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Bio-Inspired Electro-Thermal-Hygro Responsive Rewritable Systems with Temporal/Spatial Control for Environment-Interactive Information Display

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Utilization of rewritable luminescent materials for secure information storage and delivery has long been envisaged to reduce the cost and environmental wastes. However, it remains challenging to realize a temporally/spatially controlled display of the written information, which is crucial for secure information encryption. Here, inspired by bioelectricity-triggered skin pattern switching in cephalopods, an ideal rewritable system consisting of conductive graphene film and carbon dots (CDs) gel with blue-to-red fluorescence-color changes via water-triggered CDs aggregation and re-dispersion is presented. Its rewritability is guaranteed by using water ink to write on the CDs-gel and employing Joule heat of graphene film to evaporate water. Due to the highly controlled electrical stimulus, temporally/spatially controlled display is achieved, enabling on-demand delivery and duration time regulation of the written information. Furthermore, new-concept environment-interactive rewritable system is obtained by integrating sensitive acoustic/optical sensors and multichannel electronic time-delay devices. This work opens unprecedented avenues of rewritable systems and expands potential uses for information encryption/delivery.

1. Introduction

In the modern age of information explosion, data storage, and security have played an important role in the economy, as well as in our daily lives.[1] As the demands for secure information storage and delivery are growing in leaps and bounds,[2] recent research interests have been shifted to develop rewritable information carriers on the basis of smart materials whose pigment,[3] structural[4] or luminescent color[5] could be reversibly tuned by environmental signals. Such rewritable systems will help to cut down the cost of safe information storage and reduce environmental wastes. Among them, luminescent materials are particularly attractive, because the written/printed information are only visible under UV light, providing additional paper-based security data recording.[6a–c] Also, the fluorescence colors usually have quite high color saturation and are thus capable of enabling long-distance visibility, especially in low- or no-light conditions.[6d] Therefore, the past decade has witnessed a large number of luminescent rewritable systems.[7] However, many of them are primarily chemical-stimuli-responsive, in which repeatable use of the chemical inks (e.g., acids, bases, ions)[8] usually causes residual chemical accumulation and rapidly impairs their rewritable capacity. Even if there has been a few elegant systems that utilize residues-free water or heat as the stimuli,[9] it is still quite challenging to realize spatially/temporally controlled display of the written information, but such features are highly desired for some important applications such as secure information delivery or anti-counterfeiting labeling. These limitations are quite difficult to be addressed in existing systems, because innovative working mechanism and material design, but not only simple material replacement, are required.

The fascinating soft skins of cephalopods, which enable dynamic and reversible color/pattern changes with high resolution, are believed to represent a judicious inspiration for next-generation rewritable system.[10] For example, cephalopod skins have a typical multilayer structure containing different-colored chromatophore organs, which consist of one central pigment cell around a ring of innervated muscular cells.[11] Such naturally evolved architecture thus enables these pigment cells to be dynamically switched between expanded plate-like and contracted point-like states (**Figure 1**a) through the nerve impulse (bioelectricity) controlled muscular movement upon

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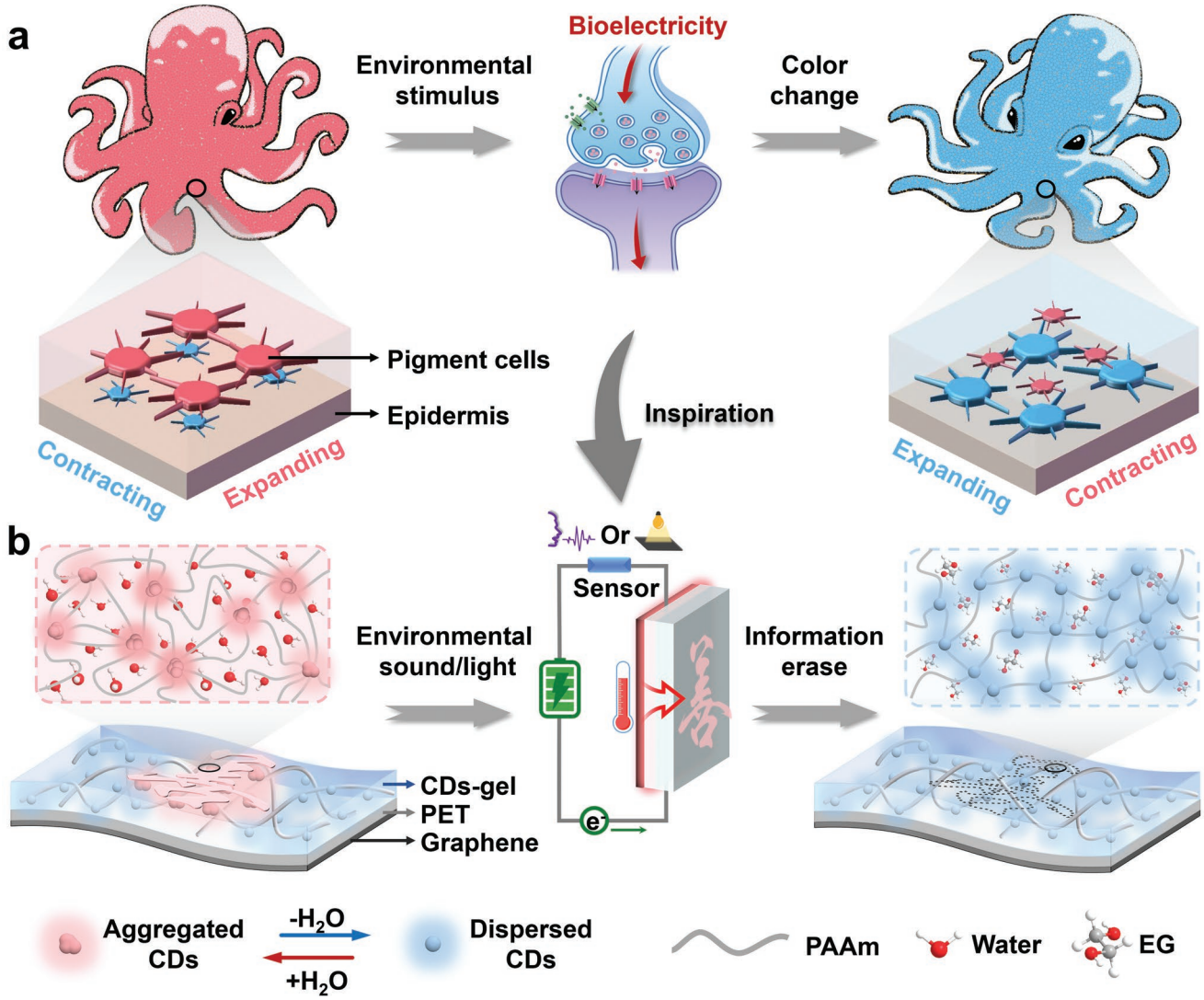

