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Excitation-wavelength-dependent fluorescent organohydrogel for dynamic information anti-counterfeiting

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ABSTRACT

Anti-counterfeiting labels with various fluorescent colors are of great importance in information encryption-decryption, but are still limited to static information display. Therefore, it is urgent to develop new materials and encryption-decryption logic for improving the security level of secret information. In this study, an organohydrogel made up of poly(*N*,*N*-dimethylacrylamide) (pDMA) hydrogel network and polyoctadecyl methacrylate (pSMA) organogel network that copolymerized with two fluorophores, 6-acrylamidopicolinic acid moieties (6APA, fluorescent ligand) and spiropyran units (SPMA, photochromic monomer), was prepared by a two-step interpenetrating method. As UV light of 365 nm and 254 nm can both cleave C_{spiro}-O bonds of SPMA, and the green fluorescence of 6APA-Tb^{3+} can only be excited by 254 nm light, the organohydrogel displays yellow and red under the irradiation of 254 nm and 365 nm, respectively. In addition to wavelength selectivity, these two fluorophores are thermal-responsive, leading to the fluorescence variation of the organohydrogel during heating process. As a result, secret information loaded on the organohydrogel can be decrypted by the irradiation of UV light, and the authenticity of the information can be further identified by thermal stimulation. Our fluorescent organohydrogel can act as an effective anti-counterfeiting label to improve the information security and protect the information from being cracked.

With the acceleration of global informatization, the protection of information integrity and privacy during storage and transmission is becoming more and more important, which is closely related with national security, social stability and people's life [1,2]. Nowadays, a variety of anti-counterfeiting materials and corresponding encryption-decryption methods have been developed to respond to the leakage of secret information and the proliferation of fake information [3–9]. Among them, fluorescent materials have a good application prospect in information storage and anti-counterfeiting due to their bright luminescence and rich colors [10–14].

As a new fluorescent material, fluorescent hydrogel has attracted extensive attention due to its diverse structure design, unique stimulus responsiveness and adjustable fluorescence performance [15–20], thus having potential application in biological imaging [21,22], bionic skin [23,24], information encryption [25–28] and so on. For example, Huang and his team reported a novel supramolecular gel with white-light-emitting performance, which was caused by the aggregation of a single chromophore. Owing to the self-healing ability based on quadruple hydrogen bonding, the hydrogels can self-assemble into complete protected information, which can be read under UV light [25]. Yi's group developed a hybrid hydrogel that combining CdTe QDs and SiO_2 PCs in a GelMA substrate. Various hidden information can be identified and authenticated due to excellent photolithography and fluorescent properties [26]. These attempts have proved that the fluorescent hydrogels can act as effective anti-counterfeiting platforms, but still limited to static information display.

Herein, the two-step interpenetrating technique [29,30] was adopted to prepare organohydrogels containing two fluorophores, exhibiting excitation-wavelength-dependent fluorescence emission. The fabricated organohydrogel was made up of thermopolymerized pDMA hydrogel network and photopolymerized p(SMA-SPMA-6APA-Tb^{3+}) organogel network (Scheme 1a, Schemes

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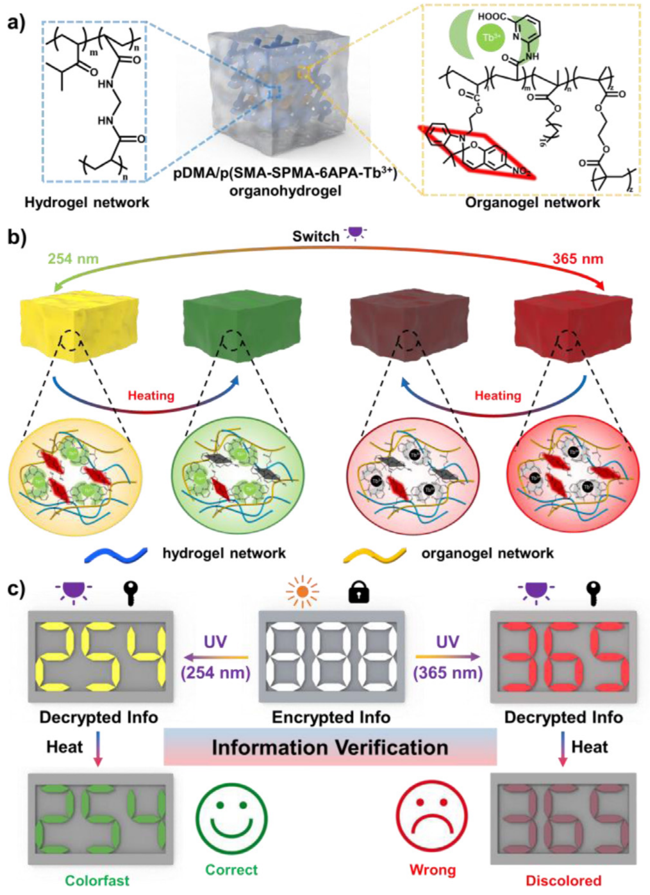

