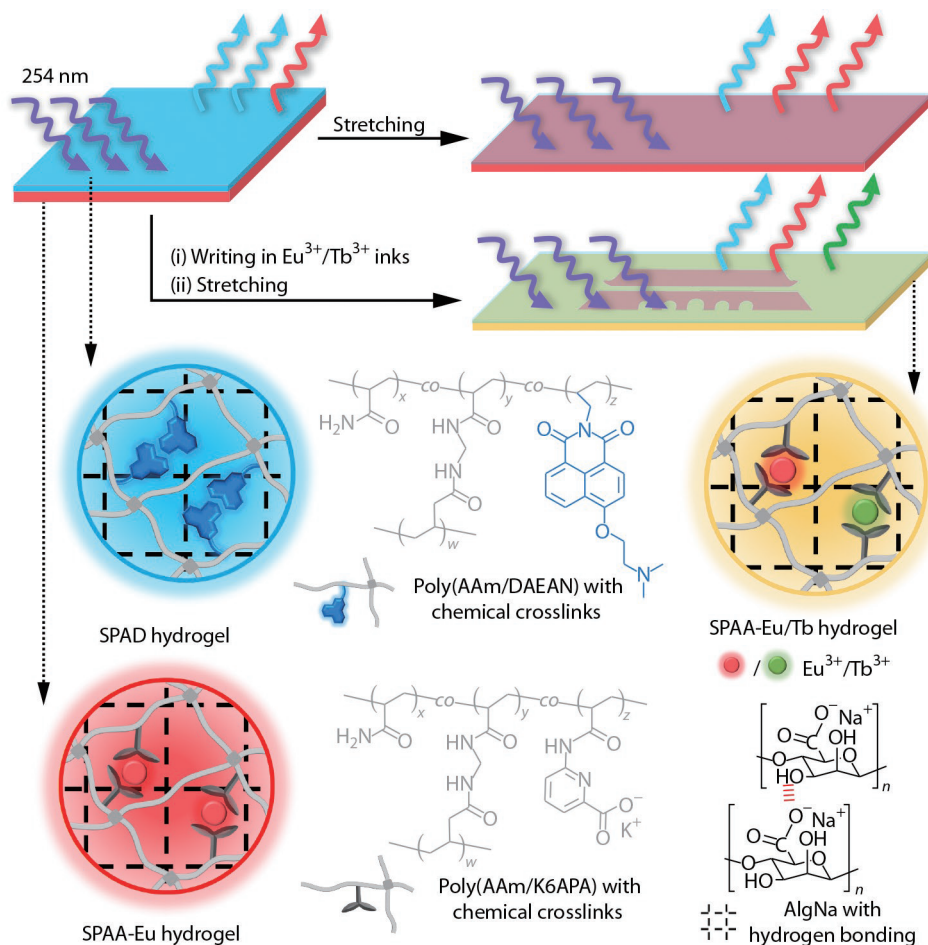
Materials

Acrylamide (AAM, 98%) and sodium alginate (AlgNa) were purchased from Sinopharm Chemical Reagent Co., Ltd. *N,N'*-methylenebis(acrylamide) (MBAA, 98%), ammonium persulfate (APS, 98%), *N,N,N',N'*-tetramethylethylenediamine (TEMED, 99%) and $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.9%) were supplied by Aladdin Chemistry Co., Ltd. $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%) and potassium hydroxide (KOH, 95%) were obtained from Energy Chemical. 6-Acrylamidopicolinic acid (6APA) and 4-(2-dimethylaminoethoxy)-*N*-allyl-1,8-naphthalimide (DAEAN) were synthesized according to the procedures described in our previous studies.^[43,44]

Fabrication of Monolayer Fluorescent Hydrogel

Synthesis of SPAA-Eu/Tb

Monomer 6APA (24 mg) was first dissolved in KOH aqueous



Scheme 1 Illustration showing the design of mechanofluorochromic double-layer hydrogel SPAD/SPAA-Eu/Tb.

solution (0.7 mL, 0.01 g/mL) to produce potassium 6-acrylamidopicolinate (K6APA), and then codissolved with monomer AAm (1.8 g), crosslinker MBAA (1 mg), initiator APS (36 mg) in deionized water (5.3 mL). The pre-polymer solution was further mixed with AlgNa aqueous solution (6 mL, 3.75 wt%), followed by the addition of initiator accelerator TEMED (12 μ L). Subsequently, the mixture was poured into self-made mold with a thickness of 0.5 mm, and free radical polymerization was carried out at room temperature for 24 h to prepare hydrogel AlgNa/poly(AAm-K6APA) (SPAA). Furthermore, the SPAA hydrogel was treated with aqueous solution of Eu^{3+} , Tb^{3+} nitrate or their mixture, affording multicolor fluorescent hydrogel SPAA-Eu/Tb. The total concentration of Eu^{3+} and Tb^{3+} was fixed at 0.05 mol/L.