Figure 1. Bioinspired design strategy for environment-interactive rewritable systems. a) Scheme of the skin allochromasia mechanism in cephalopods. Their skins have a typical multi-layer structure containing different-colored chromatophore organs, which consist of one central pigment cell around a ring of innervated muscular cells. When the environment changes, these pigment cells will be dynamically switched between the expanded plate-like and contracted point-like states through the bioelectricity-controlled muscular movement, thereby modulating the local allochromasia. b) Scheme of the bio-inspired electro-thermal-hygro responsive rewritable systems for environment-interactive information display. Acoustic/light sensors that are sensitive to environment sound/light are combined to automatically regulate the voltage on/off, so as to intelligently induce the aggregation and re-dispersion of CDs for information writing and erasing.

environmental changes, thereby modulating the local allochromasia.[12] Owing to the high accuracy of bioelectrical signal, dynamic display of delicate and colorful skin patterns was then manifested, suggesting their excellent spatial/temporal control. Also, such reversible allochromasia processes of cephalopods are taking place nearly every moment over the whole course of their lives, indicating their superb rewritable capacity. In this regard, natural cephalopod skins nearly offer all the advantages that are required for ideal rewritable information carriers, which greatly encouraged us to replicate their natural multi-layer structure and electricity-modulated color-changing mechanism in the artificial luminescent rewritable systems.

A proof-of-concept material design aiming to develop such a skin-inspired rewritable system is shown in Figure 1b. To closely mimic cephalopod skins, the illustrated system is based on flexible fluorescent gels with biotissue-like modulus and soft wet nature.[13] Fluorescent gels can also provide additional advantages such as tailored responsiveness and tunable emission colors as well as porous structures that facilitate material exchange with surroundings.[14] Therefore, there has recently been a growing research interest in developing soft wet gels for rewritable systems.[15a-b] For instance, Wu and colleagues utilized photoresponsive Ru–thioether coordination crosslinks to report smart metallopolymer organohydrogels, which potentially served as rewritable systems enabling direct pattern writing by light and easy self-erasure in the dark.[15c] We recently introduced urease into pH-sensitive fluorescent hydrogels to develop robust rewritable systems for on-demand information

encryption, because they allowed for arbitrary information writing by using acid as the ink and time-dependent erasure upon exposure to urea that gradually produces NH_3 under urease catalysis.[15d] These forefront progresses open up the possibility of utilizing soft wet gels to develop rewritable systems suitable for various applications.

As shown in Figure 1b, the fluorescent polyacrylamide gel was chemically grafted with hydrophobic and aggregation-induced emissive carbon dots (CDs) that could be switched between blue fluorescence of dispersed CDs and red fluorescence of aggregated CDs.[16a] Ethylene glycol (EG), the simplest vicinal alcohol, was employed as the solvent to infiltrate the CDs-grafted fluorescent gel (CDs-gel), because EG was nearly nonvolatile at ambient conditions and capable of forming vast hydrogen bonds with the O/N-containing moieties of polyacrylamide and CDs to ensure the environmental stability of CDs-gel. As a result, information could be facilely written on the CDs-gel as red fluorescent traces by using residue-free water as the ink to induce the formation of aggregated CDs. To mimic the unique multilayer structure and bioelectricity-modulated color/pattern display mechanism of cephalopod skins, the CDs-gel sheet was interfacial composited with conductive graphene film by using thin polyethylene glycol terephthalate (PET) film as the middle connecting layer. As illustrated in Figure 1b, upon applying voltage on the graphene layer, the generated Joule heat would spontaneously transfer to the CDs-gel layer and largely weaken the formed hydrogen bonds to accelerate water (ink) evaporation for complete information erasing to allow for another rewriting. In this way, electricity-triggered reversible aggregation and re-dispersion of CDs were realized for information writing and erasing, in analogy to the bioelectricity-triggered reversible expansion and contraction of pigment cells for skin color/pattern regulating. Owing to the highly controllable electrical stimulus in terms of amplitude and duration, spatial/temporal control of the written information was then easily achieved. Importantly, when sensitive acoustic/light sensors and multi-channel electronic timing relays device were combined to automatically regulate the voltage on/off, conceptually new environment-interactive rewritable systems were demonstrated for the first time, which enabled on-demand display of the written information and thus significantly extended their potential for advanced information encryption and smart display uses.

2. Results

2.1. Hygro-Sensitive Dynamic Carbon Dots (CDs) Dispersion And Aggregation For Reversible Fluorescence Color Regulation In CDs-Gels

The fluorescent CDs-gel was prepared by radical polymerization of vinyl-functionalized CDs, acrylamide, and *N,N′*-methylenebisacrylamide in ethylene glycol (EG) (Figure S1, Supporting Information).[16a] The crosslinked poly(acrylamide) gel matrix was chosen, owing to its electrical neutrality that can avoid the adverse influence of acids on the fluorescent intensity of CDs, as well as its nonresponsiveness that helps maintain good size stability. As illustrated in **Figure 2**a, the as-prepared CDs-gel emits blue fluorescence of the dispersed CDs under 365 nm UV light. Upon spraying water on the gel surface, these hydrophobic CDs gradually form aggregates with increasing water content in the gel, causing time-dependent fluorescence color change from blue to red. This blue-to-red emission color change was clearly evidenced by the recorded fluorescence spectra (Figure 2b), which showed the significantly enhanced red fluorescence intensity at 605 nm (≈19.6 fold). The aggregated red fluorescence of CDs-gel was able to snap back to the dispersed blue after being heated at 60 °C for 5 mins to evaporate water (Figure 2c). Direct evidence for such switch between the dispersed and aggregated states of CDs in the gel came from the transmittance tests, which showed corresponding transmittance variations from ≈89% to ≈63% and then recovery to ≈87% at 800 nm (Figure S2, Supporting Information). Importantly, such hygro-sensitive fluorescence color switch was able to be consistently cycled for many times (Figure 2d), indicating its highly reversible and repeatable nature.