Scheme 1. Schematic illustration of excitation-wavelength-dependent fluorescent organohydrogel pDMA/p(SMA-SPMA-6APA-Tb^{3+}) for dynamic information anti-counterfeiting. (a) The fluorescent organohydrogel was made up of pDMA hydrogel network and p(SMA-SPMA-6APA-Tb^{3+}) organogel network. (b) The fluorescent organohydrogel possesses excitation-wavelength-dependent fluorescent emission, which can further change colors under the stimulus of heat. (c) The fluorescent information that decrypted under UV irradiation can be distinguished by thermal stimulation.

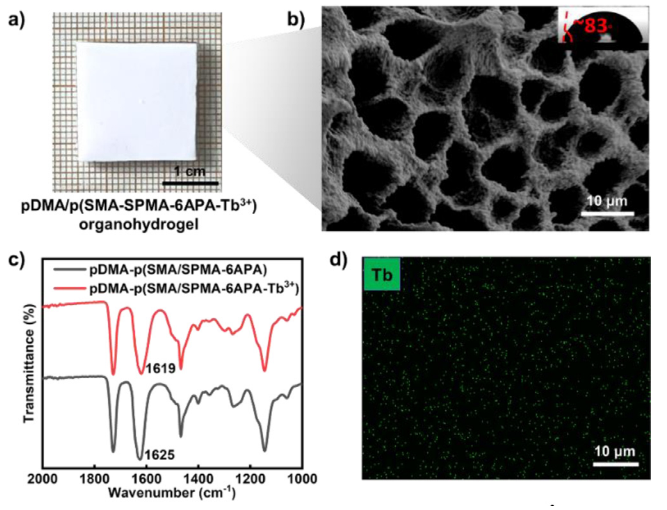

Fig. 1. Characterization of pDMA/p(SMA-SPMA-6APA-Tb^{3+}) organohydrogel. (a) Photograph and (b) cross-section SEM image and contact angle of pDMA/p(SMA-SPMA-6APA-Tb^{3+}) organohydrogel. (c) FT-IR spectra of pDMA/p(SMA-SPMA-6APA) organohydrogel that is absent or present of Tb^{3+} ions. (d) EDS mapping of Tb^{3+} in pDMA/p(SMA-SPMA-6APA-Tb^{3+}) organohydrogel.

S1-S4, Figs. S1 and S2 in Supporting information). As fluorescent complex 6APA-Tb^{3+} emits green fluorescence only at the excitation wavelength of 254 nm and spiropyran group (SPMA) can emit red fluorescence at both 254 nm and 365 nm, the prepared pDMA/p(SMA-SPMA-6APA-Tb^{3+}) organohydrogel displayed yellow fluorescence and red fluorescence under UV light at 254 nm and 365 nm, respectively (Figs. S3 and S4 in Supporting information). In addition, the ring-opened form of SPMA will turn to closed form and the fluorescence intensity of 6APA-Tb^{3+} will decrease under the stimulus of heat. Thus, the excitation-wavelength-dependent fluorescence can further be adjusted by thermal stimulation (Scheme 1b). Based on the above, our fluorescent organohydrogel can be employed for information encryption and decryption. For example, encrypted information “888” can be decrypted into different messages under corresponding UV light, “254” under the UV light of 254 nm and “365” under the UV light of 365 nm (Scheme 1c). The authenticity of the information can be identified *via* the stimulation of heat, through which the real one will turn to green and the fake one will discolor.