Synthesis of SPAD

Monomers AAm (1.8 g), crosslinker MBAA (1 mg) and initiator APS (36 mg) were codissolved in 3 mL of deionized water, and then mixed with 3 mL of DAEAN aqueous solution (0.05, 0.1 or 0.2 mg/mL). The pre-polymer solution was further mixed with 6 mL of aqueous solution of AlgNa (3.75 wt%), followed with the addition of initiator accelerator TEMED (12 μ L). Subsequently, the mixture was poured into self-made mold with a thickness of 0.3, 0.4 or 0.5 mm, and free radical polymerization was carried out at room temperature for 24 h to prepare blue fluorescent hydrogel SPAD.

Fabrication of Double-layer Fluorescent Hydrogel

First, hydrogel SPAD was dehydrated by ambient air drying for 12 h, and reached a water loss of approximately 80% initial weight. The SPAD in semi-dry state was then attached to SPAA in wet state to form double-layer fluorescent hydrogel SPAD/SPAA, which was let stand for 10 min to realize stable adhesion. Later, the SPAD/SPAA was treated with aqueous solution of Eu^{3+} , Tb^{3+} nitrate or their mixture, affording mechanofluorochromic double-layer hydrogel SPAD/SPAA-Eu/Tb.

Patterning of Double-layer Fluorescent Hydrogel

PDMS mask with certain cutout pattern was attached to the SPAA-Eu/Tb side of the double-layer fluorescent hydrogel. Aqueous solution of Eu^{3+} , Tb^{3+} nitrate or their mixture was then added onto the mask and changed the local fluorescence color. After several seconds, the sunk region was rinsed by deionized water to remove excess ions, and the residual liquid was absorbed by filter paper.

Characterizations

The fluorescent photos were taken by smart phone camera (HUAWEI P40 Pro) under a UV lamp (ZF-5, 8 W, 254/365 nm). Tensile test was conducted on Z1 Zwick/Roell Universal Testing System. Attenuated total reflection Fourier transformed infrared (ATR-FTIR) spectra were tested on a micro-FTIR spectrometer (Agilent Cary 660+620). Raman spectra were obtained from a confocal micro-Raman spectrometer (Renishaw inVia Reflex) using a LED laser (785 nm). UV transmittance spectra were acquired from a UV/Vis/NIR spectrophotometer (Perkin-Elmer LAMBDA 950). Fluorescence emission spectra were recorded by a fluorescence spectrofluorometer (HORIBA FL3-111). X-ray photoelectron spectroscopy (XPS) measurement were performed on Kratos AXIS ULTRADLD instrument with a monochromic Al K α X-ray source. The cross-section morphology

of the hydrogel was characterized by Hitachi S-4800 field-emission scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Preparation of Monolayer Fluorescent Hydrogel SPAA-Eu/Tb

In our study, fabrication of single hydrogel with suitable luminescence and high stretchability is the essential prerequisite for constructing targeted mechanofluorochromic double-layer hydrogel. To this end, specially designed multicolor fluorescent hydrogel was firstly prepared according to the synthetic route in Fig. 1(a). AAm, K6APA and MBAA crosslinker were codissolved with AlgNa in water, and free radical polymerization of the mixture was subsequently initiated by APS/TEMED at room temperature to synthesize the semi-interpenetrating network hydrogel SPAA. Typical ATR-FTIR spectrum of SPAA was shown in Fig. 1(b). Multiple stretching vibration bands of C=O bond appeared at around 1600 cm^{-1} due to the successful polymerization of three monomers and incorporation of AlgNa. More importantly, the stretching vibration bands of associative $-\text{NH}_2$ belonging to AAm (~ 3190 and ~ 3326 cm^{-1}) and associative $-\text{OH}$ belonging to AlgNa (~ 3422 cm^{-1}) were observed (Fig. S1 in the electronic supplementary information, ESI), suggesting the existence of hydrogen bonding between polymer chains. The favorable combination of chemical covalent bonds and physical interaction in polymeric network conferred excellent tensile properties to SPAA. The hydrogel could tolerate large deformation and be stretched beyond 12 times its initial length, with an elastic modulus in the order of 10^4 Pa (Fig. S2 in ESI), satisfactory for usage as mechanofluorochromic materials.