As discussed above, the reversible "dispersion-to-aggregation" transformation of hydrophobic CDs is triggered by the presence of water molecules, which break the existing hydrogen bonds between the polyacrylamide skeleton and EG to form H_2O-infiltrated polymer network. Therefore, it is important to get real-time mapping of the H_2O diffusion path in the CDs-gel surface and interior for gaining more insight into such hygro-sensitive fluorescence color-changeable process. To do this, in-situ Raman mapping was conducted. As their chemical structure indicates, there present both C–H and O–H bonds in EG, while only the O–H bonds exist in water molecules (Figure S3, Supporting Information). Therefore, it is reasonable to define a parameter I_{O-H}/I_{C-H}, the Raman intensity ratio of I_{O-H} (stretching vibration area of O–H bonds within 3060–3535 cm^{-1}) to I_{C-H} (stretching vibration area of C–H bonds within 2827–3040 cm^{-1}), for real-time water diffusion monitoring in the CDs-gel. Figure S4, Supporting Information, and Figure 2e compared the recorded Raman spectra of CDs-gel surfaces, which indicated largely increased I_{O-H}/I_{C-H} value after being exposed to water for 5 mins (Figure S5, Supporting Information). This observation was consistent with the two-dimensional (2D) mapping results, which showed an obvious color change, referring to I_{O-H}/I_{C-H}, on the CDs-gel surface with prolonging water exposure time within 5 mins (Figure 2g). These results suggest that a large quantity of water molecules have diffused into the gel surface to induce the "dispersion-to-aggregation" transformation of fluorescent CDs. Further cross-sectional 2D mapping experiments were also carried out to learn about the vertical water molecules diffusion. As summarized in Figure 2f, a prominent color change was observed after 30 mins water exposure, indicating that the water molecules have sufficiently diffused into the CDs-gel interior. These results clearly indicated that the water-triggered red fluorescent CDs aggregates are not only formed on the gel surface, but also in the gel interior.

2.2. Electro-Thermal-Hygro Responsive Rewritable Systems

The above-established repeatable fluorescence color changes in soft CDs-gel are fundamentally caused by the reversible