Owing to coexistence of hydrogel network and organogel network, the heterogenous pDMA/p(SMA-SPMA-6APA-Tb^{3+}) organohydrogel was totally opaque when the solvent was replaced with water (Fig. 1a). The cross-sectional morphology of the organohydrogel was analyzed by scanning electron microscope (SEM). As depicted in Fig. 1b, a honeycomb-like structure with pore diameters ranged from 5 μm to 15 μm was observed, which was ascribed to water-induced microphase separation of hydrophobic network in hydrophilic network. What is more, the contact angle (CA) was measured to prove the successful introduction of hydrophobic network. Compared to pure pDMA hydrogel with CA of 46° (Fig. S5 in Supporting information), the organohydrogel showed an increased CA of 83°, indicating the existence of hydrophobic network. One thing needs to be noted is that the organohydrogel shows excellent mechanical stability according to rheological behavior testing (Fig. S6 in Supporting information). Fluorescent ligand 6APA can coordinate with lanthanide ions [31,32] and emit corresponding fluorescence, which is the key for the following study in excitation-wavelength-dependent fluorescent property. The chemical structures of pDMA/p(SMA-SPMA-6APA) organohydrogel before and after the introduction of Tb^{3+} were measured by attenuated total reflection Fourier transformed infrared spectrometer (ATR-FTIR). As shown in Fig. 1c, a characteristic vibrational peak located at 1625 cm^{-1} corresponds to C=O of pyridine rings in 6APA that shifted to 1619 cm^{-1}, indicating the successful coordination between 6APA and Tb^{3+}. Besides, energy-dispersive X-ray spectroscopy (EDS) was applied for elemental mapping, which indicates the even distribution of Tb^{3+} ions in the fluorescent organohydrogel (Fig. 1d).

As there are two fluorescent monomers in the organohydrogel, excitation-wavelength-dependent fluorescence could be observed when switching the UV light between 365 nm and 254 nm. The green fluorescence of complex 6APA-Tb^{3+} could only be excited by 254 nm, while both 254 nm and 365 nm UV light can make spiropyran moieties transform from closed form (SPMA) to ring-opened form (MCMA) (Fig. 2a). Besides, the fluorescent color can also be adjusted by changing molar ratios of fluorescent monomers. When the molar ratio of 6APA to SPMA was 2:1, the organohydrogel displayed the most visible red and yellow (Fig. 2b). Furthermore, the intensity of characteristic peak on fluorescence spectra could also prove that the molar ratio of 2:1 is the optimal ratio (Figs. 2c and d), which was picked up for the following study.

As illustrated in Fig. 3a, the PL mapping spectrum revealed that there are two emission centers in the fluorescent organohydrogel, which belong to red fluorescent monomer (MCMA, 621 nm) and green fluorescent complex (6APA-Tb^{3+}, 545 nm). Since opened merocyanine units (MCMA) could convert to SPMA and the fluores-

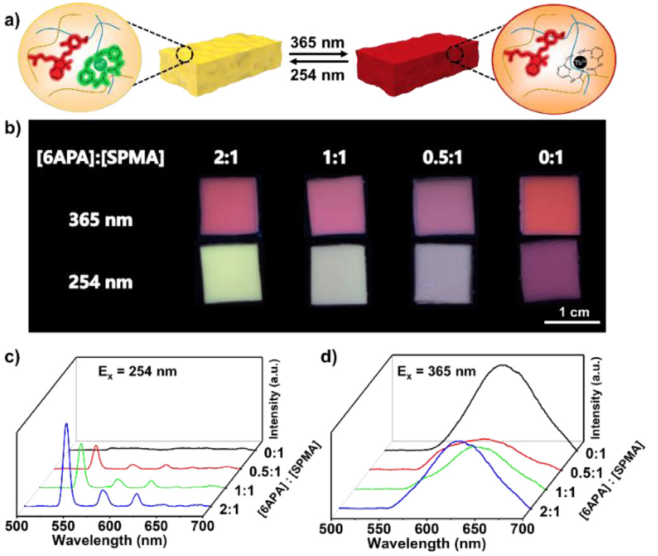

Fig. 2. Excitation-wavelength-dependent fluorescent property of pDMA/p(SMA-SPMA-6APA-Tb^{3+}) organohydrogel. (a) Illustration of the mechanism of excitation-wavelength-dependent fluorescent emission when switching between 365 nm and 254 nm. The photographs (b) and fluorescence spectra of organohydrogels with different ratios of two fluorescent monomers when exposed to UV light of 254 nm (c) and 365 nm (d), respectively. The scale bar is 1 cm.