Given that 6APA is a well-studied ligand and sensitizer to coordinate with lanthanide ions and increase their emission intensity,^[43,45,46] the as-prepared SPAA hydrogels were then facilely converted to multicolor fluorescent hydrogels by immersing them into aqueous solution of $\text{Eu}^{3+}/\text{Tb}^{3+}$ nitrate. The lanthanide-ligand coordination interaction was verified by Raman spectra. With the addition of Eu^{3+} or Tb^{3+} to SPAA, the vibration band of metal-O at around 481 cm^{-1} presented a significant enhancement, indicating that Eu^{3+} and Tb^{3+} were liable to couple with the COO^- of SPAA while K^+ was dissociative (Fig. 1c). The complexation was also evidenced by XPS. According to the fitting results, the Eu4d spectrum of the SPAA-Eu was deconvoluted into four peaks at 139.5, 134.3, 131.0 and 125.7 eV (Fig. 1d). The former two peaks were contributed by $4d_{3/2}$ and $4d_{5/2}$ of dissociative Eu^{3+} , and the latter two were attributed to bonded Eu atom with higher electron density. The Tb4d spectrum of the SPAA-Tb brought out similar split-up of peaks (Fig. S3 in ESI). Such shift of binding energy revealed the successful electron paring between lanthanide ion and ligand, accounting for the formation of stable 6APA- $\text{Eu}^{3+}/\text{Tb}^{3+}$ complex.

The fluorescent properties of SPAA-Eu/Tb were also investigated. Primarily, the emission spectra of SPAA-Eu and SPAA-Tb was intrinsic (Fig. 1e), rendering as red and green fluorescence under 254 nm UV light. When there were Eu^{3+} and Tb^{3+} with different molar ratio coexisting in the hydrogel, the emission spectra turned out to be an accumulation of the two