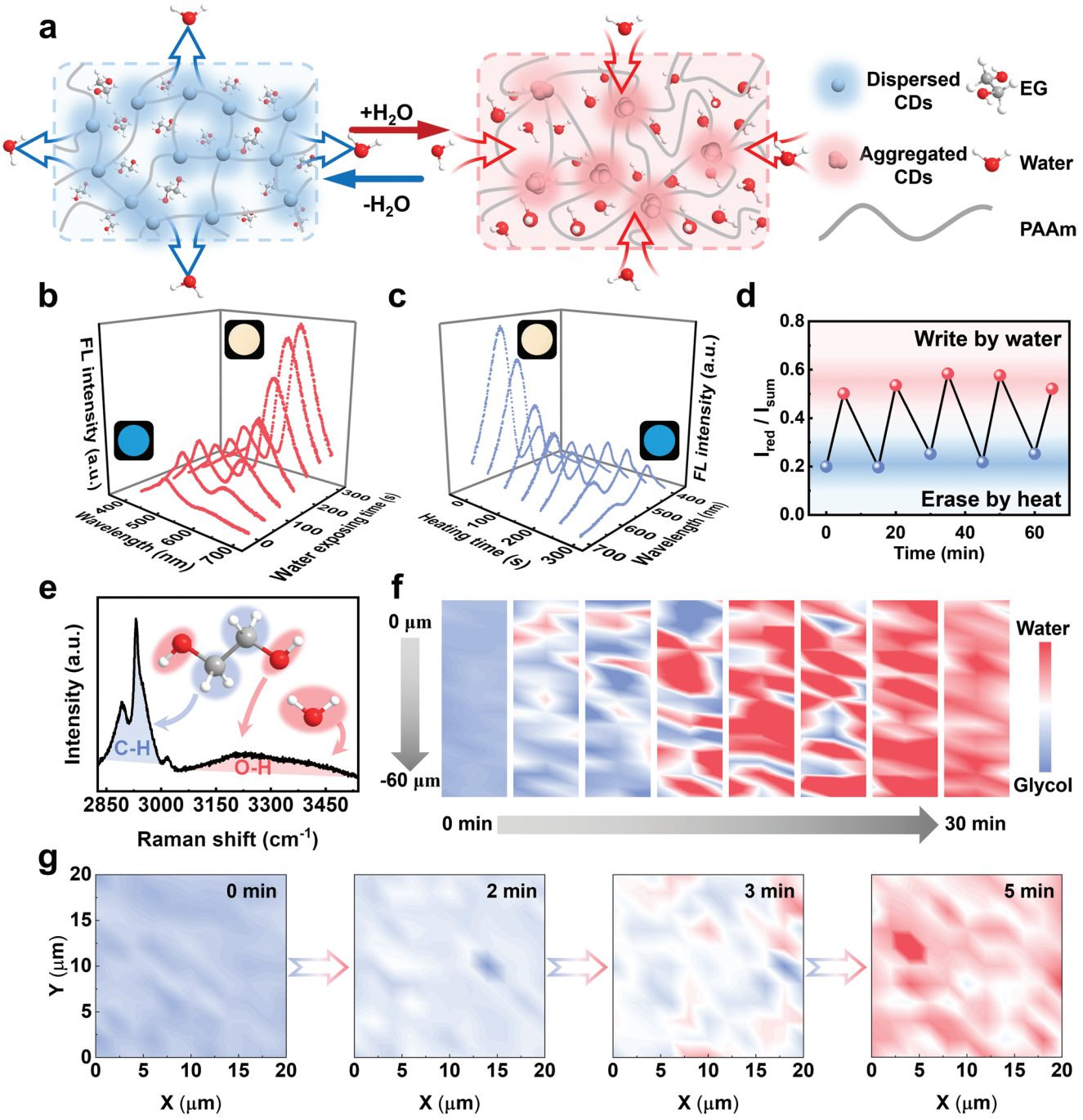

Figure 2. Hygro-sensitive reversible fluorescence color changes in CDs-gel. a) Scheme of the reversible blue-to-red fluorescence color change of CDs-gel during water absorption and dehydration. b) Fluorescence spectra (λ_{ex} = 365 nm) of the CDs-gel that are recorded at different time intervals after spraying water on the surface (0, 50, 100, 150, 200, 250, 300 s). Inset shows the fluorescent photos taken at 0 s and 300 s. c) Fluorescence spectra (λ_{ex} = 365 nm) of the water-treated CDs-gel that are recorded at different time intervals after being heated at 60 °C (0, 50, 100, 150, 200, 250, 300 s). Inset shows the fluorescent photos taken at 0 s and 300 s. d) The recorded fluorescence intensity ratio (I_{red}/I_{sum}) of CDs-gel during several writing-erasing cycles. e) Raman spectrum of the CDs-gel surface after being exposed to water for 5 mins. f) Raman mappings of CDs-gel cross-section during water exposure within 30 mins. The depth and width of the regions was 60 μm and 4 μm, respectively. g) Raman mappings of CDs-gel surface treated during water exposure within 5 mins. The color refers to the Raman band ratio ($I_{O\text{-}H}/I_{C\text{-}H}$), the red color means higher $I_{O\text{-}H}/I_{C\text{-}H}$ values. All fluorescent photos were taken under a 365 nm UV lamp.

aggregation and re-dispersion of CDs in response to the environmental water stimulus. This process is in analogy to the allochromasia phenomenon of soft cephalopod skins, which is achieved through reversible expansion and shrinking of pigment cells upon environmental changes. The key differences are the unique multilayer structure of cephalopod skins as well

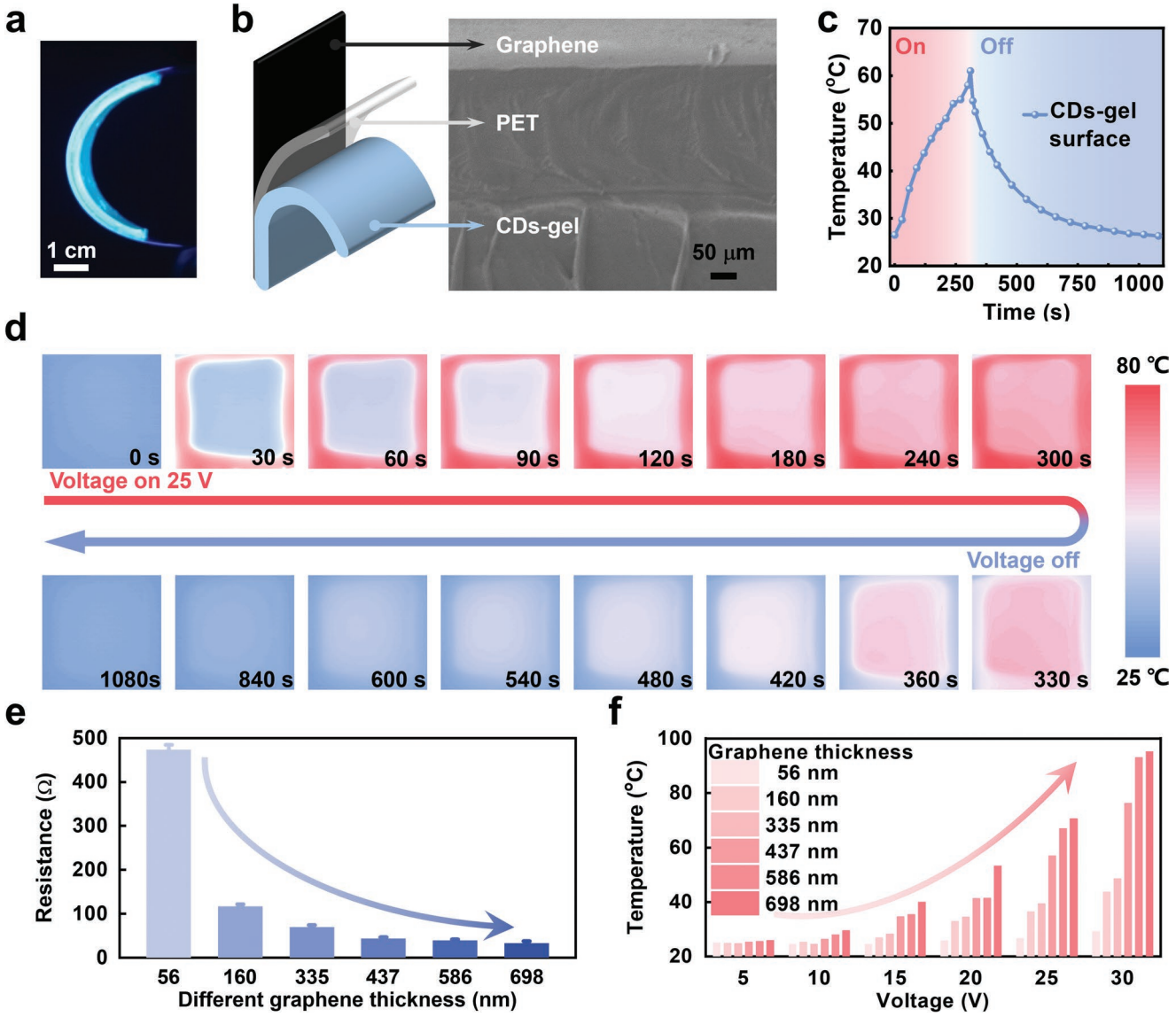

Figure 3. Electro-thermal-hygro responsive rewritable systems. a) Photo of the flexible rewritable system taken under a 365 nm UV lamp. b) Illustration of its multilayer structure and the cross-section SEM image. c) Time-dependent temperature profiles recorded on the CDs-gel layer surface upon power on-off at 25 V. d) Infrared thermography images of the CDs-gel layer surface taken at different time intervals upon power on-off at 25 V. e) Resistance changes of the conductive bilayer PET/graphene film with different graphene thickness. f) Surface temperature of these conductive bilayer PET/graphene films recorded after applying different magnitudes of voltage for 300 s.

