

# Promotion of Color-Changing Luminescent Hydrogels from Thermo to Electrical Responsiveness toward Biomimetic Skin Applications

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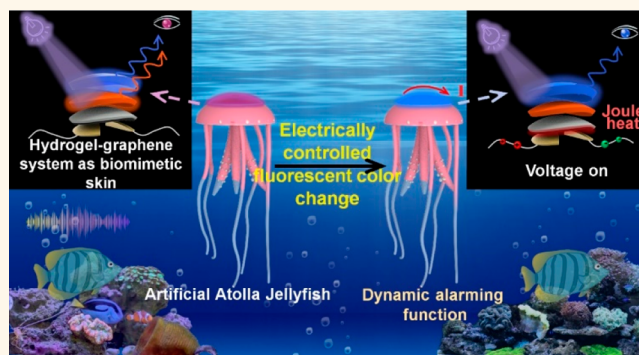
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**ABSTRACT:** The active color-changing ability of many living species has inspired scientists to replicate the optical property into soft wet and tissue-like hydrogel materials. However, the color-changing processes of most reported examples are controlled by the traditional stimuli (e.g., pH, temperature, and ions), which may suffer from the residual chemical product accumulation, and have difficulty in achieving local control and integration into the commercial robots, especially when applied as biomimetic skins. Herein, inspired by the nervous (bioelectricity) control of skin color change in cephalopods, we present an electrically powered multicolor fluorescent hydrogel system with asymmetric configuration that couples thermoresponsive fluorescent hydrogel with stacked graphene assembly (SGA)-based conductive paper through luminous paint as the middle layer. Owing to the highly controllable electrical stimulus in terms of amplitude and duration, the Joule heat supplied by SGA film can be regulated locally and in real time, leading to precise and local emission color control at low voltage. It also avoids the addition of any chemicals. Furthermore, the electrically powered color-changing hydrogel system can be conveniently integrated into the commercial robots as biomimetic skins that help them achieve desirable camouflage, display, or alarming functions.

**KEYWORDS:** hydrogels, fluorescence, stacked graphene assembly, color changes, electrothermal effect, biomimetic skins



## INTRODUCTION

Responsive color changes are commonly observed in nature. For instance, a number of living creatures, including marine mollusks, butterflies, fishes, spiders, and flowers, have evolved to utilize the tunable color changes to achieve adaptive camouflage, concealment, protection, or display.<sup>1–3</sup> These exciting phenomena have inspired scientists to replicate the responsive color-changing functionality into artificial soft synthetic materials like polymer films, elastomers, and hydrogels.<sup>4–12</sup> Given the extreme similarity between hydrogels and biotissues, i.e., the soft wet nature and tissue-like mechanical property,<sup>13–31</sup> the fabrication of smart multicolor polymeric hydrogels is of great interest as they can facilitate an understanding of these natural color change phenomena and will also be of benefit as soft biomimetic skins to enhance the function of certain machines (such as robots or prosthetics). Unfortunately, although a number of multicolor hydrogel

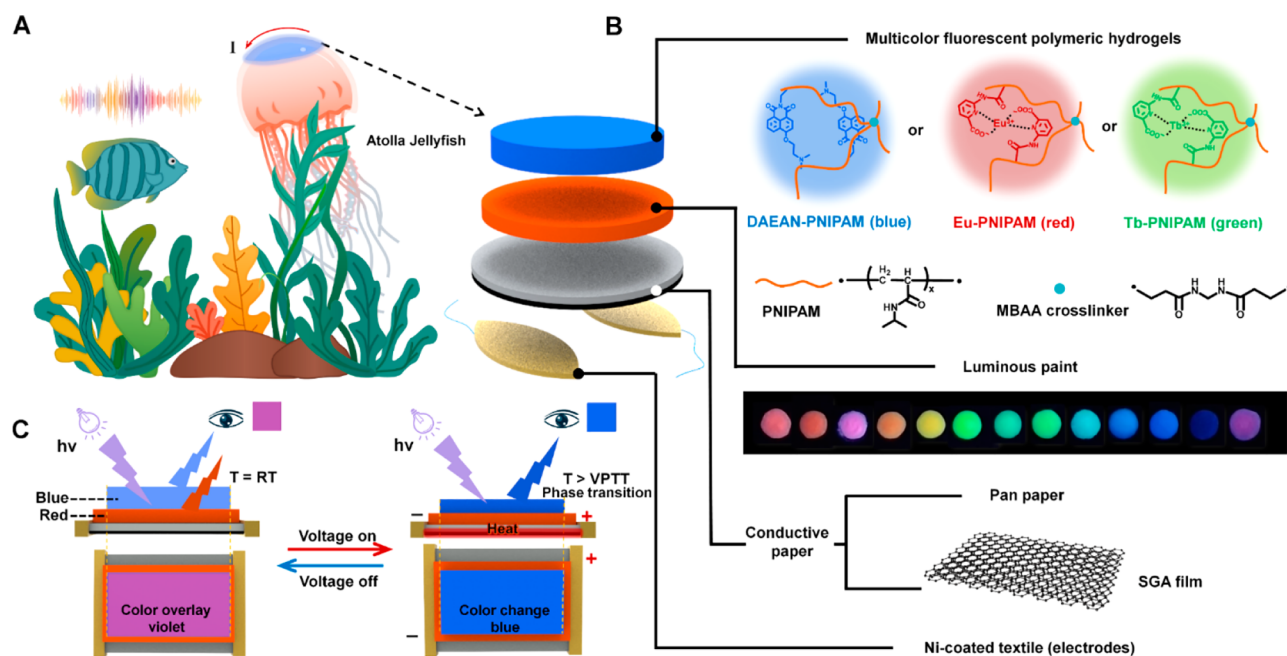
systems have been reported, applications for biomimetic skins are still little used. This might be due to the following reasons: (1) the color-changing processes of most systems are primarily controlled by traditional stimuli such as pH,<sup>32–34</sup> temperature,<sup>35–37</sup> and ions.<sup>38–40</sup> First, the color-changing behaviors of the whole hydrogels could be globally tuned, but it is usually operationally difficult to locally regulate their optical behaviors to realize the spatial/temporal color control on/within these hydrogels. (2) More importantly, they usually suffered from poor cyclic color-changing performance, especially for pH or

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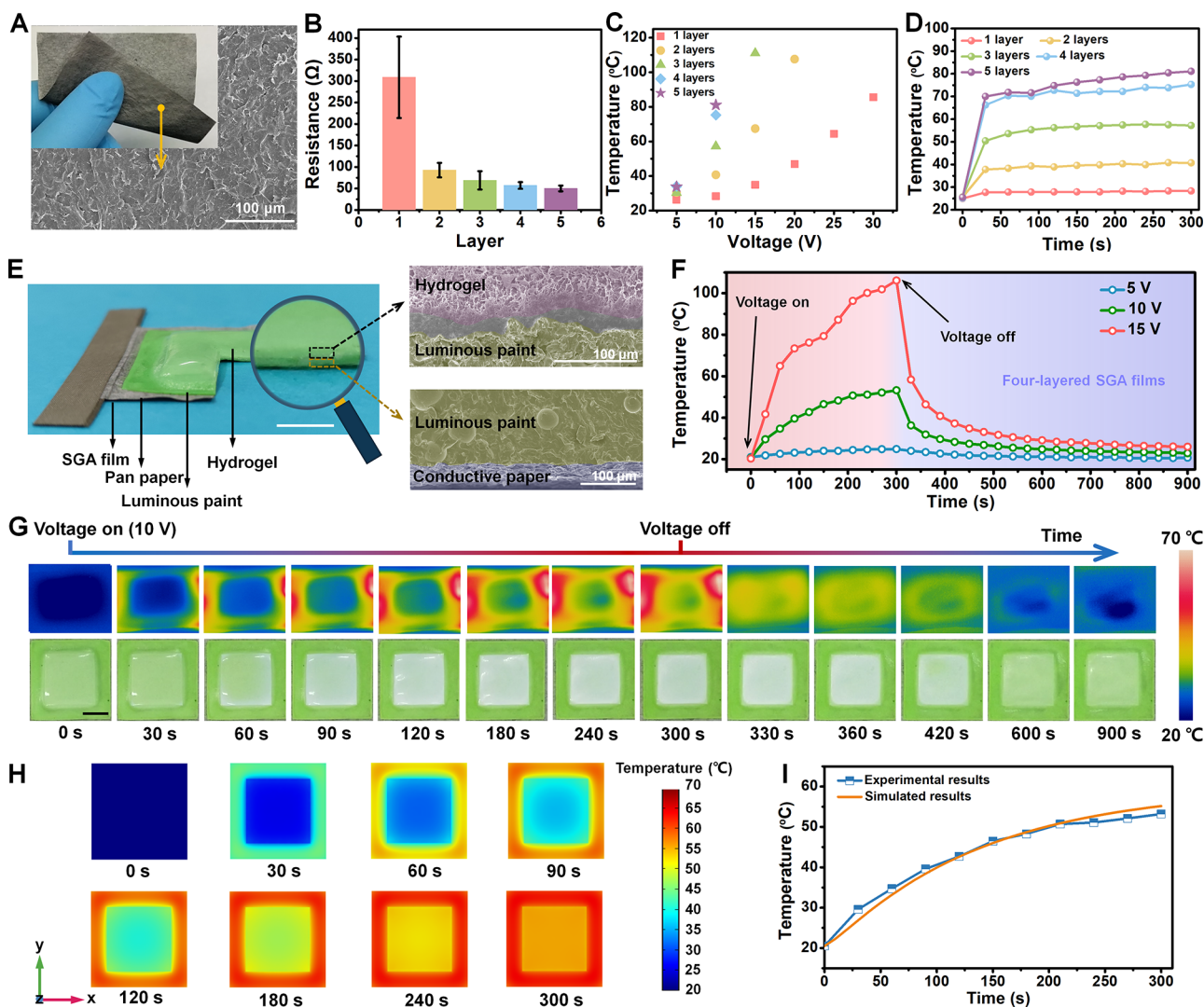