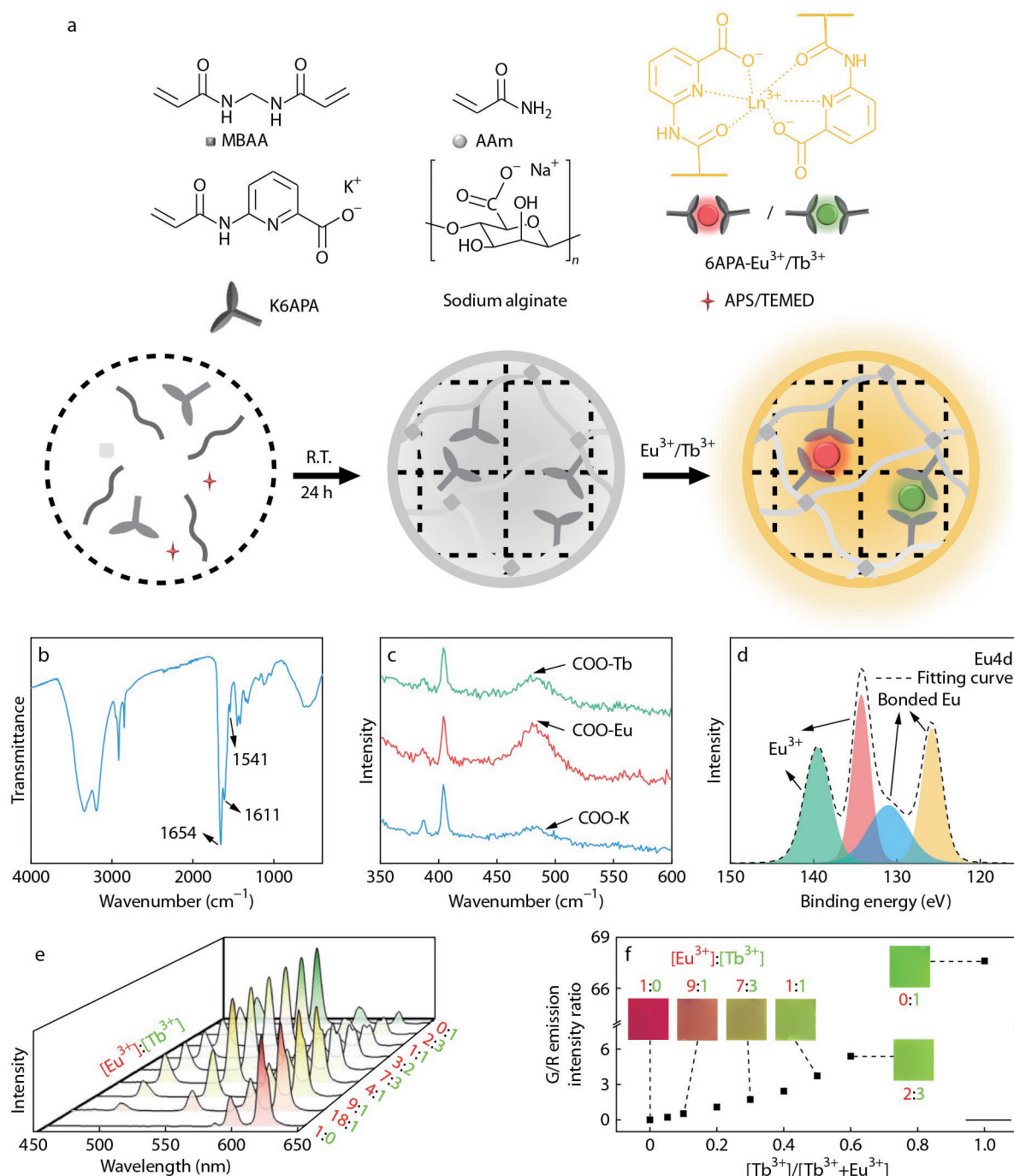


Fig. 1 Fabrication and characterization of monolayer fluorescent hydrogel SPAA-Eu/Tb. (a) Illustration of the procedure to prepare SPAA-Eu/Tb; (b) ATR-FTIR spectrum of SPAA; (c) Raman spectra of SPAA, SPAA-Eu and SPAA-Tb; (d) High-resolution XPS fitting result from Eu4d spectrum of SPAA-Eu; (e) Fluorescence emission spectra ($\lambda_{\text{ex}}=254$ nm) of SPAA-Eu/Tb with different $\text{Eu}^{3+}/\text{Tb}^{3+}$ molar ratio; (f) Green/red (G/R) emission intensity ratio as a function of $\text{Eu}^{3+}/\text{Tb}^{3+}$ molar ratio and corresponding fluorescent photos (scale bar: 1 cm).

ions' respective emission spectra, and the apparent fluorescence color was determined by the emission intensity ratio of red band and green band. As shown in Fig. 1(f), for hydrogel with a higher percentage of Tb^{3+} , its relative fluorescence intensity at 545 nm demonstrated a remarkable increase at the cost of that at 615 nm. As a result, a series of fluorescence color such as orange, yellow and greenyellow could be obtained simply by modulating $\text{Eu}^{3+}/\text{Tb}^{3+}$ molar ratio, offering various

options to the future fabrication of color-changing materials.

Construction of Double-layer Fluorescent Hydrogel SPAD/SPAA-Eu/Tb

Next, double-layer fluorescent hydrogel was prepared by employing SPAA-Eu/Tb as the bottom layer and another hydrogel SPAD as the top layer (Fig. 2a). SPAD used almost the same formulation as SPAA, and only the monomer K6APA was replaced by blue-light-emitting monomer DAEAN. Therefore,

the two hydrogels showed distinct fluorescent properties, but shared similar tensile properties (Fig. S2 in ESI). Moreover, the presence of AlgNa in both SPAA and SPAD enabled them to generate strong interfacial hydrogen bonding interaction, so that the two hydrogels could instantly adhere upon contact with each other. Considering that too much superficial water would separate the polymer chains of the two surfaces and impede their interactions, SPAD underwent moderate dehydration before it was attached to pristine SPAA to facilitate the assembly process. Later, the as-prepared SPAD/SPAA double-layer fluorescent hydrogel was treated to $\text{Eu}^{3+}/\text{Tb}^{3+}$ for further coloration. The resultant SPAD/SPAA-Eu/Tb exhibited an overlapping color of the two layers, and held the potential of mechanofluorochromism.

The mechanical stability of the double-layer fluorescent hydrogel was then studied. SEM images revealed the microarchitectures of SPAD, SPAA and SPAD/SPAA (Fig. 2b). The porous network structures of two monolayer hydrogels were also reflected in the SEM image of double-layer hydrogel. Besides,

newly born compact pores were observed on the boundary of the two layers, indicating that they were bonded tightly with no gaps in between. The interfacial bonding strength of SPAD/SPAA was characterized by T-peel test. As shown in Fig. 2(c), the interfacial peeling force per unit width was up to 100 N/m, further verifying the firm combination of SPAD and SPAA.

The tensile properties of the double-layer fluorescent hydrogel were also investigated. On the one hand, the high stretchability of SPAD and SPAA was retained by SPAD/SPAA (Fig. 2d). When $\text{Eu}^{3+}/\text{Tb}^{3+}$ were introduced to SPAD/SPAA, typical SPAD/SPAA-Eu and SPAD/SPAA-Tb both showed reductive fracture strain and multiplied elastic modulus due to the occurrence of lanthanide-ligand coordination interaction. Nevertheless, their stretching strain could still reach 700%, much higher than the required strain for mechanofluorochromism. On the other hand, the double-layer fluorescent hydrogel demonstrated decent resilience within certain strain (e.g., 200%). As shown in Fig. 2(e), the cyclic tensile curves of