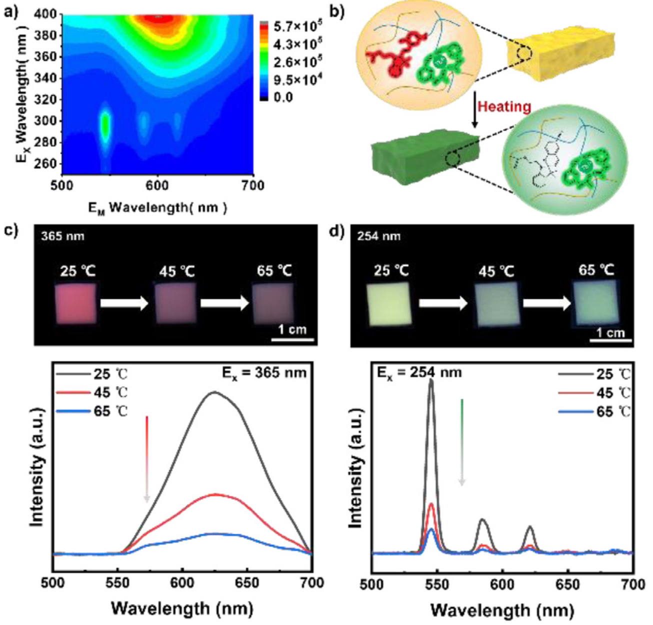

Fig. 3. Dynamic fluorescent variation under thermal stimulation. (a) PL mapping spectra of pDMA/p(SMA-SPMA-6APA-Tb^{3+}) organohydrogel. (b) Illustration of the mechanism of color change of fluorescent organohydrogel under the stimulus of heat. Photographs and fluorescence spectra of fluorescent organohydrogel under thermal stimulation: $\lambda_{ex} = 365$ nm (c), 254 nm (d). The scale bar is 1 cm.

cence intensity of 6APA-Tb^{3+} would decrease under thermal stimulation [3,33,34], the organohydrogel exhibits fluorescence variation when switching temperature (Fig. 3b). Specifically, when exposed to UV light of 365 nm, the temperature goes from 25 °C to 65 °C, the red fluorescence of organohydrogel gradually faded, accompanied with the fluorescence intensity at 621 nm decrease (Fig. 3c). In the meanwhile, the fluorescence intensity at 545 nm also decreased and fluorescent organohydrogel turned from yellow to green, which was ascribed to the overlay of two fluorescence colors (Fig. 3d).

Owing to the excitation-wavelength-dependent fluorescent property and thermal-induced fluorescence variation, a variety of information security labels could be constructed by elaborated design. First of all, four different organohydrogels, including pDMA/pSMA (white block), pDMA/p(SMA-SPMA) (red block), pDMA/p(SMA-6APA-Tb^{3+}) (green block) and pDMA/p(SMA-SPMA-6APA-Tb^{3+}) (yellow block), are fabricated and integrated to obtain corresponding anti-counterfeiting labels (Fig. 4a). For instance, the number “888” in visible light can display the number “365” or “254” under the UV light of 365 nm and 254 nm, respectively (Fig. 4b). Similarly, the word “believe” made up of green and yellow blocks under 254 nm can turn to the word “live” when exposed