**Figure 1.** Design of the electrically controlled fluorescent color changeable hydrogel–graphene system. (A) Cartoon of an Atolla Jellyfish with dynamic alarming functions that inspired the design of the hydrogel-based biomimetic color-tunable skin. (B) Schemes illustrating the structure of the electrically controlled fluorescent color changeable hydrogel–graphene system, which consisted of a fluorescent hydrogel layer, luminous paint layer, the conductive paper layer with electric-thermal effect, and flexible electrodes. Blue, red, and green fluorescent hydrogels were prepared by using DAEAN, Eu–K6APA complex, and Tb–K6APA complex as luminescent centers, respectively. The conductive paper was composed of pan paper and SGA film. (C) Schematic illustration showing the electrothermally controlled color-tunable process of the system. The blue fluorescent hydrogel and red luminous paint can be overlaid to obtain violet color. After applying suitable voltage to the conductive paper, a violet-to-blue color change was observed.

ions-controlled systems. This is because the alternate addition of chemical stimuli (e.g., acids, bases, salts) is prone to cause the residual chemical product accumulation within the hydrogels, resulting in rapidly decreasing color-changing capacity and sensitivity in the next cycle. Therefore, it is still highly desirable to develop robust multicolor hydrogel systems that can respond to “residual-free” stimulation modes and thus allow for facile local color/intensity control and better cyclic color-changing performance.

On the other hand, nature offers a drastically different strategy to control the soft skin color change of animals. One of the most famous examples is cephalopods, in which the selective activation of chromatophores is usually remotely controlled by their nervous system (bioelectricity) in response to environmental stimuli.<sup>41</sup> Inspired by this natural display strategy, we speculate whether it is possible to utilize electric stimulation to control the fluorescence color change of active multicolor changing polymeric hydrogel systems, which can easily realize remote and local control.<sup>42</sup> In addition, electrical control is an ideal “residual-free” stimulation method, effectively avoiding the residual accumulation of chemical products generated by the alternate addition of chemical stimuli (e.g., acids, bases, salts). Importantly, electrically powered color-changing systems provide notable convenience for further system control and integration, holding great potential to be facilely integrated into the electrically controlled commercial robots as biomimetic skins to achieve the desirable camouflage, display or alarming functions. However, despite its great potential, the design of electrically powered color-changing hydrogel materials is still quite challenging.

Herein, we report a robust multicolor fluorescent polymeric hydrogel system with electrically controlled fluorescent color-changing property, which can be used as a biomimetic skin to improve the performance of the commercial robots, for example, to mimic the alarm color-switching behavior of Atolla jellyfish. As illustrated in Figure 1A,B, the system with asymmetric configuration was designed and prepared by layer-by-layer assembly of the thermoresponsive fluorescent hydrogels, luminous paint, stacked graphene assembly (SGA)-based conductive papers with excellent electrothermal effect, and flexible electrodes. In this design, three kinds of fluorescent polymeric hydrogels with three primary colors (blue, red, and green) were involved. The blue fluorescent hydrogel was prepared by the radical polymerization of an AIE-active 4-(dimethylamino)ethoxy-*N*-allyl-1,8-naphthalimide (DAEAN) monomer with *N*-isopropylacrylamide (NIPAM) and methylene-bis-acrylamide (MBAA). While the red and green fluorescent hydrogels were obtained by covalently introducing Eu<sup>3+</sup> or Tb<sup>3+</sup> amidopicolinate complexes into the thermoresponsive PNIPAM network, which can exhibit intense emission through energy transfer from the ligand, potassium 6-acrylamidopicolinate (K6APA), to central Eu<sup>3+</sup> or Tb<sup>3+</sup> ions.<sup>38</sup> Emission color of the as-prepared hydrogel–graphene system was determined by the overlapping color of the fluorescent hydrogel layer and luminous paint layer. The bottom conductive paper layer was fabricated by transferring condensed SGA with good thermal conductivity and structural stability onto pan paper.<sup>43,44</sup> When an external voltage is applied to the conductive paper, Joule heat was generated to increase the temperature of the fluorescent hydrogel layer, subsequently resulting in its phase transition and light transmittance decrease. As a consequence, electrically powered