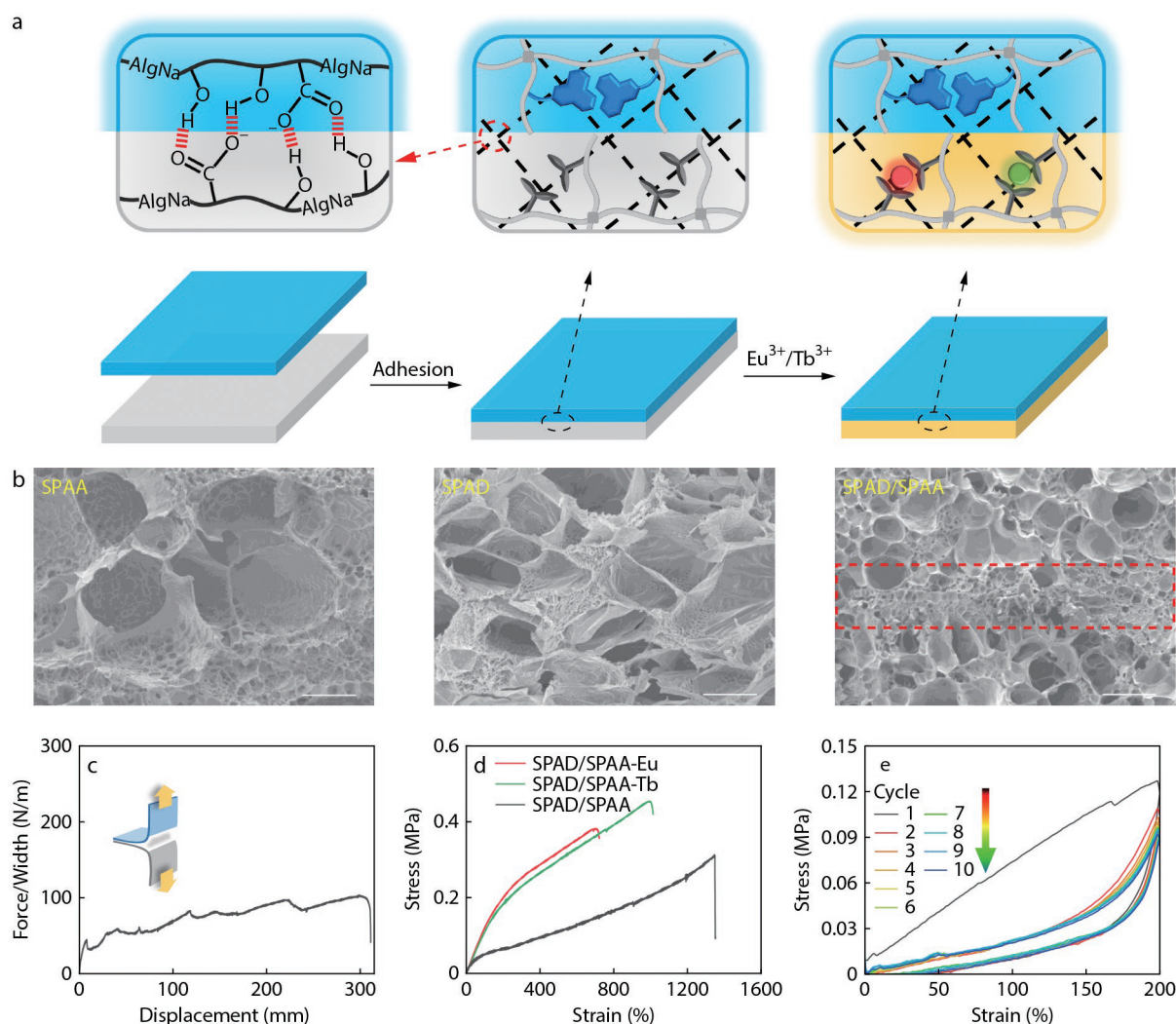


Fig. 2 Fabrication and characterization of double-layer fluorescent hydrogel SPAD/SPAA-Eu/Tb. (a) Illustration of the procedure to prepare SPAD/SPAA-Eu/Tb; (b) Cross-section SEM images of freeze-dried SPAD, SPAA and SPAD/SPAA (scale bar: 50 μm). The red dotted box indicated the boundary of SPAD and SPAA; (c) T-peel test of SPAD/SPAA; (d) Tensile stress-strain curves of SPAD/SPAA, SPAD/SPAA-Eu and SPAD/SPAA-Tb; (e) Cyclic tensile curves of SPAD/SPAA-Eu between 0% and 200 % strain.

SPAD/SPAA-Eu were basically consistent in nine cycles aside from the first cycle, which was fundamental to the good reversibility of mechanofluorochromism.

Mechanism and Optimization of Mechanofluorochromism Performance for SPAD/SPAA-Eu/Tb

As expected, SPAD/SPAA-Eu/Tb could display colorimetric changes upon mechanical stimuli. DAEAN in the top layer and 6APA-Eu³⁺/Tb³⁺ complex in the bottom layer together contributed to the overall emission of the double-layer fluorescent hydrogel, while the transmittance variation of top layer hydrogel played a dominant role in the mechanically responsive color change (Fig. 3a). When a uniaxial strain was applied, the top layer hydrogel became thin with elongation in length and allowed for more UV light to pass through, which

was absorbed by the bottom layer hydrogel to give out enhanced emission from 6APA-Eu³⁺/Tb³⁺ complex.