as the utilization of high-precision bioelectrical stimulus, thus affording facile spatial/temporal control over skin patterns. To mimic the such natural material structure and working principle, we further interfacially assembled the soft CDs-gel sheet with conductive stacked graphene assembly (SGA) film into flexible rewritable systems (**Figure 3**a) by using thin PET film as the connecting layer (see Note S1 and Figures S6–S9, Supporting Information, for detailed preparation method).[16b] The commercial PET film (thickness ≈ 0.2 mm) was chosen as the middle layer, as it not only has good flexibility for arbitrary bending, but also has well toughness for self-supporting. In a typical experiment, the flexible PET film was first used to transfer the graphene film on air/water interface to produce the bilayer PET/graphene film that were interfacially bonded via hydrophobic interactions. Subsequently, its PET side was pressed together with the CDs-gel and placed on a hot plate (80 °C) overnight. After being cooled to room temperature, CDs-gel was stably bonded to the PET film through dense interfacial hydrogen bonds between the high-density carbonyl groups in PET film and -OH/-NH_2 groups in CDs-gel. Its multilayer structure was clearly shown in the scanning electron microscope (SEM) image (Figure 3b). Upon applying voltage onto the graphene film, Joule heat was generated due to electrocaloric effect and spontaneously transferred across the middle PET layer to raise the temperature of CDs-gel layer. As the results in Figure 3c,d showed, the top CDs-gel layer was gradually heated up and reached about 61 °C within 300 s at 25 V voltage. Upon power off, the temperature spontaneously

decreased to room temperature. In this way, it is possible to regulate the aggregation and re-dispersion states of CDs by facilely switching on/off the power to precisely and continuously control the water content in the top CDs-gel layer.

Owing to the above-proposed biomimetic multilayer structure, the classic hygro-sensitive fluorescence color-changing CDs-gels have been promoted to the preferred electro-thermal-hygro responsive rewritable systems with many exciting advantages. Firstly, the electro-heat can be accurately regulated by facilely varying the thickness of graphene film (from 56±7 nm to 698±37 nm, determined by Scanning Probe Microscope measurements, See Figures S10–S12, Supporting Information), as well as magnitude of voltage and power-on time (Figure 3e,f). As a result, both the information duration time and erasing speed are able to be accurately and continuously controlled. To showcase this potential, the red fluorescent "2022" pattern was printed on the top CDs-gel layer (**Figure 4**a,b) by using water as the ink to induce CDs aggregation. At ambient conditions (no voltage), the printed fluorescent pattern was quite stable and could last for several days. Such long-time duration