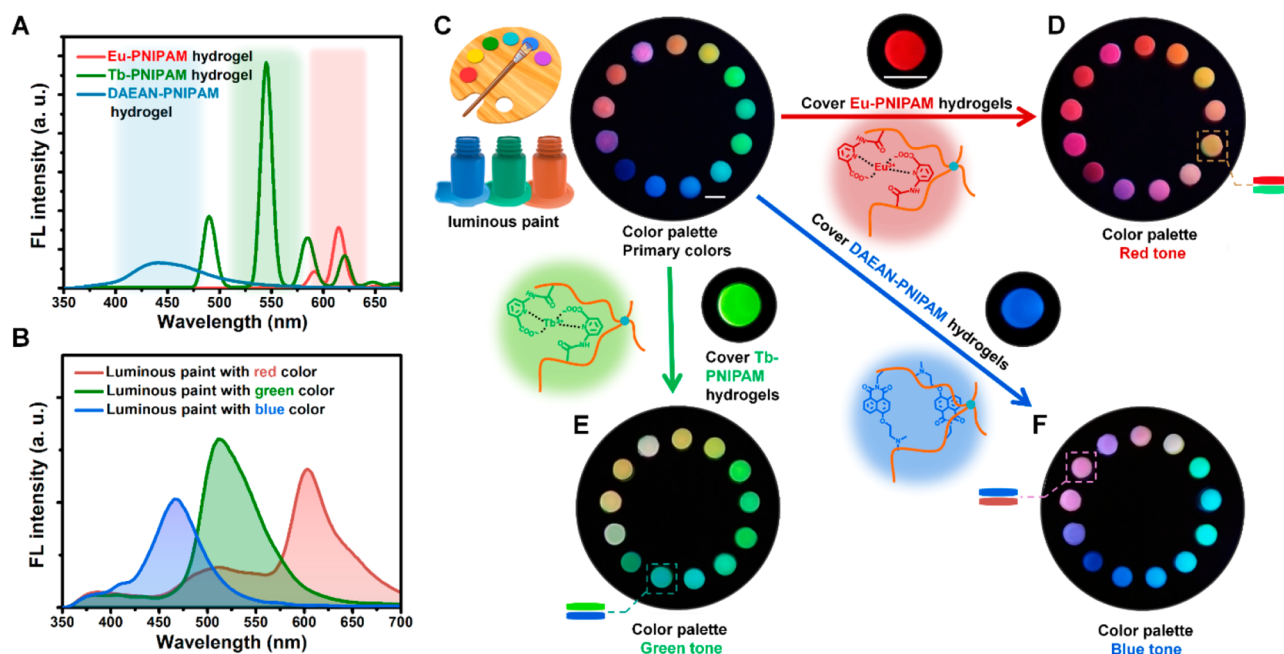


**Figure 2.** Fabrication and characterization of the electrically controlled hydrogel–graphene system. (A) SEM images of the SGA film side of conductive paper. Inset shows the corresponding digital photo. (B) Resistance of the conductive papers with different SGA layers (one to five layers). (C) Surface temperature of these conductive papers recorded after applying different voltages for 300 s. (D) Temperature change of these conductive papers as a function of power-on time at 10 V. (E) Photograph and cross-section SEM image of the device. (F) Time-dependent temperature profiles of the device recorded upon on–off of different applied voltages. (G) IR images and corresponding photographs of the device taken at different time intervals when the voltage of 10 V was applied and removed. (H) Finite element simulation of surface temperature distribution of hydrogel–graphene system with different power-on time under a voltage of 10 V. (I) Surface temperature profiles of the device by experiment and simulation under 10 V for 300 s. Scale bars in digital photos are 1 cm.

emission color change was observed (Figure 1C). By a selective combination of the luminous paint or the fluorescent hydrogel layer, it is possible to realize diverse emission color change over a wide color gamut. In addition, this remote type of electrically controlled color change was proved to be highly reversible and residual-free because no chemicals were used. On the basis of these appealing advantages, the developed color-changing hydrogel–graphene systems can serve as biomimetic skins to help the electrically powered commercial robots blend into or stand out against the background. In addition, the commercial sensor had been facily integrated with our electrically powered color-tunable system to mimic the dynamic alarming function of Atolla jellyfish through a specially designed cascading process.

## RESULTS AND DISCUSSION

**Fabrication and Characterization of the Electrically Controlled Hydrogel–Graphene System.** In our study, the color-shifting property of the fluorescent hydrogel–graphene system was triggered by continuous Joule heat generated by the conductive paper consisting of SGA film and pan paper. The condensed SGA film was assembled on the surface of water through a Marangoni spread and capillary force induced compression of graphene (Figures S1 and S2).<sup>45,46</sup> A piece of pan paper was used as the supporting material to transfer SGA film. Followed by a drying process, the conductive paper with one layer of SGA film was obtained. Then conductive papers with more layers of SGA films (two to five layers) could be prepared by repeating this transferring and drying procedure several times (Figure S2). Surfaces of both the pan paper and SGA film exhibit hydrophobicity, resulting in a decent interfacial affinity (Figure S3). SEM images of the SGA side



**Figure 3.** Overlapping color of the fluorescent hydrogel layer and luminous paint layer. (A) Fluorescence spectra ( $\lambda_{\text{ex}} = 254 \text{ nm}$ ) of different-colored fluorescent hydrogels. The red-, green-, and blue-light-emitting hydrogels were prepared from the Eu–K6APA complex, Tb–K6APA complex, and DAEAN luminogens, respectively. (B) Fluorescence spectra ( $\lambda_{\text{ex}} = 254 \text{ nm}$ ) of the luminous paint layer with green, blue, and red emission. Color palette in (C) primary color (13 colors of luminous paint), (D) red tone color (the red fluorescent hydrogels were covered on the colorful luminous paint), (E) green tone color (the green fluorescent hydrogels were covered on the colorful luminous paint), and (F) blue tone color (the blue fluorescent hydrogels were covered on the colorful luminous paint). Scale bar in digital photos is 1 cm. All fluorescent photos were taken under a 254 nm UV lamp.

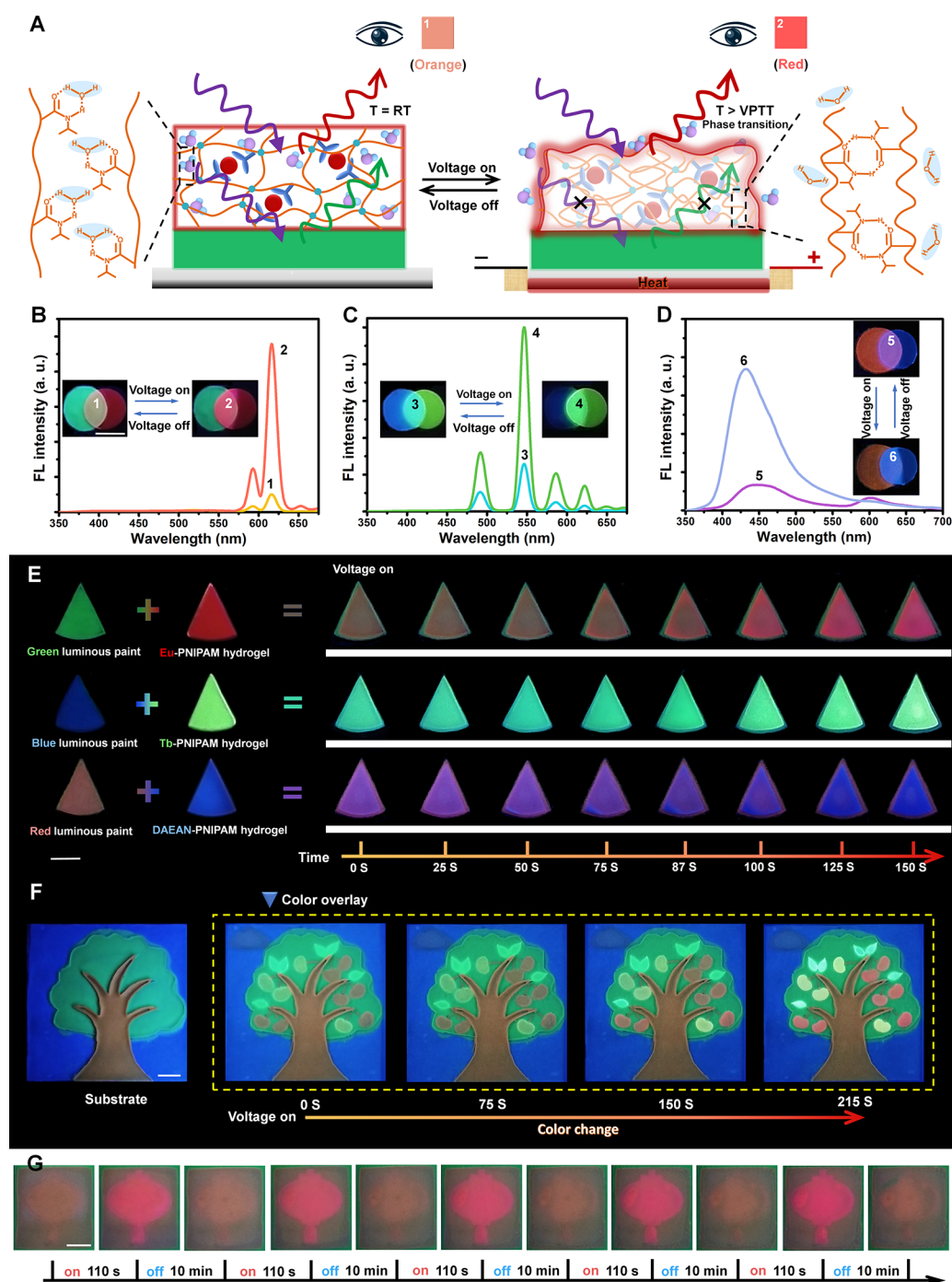
showed the closely packed structures of staggered graphene sheets (Figure 2A and Figure S4). The Raman spectrum also exhibited the structural information on SGA film with characteristic D and G bands of graphene (Figure S5). As shown in Figure 2B, the resistance of the conductive papers (35 mm  $\times$  35 mm, removing the area of electrodes) decreases with increasing SGA layers and tends to be constant above four layers, indicating that the cracks within SGA film have been gradually connected with increasing SGA layers.