On the basis of classic Lambert-Beer law, the transmittance of SPAD was closely related to DAEAN concentration and hydrogel thickness. The strain-dependent UV transmittance curves of SPAD with various DAEAN concentration and hydrogel thickness were tested (Fig. S4 in ESI) and the transmittances at 254 nm were compared (Fig. 3b and Fig. S5 in ESI). For SPAD with constant hydrogel thickness, higher DAEAN concentration led to lower initial transmittance. As stretched from 0% to 200% strain, all the hydrogels showed an ascending tendency in transmittance and a final variation of 20% or so. For SPAD with constant DAEAN concentration, larger hydrogel thickness not only brought about lower initial transmittance, but also reduced the final variation of transmittance

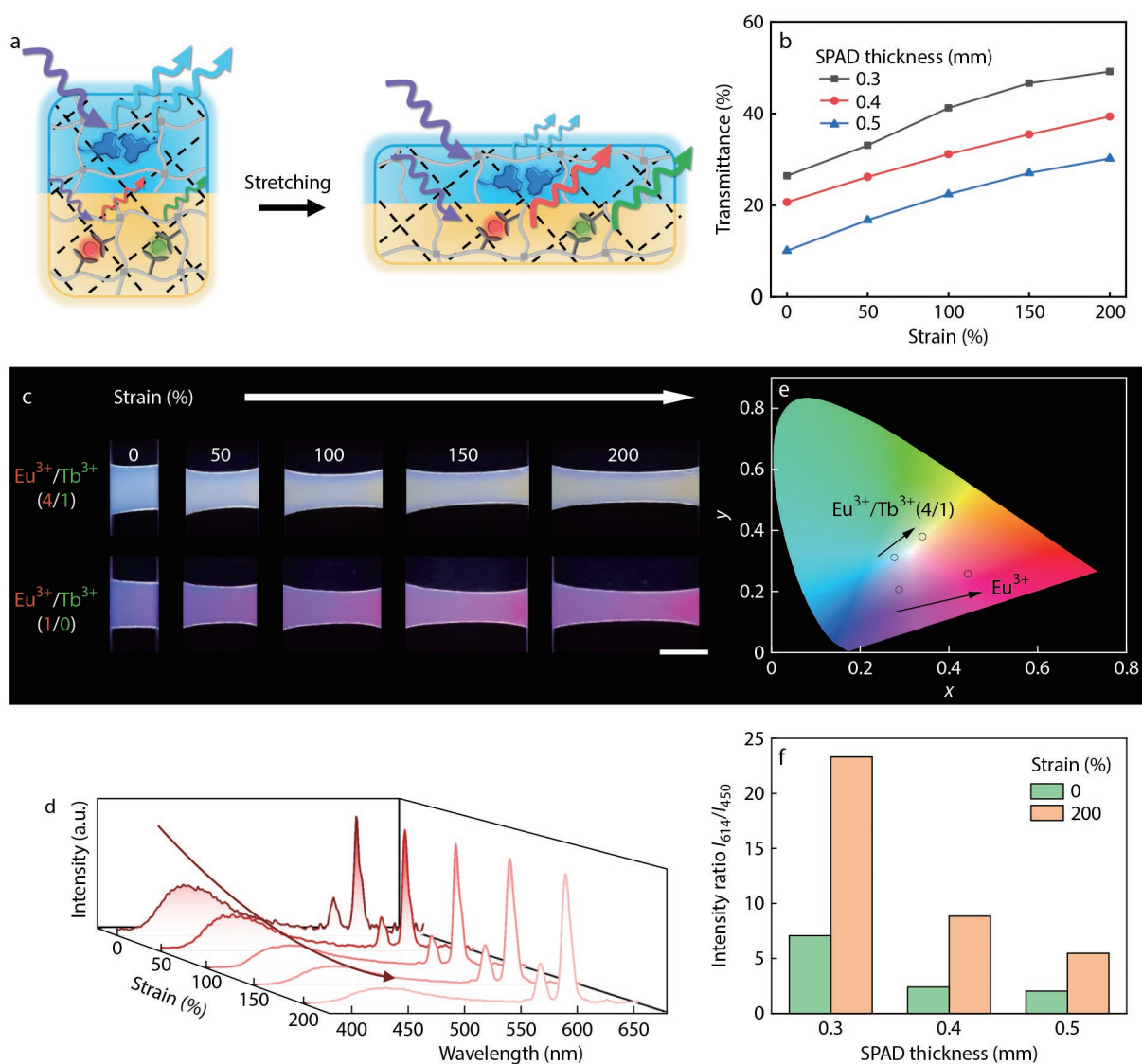


Fig. 3 Regulating the mechanofluorochromism of SPAD/SPAA-Eu/Tb. (a) Schematic mechanism of mechanofluorochromism; (b) Strain-transmittance relationship (at 254 nm) of SPAD with varied thickness; (c) Fluorescent photos showing the mechanofluorochromic change of SPAD/SPAA-Eu/Tb (scale bar: 1 cm). All the photos were taken under a 254 nm UV lamp. (d) Strain-dependent fluorescence emission spectra ($\lambda_{\text{ex}}=254$ nm) of SPAD/SPAA-Eu; (e) CIE chromaticity diagram of SPAD/SPAA-Eu and SPAD/SPAA-Eu/Tb ($\text{Eu}^{3+}/\text{Tb}^{3+}$ molar ratio of 4/1) at 0% and 200% strain; (f) Color ratio of SPAD/SPAA-Eu with varied SPAD thicknesses at 0% and 200% strain. Unless stated, the above samples used a DAEAN concentration of 0.05 mg/mL and a SPAD thickness of 0.4 mm.

tance, which would further affect the sensitivity of mechanofluorochromism. Besides, it was worth noting that the two factors also had a significant impact on the luminescence emission of SPAD. The fluorescence intensity was enhanced with increasing DAEAN concentration or hydrogel thickness (Fig. S6 in ESI), consequently influencing the initial and final color of the double-layer fluorescent hydrogel.

Subsequently, the mechanofluorochromism performance of SPAD/SPAA-Eu/Tb was characterized and optimized. Two $\text{Eu}^{3+}/\text{Tb}^{3+}$ molar ratios (1/0 and 4/1) were chosen to prepare representative double-layer fluorescent hydrogels. Fig. 3(c) and Fig. S7 (in ESI) depict their fluorescent photos in response to mechanical stimuli taken from the SPAD side. At the initial state, the fluorescence color of groups with higher DAEAN concentration or larger SPAD thickness was incline to be blue, while groups with