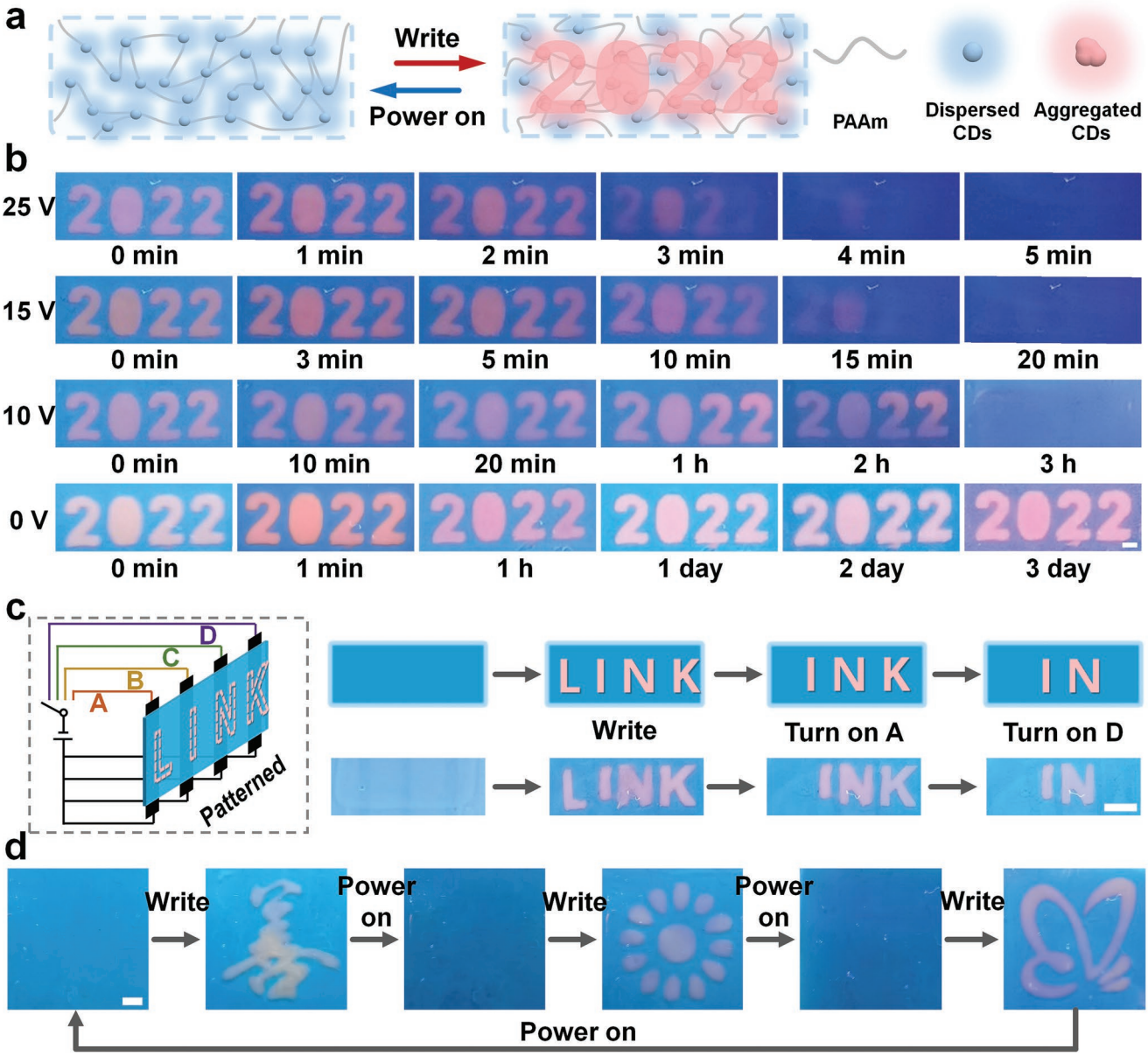

Figure 4. Demonstration of temporal/spatial information control and rewritability. a) Illustration of the water-triggered information writing and electrically controlled information erasing process in the developed rewritable system. b) Fluorescent photos showing a time-dependent display of the red fluorescent "2022" information at different voltages (0 V to 25 V), demonstrating the temporal information control capacity. c) Illustration and photos showing spatial information display of several different English letters by using the patterned graphene film layer. The graphene film beneath each letter was connected to an individual switch. d) Fluorescent photos showing the writing-erasing-rewriting capacity of our rewritable system. These patterns were written by water ink and erased by applying 25 V. All fluorescent photos were taken under a 365 nm UV lamp. Scale bars in photos is 0.5 cm.

time was believed to derive from the specially designed CDs-gel system, which utilized EG as the solvent to infiltrate the chemically cross-linked polymer network. The high-density O/N-containing groups along the polyacrylamide chain formed vast hydrogen bonds with the EG solvent and newly introduced H_2O molecules. Also, the EG molecules are known to form a variety of molecular clusters with H_2O molecules.[16c] Consequently, saturated vapor pressure of the H_2O ink was largely reduced to minimize its evaporation speed, resulting in significantly increased information duration time at ambient conditions. Importantly, upon applying voltage (e.g., 10 V), the lifetime of the written information could be regulated to a few hours, because the generated Joule heat would weaken the hydrogen bonds with water ink and the gel network to accelerate H_2O evaporation, leading to re-dispersion of the grafted CDs. Increasing the magnitude of voltage to 15 V would significantly shorten the information lifetime to about twenty minutes, while transient information with a lifespan of <5 mins could be obtained at 25 V voltage, suggesting the possibility of CDs-gel system to serve as a rewritable substance for "snapchat" communication of certain secret information. Obviously, the lifetime of the written information on this intelligent rewritable system could be defined as anticipated by facilely varying the magnitude of voltage, which were difficult to be realized in previously reported systems.

Besides, spatially-controlled display of the written information could also be guaranteed by delicately engineering the multilayer structure of our rewritable systems. To demonstrate this, one rewritable system with a patterned graphene film layer was designed. As can be seen from Figure 4c, one four-letter word "LINK" was written on the CDs-gel layer and four electric switches were connected to the graphene stripes beneath each letter. As a result, when turning on Switch A, letter "L" would be selectively erased by the electro-heat, leading to the display of the three-letter word "INK". Similarly, another two-letter word "IN" would be successively displayed after turning on Switch D. In this way, spatial information control was demonstrated for our rewritable system.

Further, this electro-heat-regulated rewritable system was also proved to be residue-free, thus holding great potential to enable numerous writing-erasing-rewriting cycles in theory. As can be seen from Figure 4d, the Chinese character "善", which was clearly written on the blank CDs-gel layer by water ink, was capable of being completely erased upon applying a voltage to generate Joule heat that accelerated water ink evaporation. Then, the sun profile could be well rewritten and wholly erased to allow for the successive reprinting of the butterfly profile. Such well-established rewritable capacity was derived from the delicately designed CDs-gel composition. For one thing, the employment of aggregation-induced emission active CDs made it possible to use clean and pollution-free water ink to write or print information. For another, the vast hydrogen bonds between water ink and the gel network were spontaneously weakened at elevated temperature, thus allowing for full evaporation of water ink to erase the written information. In addition, the minimum line width of these water-written fluorescent patterns on CDs-gel layer was found to be ≈0.7 mm (Figure S13, Supporting Information).

The bio-inspired electricity-controlled rewritable systems, characterized with an unprecedented combination of spatial/temporal information control and good rewritability, further enlightened us to explore their environment-interactive display functions. Compared with traditional stimuli such as water or heat, the electrical stimulus provides notable convenience for joint use with the commercial sensors and multichannel electronic timing relays devices. To show this potential, **Figure 5**a,b showed a "peacock" paint example, in which the "feather" parts were printed by water ink and other parts were made by commercial luminous paints as the control experiment. In order to realize the environment-interactive display of this "peacock" paint, an acoustic sensor (AS) and a three-channel electronic timing relays (TCETR) device were connected with the bottom patterned graphene film layer according to the circuit schemed in Figure 5a. In this design, power on/off of the graphene circuits A, B, and C was intelligently controlled by the pre-edited program in the combined AS-TCETR device. At normal decibel, all these three graphene circuits were powered off so as to enable stable display of the whole "peacock" paint (Figure 5b-ii). But when the surrounding voice became higher than a pre-set value, the combined AS-TCETR device would be activated to immediately switch on the graphene circuit A. As Figure 5b-iii showed, the outer "feather" parts would be erased first due to the electro-heat generated by graphene circuit A. According to the pre-edited program in the AS-TCETR control device, graphene circuit B would be automatically powered on after 10 mins in order to erase the middle "feather" parts (Figure 5b-iv), and graphene circuit C was finally turned on to erase the inner "feather" parts (Figure 5b-v). In this way, the environmental sound-interactive stepwise information display was successfully achieved in our electrically powered rewritable systems. Note that such "peacock" pattern could be rewritten on the CDs-gel by using water as the ink to enable another stepwise erasure process, suggesting its possibility to allow for a rewritable display of the "peacock" image. Besides the sound, environmental light-interactive on-demand information display could also be easily guaranteed by the joint use of a light sensor (LS) and five-channel electronic timing relay device (Note S2 and Figures S14–S16, Supporting Information).