The electrothermal performance of the conductive papers was then investigated. Figure 2C shows the surface temperature variation of these conductive papers after applying different voltages for 300 s. It was found that the temperature was positively related to the SGA film layers and applied voltages. When the applied voltage is fixed (taking 10 V as example), the temperature of all conductive papers rises rapidly within the first 30 s and soon reaches a plateau (Figure 2D and Figure S6). For conductive papers with four and five layers of SGA film, the temperature can increase to nearly 70 °C, which is much higher than the volume phase transition temperature (VPTT) of poly(*N*-isopropylacrylamide) (PNIPAM) hydrogel. Therefore, the conductive paper containing four-layered SGA films (with a thickness of about 32.5  $\mu\text{m}$ ) was chosen to construct the color-tunable hydrogel–graphene systems in the following study (Figure S7). The VPTT of PNIPAM-based fluorescent hydrogel is about 33 °C, which is similar to that of the previously reported PNIPAM hydrogels (Figure S8).<sup>47</sup>

By using the conductive paper as base substrate, an electrically controlled fluorescent color changeable hydrogel–graphene system was then fabricated by a layer-by-layer composite approach. As shown in Figures S9 and S10, luminous paint was first coated on the paper side of conductive paper. In this design, the luminous paint not only provides a

base color but also protects the conductive SGA films from interference of the water-swollen hydrogel layer. Subsequently, the thermoresponsive fluorescent hydrogel layer, which was pre-prepared by radical polymerization of fluorescent monomer, NIPAM monomer, and MBAA cross-linker, was placed onto the luminous paint to construct the whole device. In order to enhance the interfacial adhesion between the fluorescent hydrogel layer and luminous paint layer, the PVA glue was applied between the two layers. After several freezing and thawing cycles, their interfaces were stably bonded with the interfacial peeling force exceeding 18 N m<sup>-1</sup> per unit width (Figure S11). In addition, the hydrogel–graphene device can be easily folded, bent, and twisted, indicating its good flexibility (Figure S12). The multilayered structure of the as-prepared device, as well as SEM images of the microarchitectures of each layer, are depicted in Figure 2E and Figure S13.

The temperature profiles of the device recorded upon on–off of different applied voltages were then related to the transmittance of the thermoresponsive hydrogels (Figure 2F,G and Figure S14). At relatively low voltage (e.g., 5 V), the temperature rise was small. The Joule heat generated by conductive paper was not enough to induce the phase transition of hydrogel. At appropriate voltages (e.g., 10 V for the device with 35 mm  $\times$  35 mm conductive paper), the temperature soon reached 40 °C within 100 s and then gradually increased to  $\sim$ 53 °C after 300 s. As a consequence, the hydrogel on the top layer underwent noticeable phase transition accompanied by a significant transmittance decrease. In order to further demonstrate that the Joule heat generated by SGA film can supply energy for the entire device, we analyzed the temperature change of our hydrogel–graphene system under a voltage of 10 V by finite element simulation, which was highly consistent with the experimental results

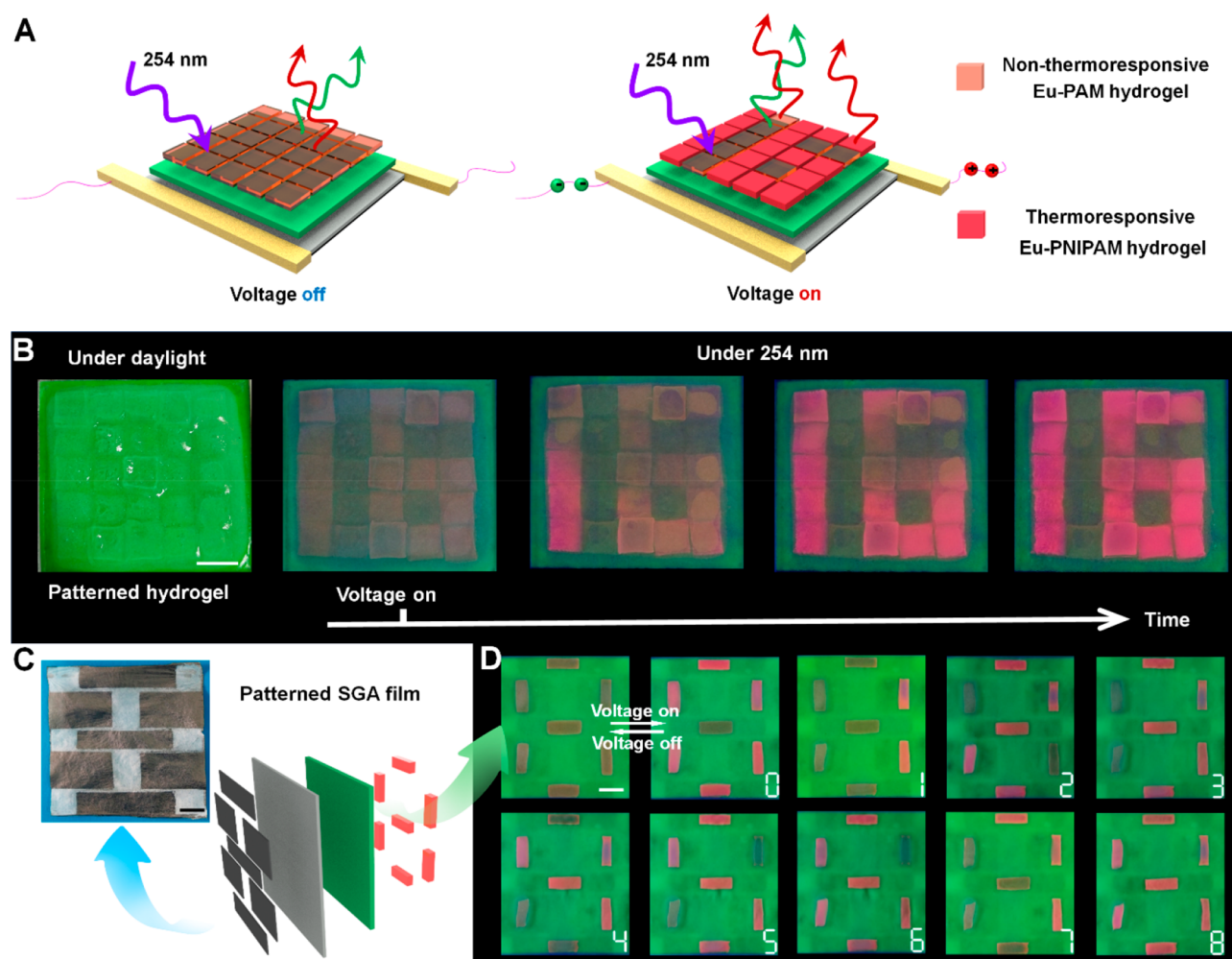


**Figure 4.** Studies on the electrically controlled fluorescent color changeable process. (A) Schematic illustration showing the proposed mechanism for the electrically controlled orange-to-red emission color change of the system. (B–D) Fluorescence spectra ( $\lambda_{\text{ex}} = 254 \text{ nm}$ ) of the overlapping areas before and after applying the voltage. (E) Images showing the electrically controlled fluorescent color changeable process of various samples under the voltage of 11 V. (F) Digital photographs showing the fruit-ripening process of an artificial cherry tree under the control of electric heat. The background pattern was created with the luminous paint. Eu–PNIPAM and Eu/Tb–PNIPAM ( $\text{Eu}^{3+}/\text{Tb}^{3+} = 3:1$ ) hydrogels were used to fabricate the red and yellow fruits, respectively. Tb–PNIPAM hydrogels were used to fabricate green leaves. (G) Photos showing the cyclic color-changing process of the fluorescent hydrogel–graphene system, which was triggered by on–off of electric powers. The color-tunable area with a lantern shape was fabricated by thermoresponsive Eu–PNIPAM hydrogel, and the rest of the patterns were fabricated by nonresponsive Eu–PAM hydrogel. Scale bars in digital photos are 1 cm. All fluorescent photos were taken under a 254 nm UV lamp.

(Figure 2H,I and Figure S15). When the voltage was turned off, the hydrogel layer gradually recovered to the transparent state as expected. If the voltage was too high (e.g., 15 V), the temperature could rapidly exceed 100 °C that might bring damage to the device. These results highlight that the applied

voltage should be selected within an appropriate range for a given device.