lower DAEAN concentration or smaller SPAD thickness might have presented a certain degree of red or yellow. When the strain reached 200%, quite different fluorescence colors were attained from the double-layer fluorescent hydrogels, and only groups with moderate DAEAN concentration and SPAD thickness manifested conspicuous color changing from blue to bright red or yellow. These results were evidenced by a series of fluorescence emission spectra (Fig. 3d and Fig. S8 in ESI) and CIE chromaticity diagrams (Fig. 3e and Fig. S9 in ESI). Moreover, the mechanofluorochromism performance was evaluated from a quantitative point of view. As shown in Fig. 3(f) and Fig. S10 (in ESI), the color ratio of the double-layer fluorescent hydrogel, defined as the intensity ratio of red/green emission (614 nm/545 nm) from bottom SPAA-Eu/Tb to blue emission (450 nm) from top SPAD, experienced varying degrees of increase

when subjected to stretching strain. Taking both the initial color and color changing ability into consideration, the group with a DAEAN concentration of 0.05 mg/mL and a SPAD thickness of 0.4 mm was determined to be optimal and would be used in the following study of application.

Force-triggered Display of Fluorescent Patterns

The fluorescence color of SPAA-Eu/Tb could be changed by adding proper amount of Eu^{3+} or Tb^{3+} due to the reversible dissociation/reassociation of 6APA- $\text{Eu}^{3+}/\text{Tb}^{3+}$ complex. Thus, it is viable to fabricate multicolor SPAD/SPAA-Eu/Tb with on-demand patterning. As shown in Figs. 4(a) and 4(b), a particular red pattern was loaded onto the yellow SPAA-Eu/Tb ($\text{Eu}^{3+}/\text{Tb}^{3+}$ molar ratio of 4/1) substrate using the aqueous solution of Eu^{3+} as ink. Customized PDMS mask was employed to hinder the diffusion of ions and ensure the independence of each color. Owing to the shielding effect of top SPAD, the double-layer fluorescent hydrogel at unstretched state appeared to be blue as a whole. In the presence of stretching strain, the UV transmittance of top SPAD rose to high enough to excite the bottom SPAA-Eu/Tb, so that the fluorescent pattern of a red Chinese character for “force” against yellow background gradually manifested. Similar force-triggered display of fluorescent patterns was demonstrated in the case of other two mechanofluorochromic double-layer fluorescent hydrogels (Figs. 4c and 4d), where a letter string of “CJPS” and a sketch of palace were observed on SPAD side in response to mechanical stretching.