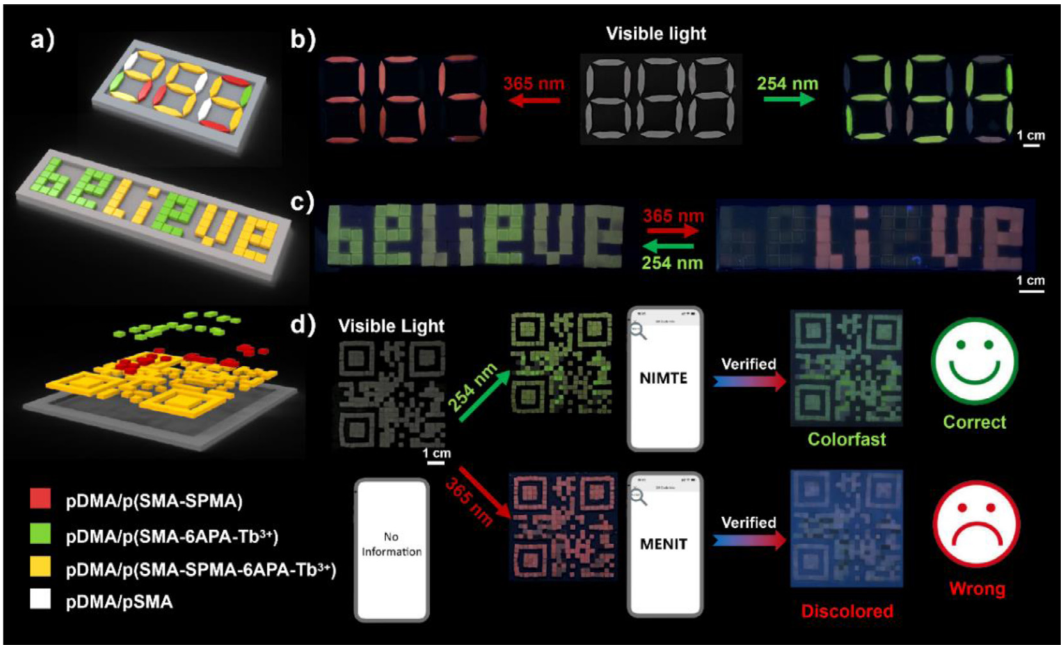

Fig. 4. Dynamic information anti-counterfeiting based on fluorescent organohydrogels. (a) The elaborate design of number, letters and QR code based on various fluorescent organohydrogels. Programmed number “888” (b) and word “believe” (c) display different information under irradiation of 254 nm and 365 nm, respectively. (d) The QR code can be decrypted and scanned by smartphones under UV light, which can further be told the true from the false by thermal stimulation. The scale bar is 1 cm.

to UV light of 365 nm (Fig. 4c). Moreover, a complicated QR code without any information in visible light was fabricated by assembling pixelated organohydrogel blocks (Fig. 4d). The hidden information can be revealed under UV light of different wavelengths. The information decrypted under 254 nm UV light can be scanned by a smartphone and present the message of "NIMTE", while under 365 nm UV light the scanned information is "MENIT". Furthermore, the authenticity of the decrypted messages can be identified by thermal stimulation, in which the colorfast information is true and the discolored information is false. Through excitation wavelength selection and temperature verification, the organohydrogel-based information security labels have a higher level of information encryption.

In summary, we presented a series fluorescent organohydrogels with novel encryption-decryption logic for constructing anti-counterfeiting labels. The fluorescent organohydrogel pDMA/p(SMA-SPMA-6APA-Tb^{3+}) containing 6APA-Tb^{3+} (green fluorescent complex, $E_x = 254$ nm) and SPMA (red fluorescent monomer, $E_x = 254$ nm and 365 nm) was prepared *via* a two-step interpenetrating technique. Due to the excitation-wavelength-dependent fluorescent property, our organohydrogel exhibits red fluorescence and yellow fluorescence under the irradiation of 365 nm and 254 nm, respectively. Besides, opened merocyanine units exhibit thermal-induced ring-closing process and the fluorescence intensity of 6APA-Tb^{3+} also be decreased by heat, thus the fluorescence of organohydrogel showed a yellow-green transition and an attenuation of red fluorescence under 254 nm and 365 nm, respectively. Given that the fluorescent color is excitation-wavelength-dependent and thermal-responsive, information based on different organohydrogels can be loaded and encrypted. The hidden information can be read by ultraviolet light irradiation, and the authenticity of the information can be further identified by heating. In a word, the proposed novel fluorescent organohydrogels and corresponding encryption-decryption strategy provides a new insight in improving the security level of information.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2023.108347.

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