**Electrically Controlled Fluorescent Color-Changing Process.** As the multilayered device contained one luminous paint layer and another fluorescent hydrogel layer, its initial

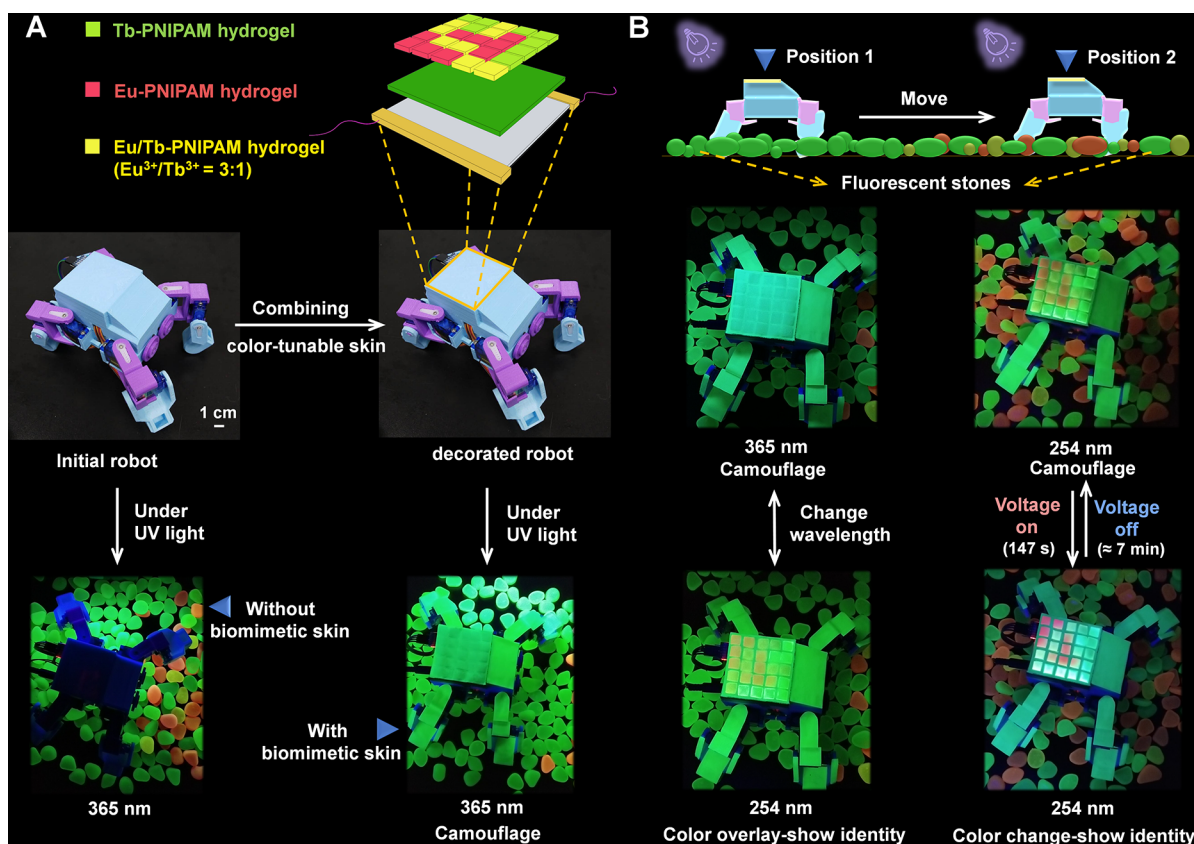


**Figure 5.** Patterned display and local control studies. (A) Schematic illustration of the device with a patterned hydrogel layer as well as the images that depict the on-demand display of specific information under electric heating control (B). Within the hydrogel array, the parts of the “16” pattern were fabricated by thermoresponsive Eu–PNIPAM hydrogel blocks, while the remaining parts were prepared by nonresponsive Eu–PAM hydrogels. (C) Schematic illustration of the device with patterned hydrogel and patterned SGA film. Each part of the patterned SGA film was controlled by a single switch for independently regulating the Joule heat of the corresponding hydrogel blocks. (D) Digital photographs showing the on-demand display of certain numbers by local control of the generated Joule heat. Scale bars in digital photos are 1 cm. All fluorescent photos were taken under a 254 nm UV lamp.

emission color was determined by the spectral overlapping of two layers. To produce diverse-colored fluorescent systems, we first specially designed three different luminogens (Figure 3A), which were then covalently incorporated into the chemically cross-linked PNIPAM matrix to prepare three types of polymeric hydrogel layers with red, green and blue emission color, respectively. As shown in Figure 3B–D, when the green luminous paint layer was covered by the red fluorescent Eu–PNIPAM hydrogel layer, an orange fluorescent device was obtained. Likewise, a cyan-light-emitting system was achieved by covering the blue luminous paint layer with a green fluorescent Tb–PNIPAM hydrogel layer, while violet fluorescence was obtained by covering red luminous paint layer with blue fluorescence DAEAN-PNIPAM hydrogel layer, which is marked in Figure 3E,F. Furthermore, diverse overlapping colors could be realized through a selective combination of different-colored fluorescent hydrogel layer with a color palette composed of 13 types luminous paint (Figure 3C–F).

Next, to systematically investigate the electrothermal fluorescence color-changing properties of the device, three

kinds of overlapping colors marked in Figure 3 were chosen according to RGB color additive method. Figure 4A,B illustrated the color-changing process of the system prepared by partially covering a circle-shaped green luminous paint layer with a red fluorescent Eu–PNIPAM hydrogel layer. It was found that upon applying voltage, the hydrogel layer underwent phase transition owing to the Joule heat generated by SGA films. As a result, a prominent color shifting from orange to red was observed in the overlapping area. This color-tunable phenomenon can be explained as follows: at the initial state, the thermosensitive fluorescent hydrogel allows the incident light (UV light) to pass through the fluorescent hydrogel layer to excite the luminous paint layer. The emission color of the system thus comes from the spectral overlapping of these two luminescent layers. After applying an appropriate voltage on the SGA films, the Joule heat-induced temperature rise ( $T > VPTT$ ) leads to the phase transition of PNIPAM-based fluorescent hydrogel layer. Meanwhile, light transmittance of the hydrogel decreases significantly, which largely blocks both the incident light and emission light of the luminous paint. In addition, the fluorescence intensity of the