On account for the as-established environmental sound/light-interactive rewritable systems, on-demand regulation of information display that suits anti-counterfeiting applications was further demonstrated. In a typical example, a water-written Chinese character "树" was printed on the rewritable system with a patterned graphene film layer (Figure 5c). Note that graphene film A was connected with a circuit with an AS, while graphene film C was connected with a circuit with a LS (Figures S17,S18, Supporting Information). As a result, the Chinese character "对" was displayed at elevated voice decibel, while the Chinese character "权" was observed when shading light on the LS (Figure 5d). Furthermore, another different Chinese character "又" was displayed under the input of both acoustic and light cues. In this way, not only distinct characters information, but also their display sequence could be successfully programmed upon different environmental sound/light changes, largely enriching the multi-functionalities and potential uses

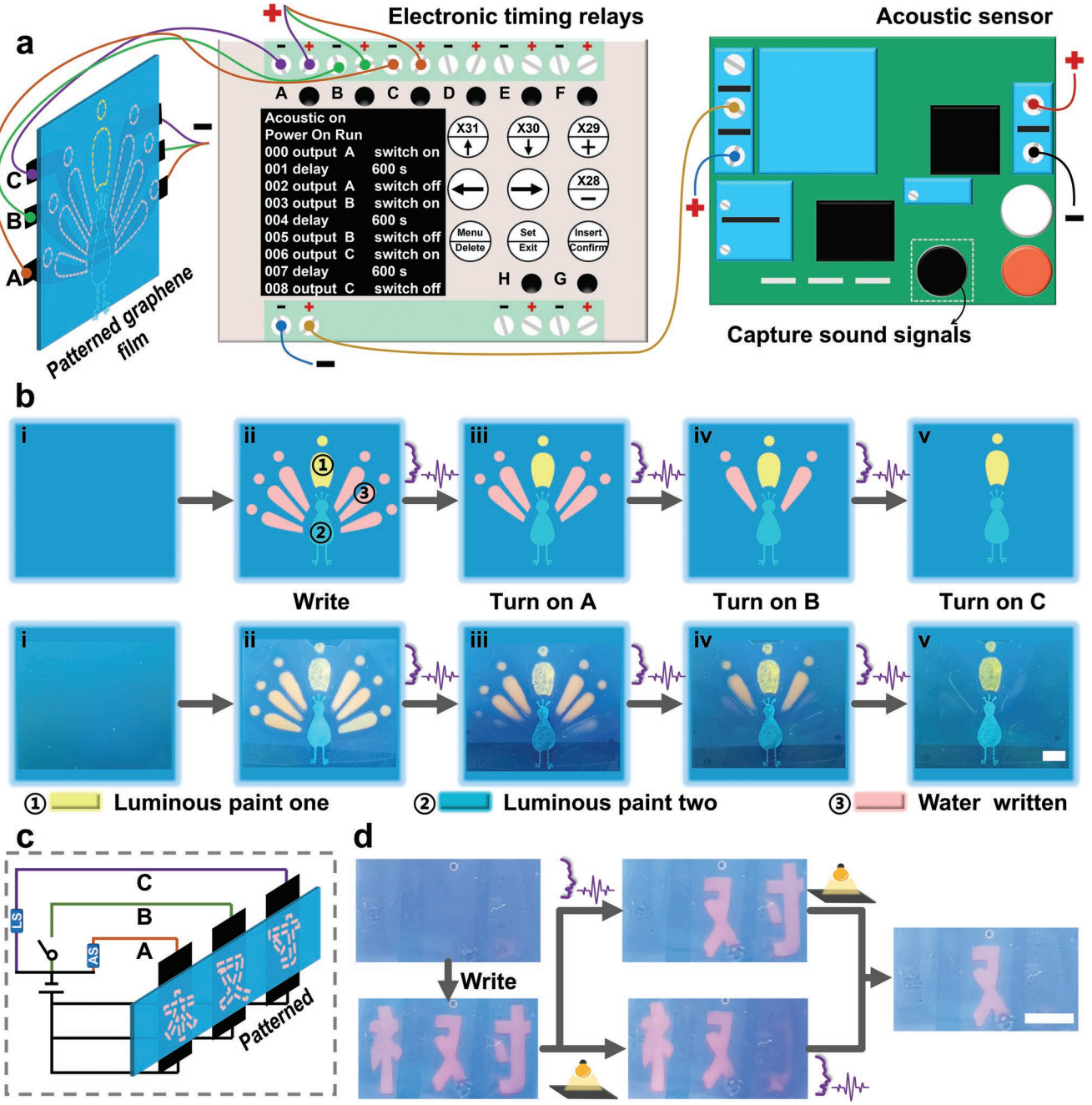

Figure 5. Environment-interactive information display. a) Schematic circuit of electrically controlled rewritable system, in which an AS and a TCETR device were connected with the bottom patterned graphene film layer. b) Illustration (upper) and fluorescent photos (lower) showing environmental sound-interactive display of a dynamic "peacock" pattern. c) Schematic circuit of electrically controlled rewritable system, in which both AS and LS were combined with the bottom patterned graphene film layer. d) Fluorescent photos showing environmental sound/light-interactive display of different Chinese characters. When different environment sound/light signals change, a series of Chinese characters with different meanings were decrypted in sequence. All fluorescent photos were taken under a 365 nm UV lamp. Scale bars in photos is 1 cm.

of rewritable systems. Moreover, after the complete erasure of these "木", "又" and "寸" characters by Joule heat, the bottom graphene films are wide enough to allow the re-writing of any other Chinese characters on the top CDs-gel, suggesting its possibility to serve as a rewritable system to facilitate environmental sound/light-interactive on-demand information encryption.

3. Conclusion

In this study, we have learned from the natural multilayer structure and bioelectricity-controlled mechanism of soft cephalopod skins to develop robust luminescent rewritable systems that combine the merits of spatial/temporal information control and rewritability. The developed systems have the

biomimetic multilayer structure, including the hygro-sensitive fluorescence color changeable CDs-gel sheet as the upper layer and the bottom conductive graphene film layer that are bonded together by using soft PET film as the middle layer. In this device, arbitrary information could be repeatedly written or printed on the top CDs-gel layer by using water as the ink and employing electroheat to de-ink. Remarkably, temporal/spatial control of the written information, which have hardly been achieved before, could be realized by facilely patterning the graphene film layer or varying magnitude of voltage and power on time. Especially, when the signal reception units (acoustic/optical sensors) were further integrated, conceptually new environment-interactive rewritable systems were realized, which behaved like natural cephalopod skins to display different patterns in response to environmental light/sound signal changes.