Besides, it was worth mentioning that the fluorescence emission of SPAD/SPAA-Eu/Tb was dependent of excitation light. Under UV light with other wavelength (e.g., 365 nm), the fluorescence colors of both SPAD and SPAA-Eu/Tb turned out

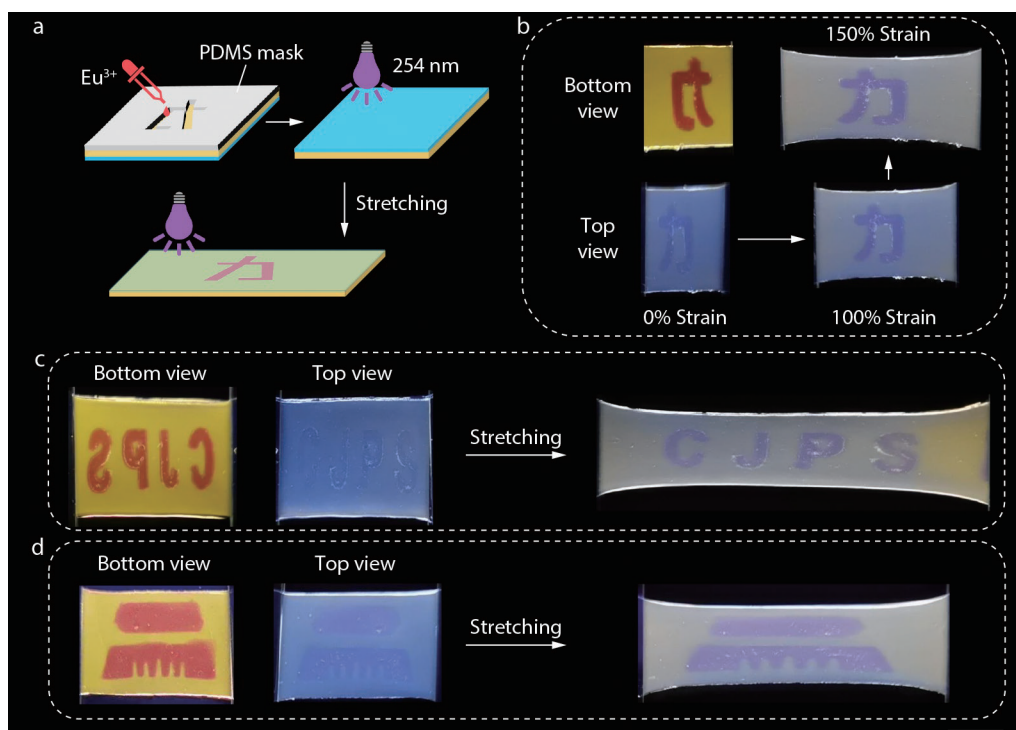


Fig. 4 Smart display of fluorescent patterns on SPAD/SPAA-Eu/Tb upon stretching. (a) Illustration of the procedure to prepare patterned SPAD/SPAA-Eu/Tb. (b–d) Fluorescent photos showing the concealment and disclosure of patterns in response to external force (scale bar: 1 cm). All of the photos were taken under a 254 nm UV lamp.

to be blue, so that no mechanofluorochromism or fluorescent pattern could be observed from the double-layer fluorescent hydrogel (Fig. S11 in ESI), which was quite different from the phenomena under 254 nm UV light. Therefore, the hidden fluorescent patterns could be revealed only if specific UV light and stretching strain simultaneously acted on SPAD/SPAA-Eu/Tb, suggesting the potential of such hydrogel-based platforms for information encryption.

CONCLUSIONS

In summary, we reported a novel mechanofluorochromic hydrogel, SPAD/SPAA-Eu/Tb, that was facilely prepared by the combination of two individual fluorescent hydrogels via interfacial hydrogen bonding. The apparent color of the double-layer fluorescent hydrogel was contributed by the blue emission from top SPAD and the red/green emission from bottom SPAA-Eu/Tb together. With an increase of stretching strain, the top layer hydrogel gradually became thinner due to Poisson's effect, accompanied by higher UV transmittance and weaker blue emission intensity. Meanwhile, the emission of the bottom hydrogel was enhanced and remarkably changed the relative intensity ratio of the two hydrogel layers, which was eventually reflected in the variation of apparent color. Based on the above mechanism, the mechanofluorochromism performance of SPAD/SPAA-Eu/Tb was possible to be controlled by regulating the initial thickness and DAEAN concentration of SPAD, including programmable initial color, sensitivity of mechanofluorochromism and color at a given strain. Furthermore, the multiple selectivity of SPAA-Eu/Tb color enabled the construction of patterned hydrogel. Thus, SPAD/SPAA-Eu/Tb capable of mechanofluorochromism was considered as a promising candidate to develop smart display and encryption devices. In addition, the method of constructing double-layer hydrogel in our study was assumed to be universal. Other fluorescent monomers, especially those with extra responsiveness, could be introduced to the system for more useful mechanofluorochromic materials.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2885-z>.

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