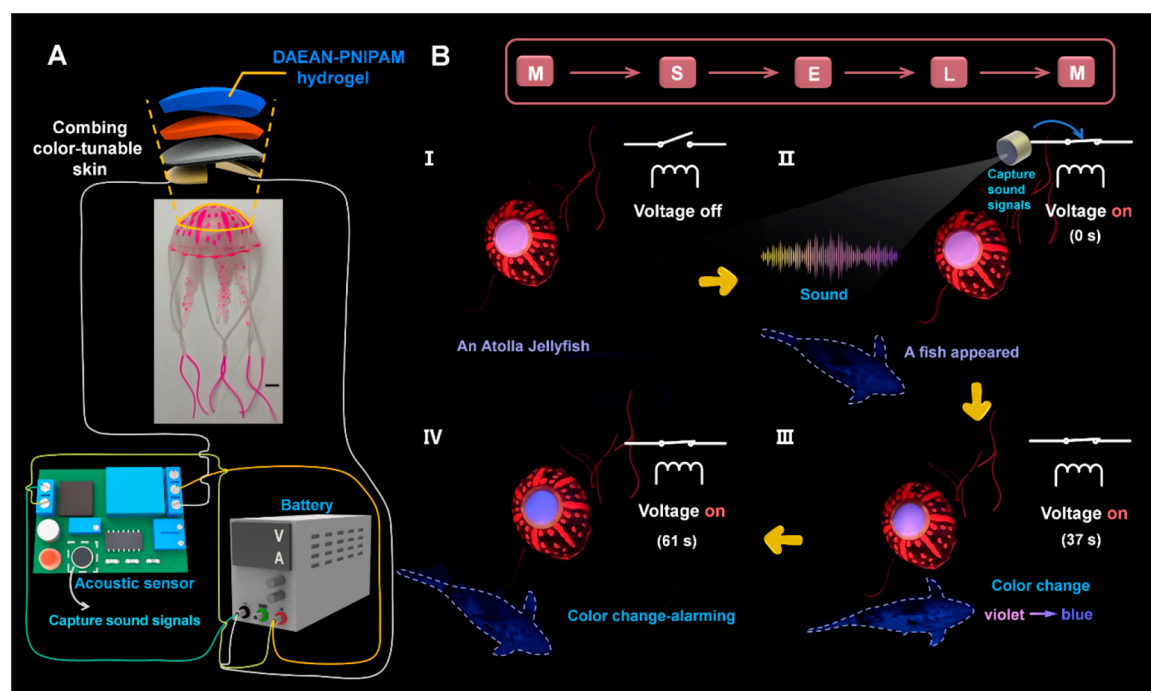
**Figure 6.** Application as the biomimetic skin that helps the commercial robot realize camouflage and display functions. (A) Illustration showing the multilayered structure of the hydrogel-based biomimetic skin, as well as the photos of the commercial robot and decorated robot. The hydrogel layer of biomimetic skin was a  $5 \times 5$  square array consisting of red (Eu-PNIPAM), green (Tb-PNIPAM), and yellow (Eu/Tb-PNIPAM ( $\text{Eu}^{3+}/\text{Tb}^{3+} = 3:1$ )) fluorescent hydrogel blocks. (B) Photos showing the switch between the camouflage and display modes of the decorated robot when triggered by either different excitation light or the stimuli of electric heat. On position 1, the state of the decorated robot could change from camouflage to display through switching excitation wavelength from 365 to 254 nm on the green fluorescent stones. The decorated robot walked from position 1 to position 2, and the background underneath changed from green fluorescent stones to multicolor fluorescent stones. Under a 254 nm UV lamp, the state of the decorated robot could change from camouflage to display through application of suitable voltage.

fluorescent polymeric hydrogels with three primary colors increased obviously in this process (Figure S16). This is mainly attributed to the reduced hydration effect of the red/green-light-emitting lanthanide complexes and enhanced AIE effect of the blue-light-emitting AIEgens in the volume phase transition hydrogels with more compact polymer chains.<sup>48–50</sup> Therefore, the emission color of the device mainly comes from the fluorescent hydrogel layer, resulting in a noticeable orange-to-red emission color change. By a selective combination of different-colored fluorescent hydrogel layer and luminous paint layer, interesting cyan-to-green and violet-to-blue color-changing processes were also achieved under the stimulus of Joule heat. These results are evidenced by the fluorescence spectra and CIE coordinate changes (Figure 4C,D and Figure S17). Similar phenomena were observed under 365 nm (Figure S18). Notably, the Eu-PNIPAM and Tb-PNIPAM hydrogels are nearly nonfluorescent under 365 nm light excitation because the picolinate chromophore of the K6APA ligand has only a small conjugation unit that has no absorbance band above 300 nm.<sup>38</sup> Therefore, the device displayed the color of luminous paint under 365 nm UV light. When a voltage was applied, the recorded luminescence intensity was significantly reduced, which further demonstrated that the

emission light of the luminous paint layer could be blocked by the phase-transitioned hydrogel layer.

In addition, a colorful disk with seven sectors was designed, which displayed stunning rainbow colors under the stimulus of Joule heat (Figure S19). The color-changing processes for three sectors are exhibited in Figure 4E. At 11 V, an obvious color change of samples was observed with the prolongation of power-on time. This process was reversible and could be repeated for several times upon on-off switching of the electric powers (Figure 4G). Furthermore, the electrically controlled fluorescent hydrogel-graphene system featuring richer color variations was also demonstrated. As can be seen from Figure 4F and Movie S1, luminous paint was used to construct a cherry tree while different-colored fluorescent hydrogels were used to prepare fruits and leaves. Upon 254 nm excitation, the fruit of the cherry tree appeared orange and yellow-green, indicative of immature state. When an electric voltage of 16 V was applied, the color of the fruits gradually changed to bright red and yellow, which simulated the process of fruit ripening.

**Patterned Display and Local Control Studies.** Having demonstrated the feasibility of utilizing the electrothermal stimuli to control emission color of hydrogel-graphene systems, we further constructed patterned fluorescent hydrogel



**Figure 7.** Application as the biomimetic skin that helps the artificial Atolla Jellyfish realize the dynamic alarming function. (A) Illustration showing the multilayered structure of the hydrogel-based biomimetic skin, as well as the photos of artificial Atolla Jellyfish that integrated electrically controlled fluorescent color changeable hydrogel–graphene system, soft jellyfish model, acoustic sensor, and battery into one system. (B) Photos showing the dynamic alarming function of artificial Atolla Jellyfish through a bioinspired M→S→E→L→M (mechanical–sonic–electric–luminous–mechanical) cascading process. I: An Atolla Jellyfish with a violet-light-emitting top floated in water. II: The sound signal generated from the mechanical fish was captured by the acoustic sensor, resulting in an automatic connection to the circuit of biomimetic skin to produce electric heating. III: A gradual violet-to-blue emission color change was observed for the artificial jellyfish dome under the stimulus of Joule heat. IV: The violet-to-blue color-changing process produced an alarming signal to make the fish swim away. The surface of mechanical fish was coated with blue luminous paint. Scale bar in digital photos is 1 cm. Photos were taken under a 254 nm UV lamp.

device that allowed for the on-demand display of specific information under electric heating control. Given that non-thermosensitive polyacrylamide (PAM)-based hydrogels are not sensitive to Joule heat, they are suitable candidates for preparing control groups of thermosensitive PNIPAM-based hydrogels. The array consisting of Eu–PNIPAM and Eu–PAM hydrogel blocks was transparent under daylight. However, the specific regions constructed by thermosensitive Eu–PNIPAM hydrogels started to change color while the rest of the parts remained unchanged after applying voltage under 254 nm UV light, which could reveal the hidden pattern. As a result, a 5 × 5 square array of red-light-emitting hydrogels was constructed in the system. Within the hydrogel array, the parts of a “16” pattern were fabricated by thermoresponsive Eu–PNIPAM hydrogel blocks, while the remaining parts were prepared by nonresponsive Eu–PAM hydrogels (Figure 5A,B and Movie S2). As expected, the “16” number pattern was utterly invisible under natural visible light and fuzzy under 254 nm UV light at RT. Interestingly, upon applying the voltage, the luminescence color of the Eu–PNIPAM hydrogel blocks gradually switched from orange to red, whereas the emission color of other parts remained unchanged, thus resulting in a display of the previously typed-in information. Besides, since the SGA films can also be patterned, another mode of patterned display device was demonstrated through the local electric heating control. As depicted in Figure 5C, a patterned SGA film consisting of seven separate zones was coated on one paper through a mask. Each zone was controlled by a single switch

for independently regulating the Joule heat of the corresponding hydrogel blocks (Figure S20). Benefiting from the color tunability property of our device, the numbers from 0 to 8 were successfully displayed in order by selectively turning on/off the respective electrical heating modules (Figure 5D). These results suggest that our electrically controlled fluorescent color changeable hydrogel–graphene system holds great potential for smart display, anticounterfeiting, sensing, and biomimetic skin.