The key to enable the preferred spatial/temporal control and rewritability of our rewritable systems was derived from the imitation of bioelectricity-regulated reversible expansion and contraction of pigment cells that are vertically arranged in natural cephalopod skins. Thanks to biomimetic multilayer structure of the developed rewritable systems, electricity-triggered reversible aggregation and dispersion of fluorescent CDs in the upper CDs-gel layer was achieved via the generated Joule heat of the bottom graphene film, resulting in excellent rewritability. Additionally, the highly controllable electrical stimulus in terms of amplitude and duration spontaneously brought such merits as spatial/temporal control of the written information. As a result, time-stamped information display and environment-interactive multiple-output functions, which have been highly desired but never achieved before, were observed, thus significantly promoting the development of luminescent rewritable systems. Our rewritable systems with regulated lifetime and interactive display features are expected to be applied in fields where the written information should disappear within a pre-set time period, such as for waybills and secret information delivery. As such, people's privacy and secret information would be better protected.

4. Experimental Section

Materials: Ammonium persulphate (APS, 99%) was obtained from Shanghai Macklin Biochemical Co. Ltd. Dimethyl sulfoxide (DMSO, 99.0%), acrylamide (AAm, 98%), *N,N′*-methylenebisacrylamide (MBAA, ≥98.0%), and ethylene glycol (EG, 99.0%) were purchased from Aladdin Chemistry Co. Ltd. All materials were used without further purification. Vinyl-functionalized CDs were synthesized according to the procedures described in previous study.[16a]

Instruments and Measurements: The digital photographs of the gels were taken under UV lamps (ZF-5, 8 W, 365 nm) using a smartphone (HUAWEI P40 Pro). Steady-state fluorescence measurements were carried out by a Horiba FL3-111 fluorescence spectrophotometer at room temperature with a 450 W Xenon lamp. Transmittance spectra were measured on a UV-Vis spectrophotometer (Lambda 950, Perkin–Elmer). Static water contact angles were probed using a contact angle meter (OCA25, Data-physics) using a 3 µL droplet of water as an indicator. Raman scattering measurements were taken by a Raman system (in Via-reflex, Renishaw) with 785 nm excitation wavelength. An infrared thermal camera (Optris PI 400) was employed to capture the real-time recording of the surface temperature and infrared images under different input voltages. The surface and cross-section morphologies of the multilayered structure of CDs-gel/PET/graphene were performed by a field-emission scanning electron microscopy (SEM, S-4800, Hitachi) with an accelerating voltage of 5.0 kV. Scanning Probe Microscope (SPM) measurements were conducted using Dimension 3100 SPM (Vecco, USA) in a PeakForce tapping mode.

Synthesis of the CDs-Gels: Vinyl-functionalized CDs (fluorescent monomer, 0.04 g) was dissolved in 0.5 mL DMSO (denoted as solution A). Then, AAm (monomer, 1.00 g), MBAA (crosslinker, 0.01 g), and APS (thermoinitiator, 0.01 g) were dissolved in 4 mL EG (denoted as solution B). Subsequently, solution A and B were mixed well by vortexing. The precursor solution was added into the molds with two quartz glass plates and a 2-mm thick silicon plate. Finally, the system was transferred into an oven at 65 °C to polymerize for 6 h to obtain the CDs-gel.

Preparation of the Conductive Bilayer polyethylene glycol terephthalate (PET)/Graphene Film: The conductive bilayer PET/graphene film was fabricated according to the previous study.[16b] Typically, a certain amount of graphene stocks was mixed with ethanol and then ultrasonicated for 6–10 h to form a uniform dispersion (1.5 mg mL^{-1}). Then, the as-prepared graphene/ethanol dispersion (30 mL) was sprayed onto the water surface, which resulted in an ultrathin graphene film evenly located at the air/water interface. Next, a piece of taper porous sponge was inserted into water to form the stacked graphene assembly (SGA) film. Then, a piece of PET film was cut into 8 cm × 8 cm, and inserted into water to transfer graphene film, followed by a drying process (60 °C, 10 mins) to obtain the bilayer PET/graphene with one SGA layer. Repeating such transferring and drying steps would produce the bilayer PET/graphene with different SGA layers (from one to six).

Preparation of the Electrically Controlled Rewritable System: First, the as-prepared CDs-gel was adhered to the PET side of the as-prepared bilayer PET/graphene film with five SGA layers. Second, the system was placed on the hot plate (80 °C) overnight with the graphene side down to evaporate EG. Third, Ni-coated textile electrodes were connected to graphene film layer of the system.

Writing Process of the Electrically Controlled Rewritable System: Information was written on the CDs-gel layer by using water the ink. Taking the writing of "2022" information as an example, one silicon rubber mask with a "2022" pattern was first prepared by a laser cutting machine. The mask was then clinged on the CDs-gel layer, followed by spraying water on the gel surface. As such, red fluorescent "2022" information quickly appeared within 3 mins because of the water diffusion that triggered the CDs aggregation. Other information was printed by using different silicon rubber masks.

Experiments to Determine the Minimum Line Width of Water-Written Fluorescent Patterns on CDs-Gel Layer: Red fluorescent line patterns were written on the CDs-gel layer by using water as the ink with the assistance of silicon rubber masks. Specifically, the silicon rubber masks with different line pattern widths (3 mm, 2 mm, 1 mm, 0.7 mm, 0.5 mm, 0.3 mm, and 0.2 mm, respectively) were first prepared by a laser cutting machine. These masks were then clinged on the CDs-gel layer, followed by spraying water on the gel surface. As such, red fluorescent lines quickly appeared within 3 mins because of the water diffusion that triggered the CDs aggregation. It was found that the minimum line width of these water-written fluorescent patterns on CDs-gel layer was found to be ≈0.7 mm.

Statistical Analysis: The error bars of experimental data were presented with mean ± standard deviation (SD), and all experiments were repeated at least three times. Images taken by mobile phones were processed by edge extraction, brightness, and contrast in the article. The software of Excel was employed to conduct a one-way analysis of variance (one-way ANOVA) and the difference among samples was considered to be important when the calculated p-value was <0.05.

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.

Data Availability Statement

Research data are not shared.

Keywords

color changes, environment-interactive, fluorescence, gels, rewritable systems

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