**Application as Biomimetic Skins.** Given the above-mentioned excellent features, including modular design principle, remote controllable diverse color change, on-demand display, and local control behavior, our electrically controlled fluorescent color changeable hydrogel–graphene system was then used as biomimetic skin. As is well-known, it is worthwhile to develop suitable biomimetic skins to help robots blend into the background (camouflage) or stand out against the background (display) in real work environments.<sup>1,51–53</sup> For example, camouflaged robots may hide and protect themselves, which makes them easy to perform reconnaissance missions, while displayed robots may show their identity to aid location from poorly lit or cluttered environments. Notably, our device shows multicolor variations under electric heat, which has been proved to be a residual-free, remotely controlled, and reversible stimulus. In addition, it can be potentially integrated with the existing electro-mechanical systems to develop biomimetic intelligent color-changing robots. To this end, the as-prepared flexible



electrically controlled color-tunable hydrogel–graphene system was decorated onto the surface of one commercial robot to serve as the biomimetic skin (Figure 6A). The green-light-emitting luminous paint layer was used as the substrate in the biomimetic skin. The hydrogel layer was fabricated by lanthanide-coordinated fluorescent hydrogels whose emission color can be modulated by varying the  $\text{Eu}^{3+}/\text{Tb}^{3+}$  molar ratio of the mixed solutions under 254 nm UV light.<sup>38</sup> Specifically, red (Eu–PNIPAM), green (Tb–PNIPAM), and yellow (Eu/Tb–PNIPAM ( $\text{Eu}^{3+}/\text{Tb}^{3+} = 3:1$ )) fluorescent hydrogel blocks were used to construct a  $5 \times 5$  square array. As shown in Figure 6A, since the hydrogel layer was nearly nonfluorescent under 365 nm illumination, the decorated robot primarily displayed the green fluorescence of the bottom luminous paint layer, which made the decorated robot merge into the background composed of green fluorescent stones. Furthermore, the camouflage mode of the biomimetic skin decorated on the robot could be facily switched to the display mode by changing the excitation wavelength from 365 to 254 nm on position 1. It is because the hydrogel blocks displayed colorful patterns under 254 nm UV light, which is obvious against the background of green fluorescent stones (Figure 6B). When the decorated robot walked from position 1 to position 2, the biomimetic skin displaying colorful patterns under a 254 nm UV lamp would enable the robot to achieve camouflage behavior again on the multicolor fluorescent stones. Moreover, when suitable voltage was applied, both the obvious color-change and emission-intensity enhancement would make the decorated robot in high contrast to the background. As a result, the identity of the robot was shown. In this way, we preliminarily demonstrated that the developed electrically powered color-changeable hydrogel–graphene system could potentially serve as efficient biomimetic skins that assist the robots to accomplish tasks in complex natural environments.

Some animals are known to display striking bioluminescent patterns for alarming use in order to protect themselves when in danger. For example, the body of the Atolla jellyfish emits conspicuous light when captured by the predator, hoping to drive away the current predator. To mimic this interesting biological behavior in artificial systems, we tried to conformally cover the top of a commercially available soft jellyfish model with a flexible biomimetic skin consisting of blue DAEAN-PNIPAM hydrogel and red luminous paint (Figure 7A). In order to realize the entire alarming function, an acoustic sensor was introduced in the system that can automatically connect the circuit by sound signal. As shown in Figure 7B and Movie S3, the biomimetic Atolla jellyfish with a violet-light-emitting top could float independently in water. Subsequently, a mechanical fish (the triggering source) was made to gradually approach the biomimetic jellyfish. When the sound signal generated from mechanical vibration of the mechanical fish was captured by the acoustic sensor, it would result in an automatic connection to the circuit of biomimetic skin to produce electric heating. As a consequence, a gradual violet-to-blue emission color change was observed for the artificial jellyfish dome. This dynamic color-changing process produced an alarming signal to make the fish swim away. Similarly, the alarm color of a butterfly was also achieved by integrating our biomimetic skin with a light sensor (Figure S21 and Movie S4). In this way, we successfully demonstrated a bioinspired  $M \rightarrow S \rightarrow E \rightarrow L \rightarrow M$  cascading process, where M corresponds to mechanical movement of mechanical fish, S denotes the sound signal, E represents the electric power, and L denotes

the luminous ability of our biomimetic skin. These self-regulated systems manifest the developed electrically powered color-changeable hydrogel–graphene systems hold great potential to serve as the biomimetic skins that help the soft robots accomplish certain practical functions such as camouflage and alarming. In addition, it is very important to reduce the color-changing time of the device after applying the voltage for its application as biomimetic skins. The color-changing time of the developed device is determined by the phase transition rate of the hydrogel layer, which is controlled by Joule heat. According to the equation of the Joule's Law that  $Q = U^2 R^{-1} t$  ( $Q$  represents the quantity of heat transferred from electric energy;  $U$  is the voltage;  $R$  is the resistance;  $t$  is the time), the key to reducing the color-changing time is to regulate the voltage and resistance of the device. Several strategies are briefly summarized as follows: increasing the applied voltage in appropriate range; selecting the materials with better conductivity to construct the conductive layer of the device; increasing the concentration of conductive materials; increasing the thickness of conductive layer; reducing the size of the conductive layer within a reasonable range; reducing the contact resistance.

## CONCLUSIONS

In summary, we have presented the design and fabrication of an electrically controlled multicolor fluorescent hydrogel system that can be used as biomimetic skins to mimic the physiological functions of living organisms' skins and help the robots realize active camouflage, display, and alarm functions. The key to fabricating the device is the heterogeneous integration of thermoresponsive fluorescent hydrogel, luminous paint, and SGA-based conductive paper into a whole system. When applying suitable voltage to the conductive paper layer, the generated Joule heat induces the phase transition and large transmittance loss as well as fluorescence enhancement of fluorescent hydrogel layer. As a result, the luminescence from the luminous paint layer is heavily blocked, leading to the overlapping color change of the whole device under the electrothermal stimulus. Furthermore, through a rational selection of fluorescent hydrogel layer and luminous paint layer, the diverse color tunability from orange to red, or from cyan to green, or from violet to blue, could be facily realized merely by controlling the applied voltages. Toward practical applications, our electrically controlled fluorescent hydrogel–graphene system was proved to be capable of serving as biomimetic skin to help the commercial robots achieve the desirable camouflage and display functions. Furthermore, an artificial Atolla jellyfish example was demonstrated, which could mimic the color-changing alarming process of this living creature through a bioinspired  $M \rightarrow S \rightarrow E \rightarrow L \rightarrow M$  cascading process. Despite the fact that the presented demonstrations are still simple and preliminary in terms of functions, we believe that our study could provide another useful design strategy for smart bionic soft robots and human-machine interaction.

The key point of the present system is the utilization of electric stimulation, which is “residual-free” and allows for remote and local control to induce fluorescence color change, in contrast to the previously reported multicolor fluorescent hydrogels that are primarily triggered by traditional stimuli such as pH, temperature and metal ions.<sup>54</sup> This kind of electrically controlled system avoids the accumulation of chemicals (e.g., inorganic salts) that may cause the degradation

of color-change performance. Additionally, compared with the traditional temperature stimulation directly controlled by thermos/temperature such as changing the ambient temperature of the device through a thermostatic heater, our approach promises the remote and local regulation through finely adjusting the voltage and power-on time to precisely manage the generated Joule heat. Furthermore, a built-in power supply and Bluetooth module can be potentially introduced into the hydrogel–graphene system in a next step in order to achieve full wireless remote control. Furthermore, due to the versatility of the electric signal, the circuit of our fluorescence hydrogel device can be easily connected with various commercial sensors and electromechanical systems. These benefits are significant for construction of further smart biomimetic robots with advanced camouflage, display, and alarming abilities or other capabilities that were not possible before, which are expected to enable the commercial robots to better perform tasks such as exploration, monitoring, or even rescue missions in a natural environment.

Finally, the proposed construction strategy of our electrically controlled fluorescent color-changeable hydrogel systems proves to be general. The materials of the luminescent layer are not limited to the utilized fluorescent hydrogels. This design principle is generally applicable to other soft color-changing materials such as structural color materials with temperature response and elastomers loaded with thermochromic pigment. Additionally, besides graphene, other types of conductive materials could also be employed to generate Joule heat, including carbon nanotubes, MXene and even heating wire.<sup>42,55,56</sup> Therefore, it is believed that the proposed strategy is generally attractive to researchers and will inspire future research to build more advanced systems with a broad potential application in the area of materials science.

## EXPERIMENTAL METHODS

**Material.** Graphene (GR, 5 wt %) was purchased from Ningbo Morsh Technology Co., Ltd. Poly(vinyl alcohol) (PVA-124, 98–99% hydrolyzed, average  $M_w$  105600–110000), acrylamide (AM, 98.0%), and pan papers were obtained from Sinopharm Chemical Reagent Co. Ltd. *N*-Isopropylacrylamide (NIPAM, 98.0%) and 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (I2959, >98.0%) were purchased from TCI (Shanghai) Development Co., Ltd. *N,N'*-Methylenebis(acrylamide) (MBAA, ≥98.0%), ammonium peroxodisulfate (APS, ≥ 98.0%), *N,N,N',N'*-tetramethylethylenediamine (TEMED, 99.0%) and  $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (99.9%) were provided by Aladdin Chemistry Co. Ltd.  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.9%) and potassium hydroxide (KOH, 95.0%) were supplied by Energy Chemical. The luminous paint was purchased from Jinan Huancai Trading Co. Ltd. The ligand monomer potassium 6-acrylamidopicolinic acid (K6APA) and the AIE-active monomer 4-(2-dimethylaminoethoxy)-*N*-allyl-1,8-naphthalimide (DAEAN) were synthesized according to the procedures described in our previous study.<sup>38,57</sup>

**Preparation of Conductive Papers.** The conductive papers were fabricated according to our previous study.<sup>45,46</sup> First, the graphene flakes were added to anhydrous ethanol and mixed under ultrasonication for several hours to form a 1.5 mg mL<sup>-1</sup> dispersion. Then, a certain volume of the as-prepared dispersion was sprayed on to the water surface by a spray pot, which resulted in a uniform and ultrathin graphene-based film located at the air/water interface. Next, a piece of porous absorbent sponge was inserted into water along the wall of the container in order to break the equilibrium of the surface tension. The area of the preassembled graphene film then obviously decreased to form a condensed SGA layer. The compression procedure was repeated until the SGA film could not be condensed further. The wet pan paper cut into appropriate shape was conformally fixed on a glass substrate. Using the lift-up transferring

method, the condensed SGA film floating on air/water interface was transferred to the surface of paper, followed by a drying process (60 °C) to obtain one-layered conductive paper. The transferring and drying procedures were repeated many times, so that a series of conductive papers containing different-layered SGA films were fabricated (one, two, three, four, and five layers). Finally, the as-prepared conductive paper was sandwiched by two PTFE sheets and then placed into a baking oven. After heat pressing at 60 °C for 15 min, a flat conductive paper was obtained.

**Fabrication of the Fluorescent Polymeric Hydrogels.** The different-colored fluorescent polymeric hydrogels were prepared by radical polymerization. To prepare Eu–PNIPAM and Tb–PNIPAM hydrogels, NIPAM (monomer, 1166 mg), 6APA (fluorescent monomer, 20 mg), MBAA (cross-linker, 5.83 mg), I2959 (photo-initiator, 11.66 mg), and KOH (5.84 mg) were first dissolved in deionized water (6.61 mL). Next, the mixture was added into the self-made molds consisting of two quartz glass plates and a 0.8 mm thick silicon plate. Then ultraviolet irradiation (250 W, 365 nm) was applied for 10 min to produce cross-linked polymer networks. After that, the obtained PNIPAM–K6APA hydrogels were immersed in aqueous solutions of  $\text{Eu}^{3+}$  or  $\text{Tb}^{3+}$  (0.1 M) for 15 min at RT to produce the red fluorescent Eu–PNIPAM and green fluorescent Tb–PNIPAM hydrogels. The yellow-light-emitting Eu/Tb–PNIPAM hydrogel was prepared by immersing the PNIPAM–K6APA hydrogels into mixed solutions of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  (molar ratio of 3:1). To produce the blue fluorescent DAEAN–PNIPAM hydrogel, NIPAM (monomer, 1166 mg), MBAA (cross-linker, 5.83 mg), APS (thermal initiator, 11.66 mg), and 6.61 mL of aqueous DAEAN solution (luminescent monomer, 0.1 mg mL<sup>-1</sup>) were mixed. After the addition of TEMED (initiator accelerator, 10 μL) in the mixture, the radical polymerization was carried out at 4 °C in the self-made molds mentioned above for 24 h. Afterward, the hydrogels were immersed in the deionized water to remove impurities. Similar procedures were used for the fabrication of corresponding PAM-based fluorescent hydrogels.

**Fabrication of the Embedded Patterned Hydrogels.** The embedded patterned hydrogels were prepared by two-step polymerization: First, the precursor solution of Eu–PNIPAM hydrogel was added into the self-made molds including a 0.8 mm thick silicon plate with hollow lantern pattern sandwiched by two quartz glass slides. After UV polymerization, the Eu–PNIPAM hydrogel with lantern pattern was obtained. Then the original silicon plate was removed and a larger silicon plate with hollow rectangular shape was used. Next, the precursor solution of Eu–PAM was transferred to the molds, followed by the second photopolymerization. Finally, the embedded patterned hydrogel was peeled off from the molds and immersed in aqueous solutions of  $\text{Eu}^{3+}$  ions to define the fluorescent colors.

**Fabrication of the Electrically Controlled Fluorescent Color-Changeable Hydrogel–Graphene System.** First, the luminous paint layer was assembled onto the conductive paper substrate. Typically, the as-prepared conductive paper was placed on a PTFE sheet with the SGA side facing down. Then the luminous paint was uniformly scraped on the pure paper side of conductive paper by plastic blade, whose shape and size were controlled by the silicon plate (0.8 mm thick). Subsequently, the deposited viscous luminous paint was cured at 35 °C for 6 h. Then Ni-coated textile electrodes were connected to the conductive paper. Second, the PVA glue (10 wt %) was coated on the surface of the luminous paint layer and the fluorescent hydrogel layer. The two surfaces were connected to each other. After several freezing–thawing cycles, the fluorescent hydrogel layer was firmly adhered to the surface of luminous paint layer. In this way, the soft electrically controlled fluorescent color changeable hydrogel–graphene system was fabricated.

**Characterization.** The color-changing process of the devices was recorded by a smart phone camera under UV lamps (ZF-5, 8W, 254 or 365 nm). Steady-state fluorescence spectra were measured by a Hitachi F-4600 fluorescence spectrofluorometer with a xenon lamp (150 W). The morphology of the sample was characterized by a field-emission scanning electron microscope (SEM, Hitachi S-4800). The Raman scattering measurements were taken by a Raman system (in

Via-reflex, Renishaw) with 532 nm excitation wavelength. The VPTT of the fluorescent hydrogels were characterized by differential scanning calorimeter (DSC, Netzsch DSC-214) under nitrogen atmosphere with a heating rate of 1 °C/min. The interfacial peeling force was measured by a Zwick Z1.0 universal testing machine with a peeling rate of 50 mm min<sup>-1</sup>. A UV-Vis spectrophotometer (TU-1810, Purkinje General Instrument Co., Ltd.) was used to test the optical transmittance of the fluorescent hydrogels. Static water contact angles were probed using a contact angle meter (OCA25, Data-physics) using a 3 μL droplet of water as an indicator. An IR thermal camera (Optris PI 400) was employed to capture the real-time recording of the surface temperature and IR images under different input voltages. The data was analyzed by PI connect software. Finite element analysis was carried out to simulate the temperature distribution of the hydrogel-graphene system under the voltage of 10 V by COMSOL Multiphysics 5.5.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.1c02720>.

Process of fruit ripening in artificial cherry trees (MP4)

Patterned display capability of hydrogel-graphene system (MP4)

Dynamic alarming function of artificial Atolla jellyfish (MP4)

Dynamic alarming function of the artificial butterfly (MP4)

Photos of SGA film on the surface of the water; sketch of conductive paper fabrication; water contact angles, SEM images, Raman characterization, IR images and film thickness of the conductive papers; DSC curve of the hydrogel; schematic illustration and photos of the hydrogel-graphene system fabrication; interfacial toughness measurement and SEM images of hydrogel-graphene device; transmittance and fluorescence characterization of hydrogels at RT and 60 °C; finite element simulation of cross-section temperature distribution of hydrogel-graphene system; CIE (1931) coordinate diagrams before and after adding voltage; extended fluorescence analysis ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ); extended demonstration of electrically controlled fluorescent color change (PDF)

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W.L. and T.C. proposed the idea and supervised the project. S.W., W.L., and T.C. designed the experiment. S.W., H.Q., H.S., H.L., H.Y., D.Z., J.Z., P.T., and Y.W. performed the fabrication, characterizations, and analysis. S.W., W.L., and T.C. wrote the manuscript. All authors discussed the results

and commented on the manuscript. The manuscript was written through contributions of all authors.

## Notes

The authors declare no competing financial interest.

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