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Ionotronic Luminescent Fibers, Fabrics, and Other Configurations

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A family of recently developed devices, hydrogel ionotronics, uses hydrogels as ionic conductors, and uses hydrophobic elastomers as dielectrics. This development has posed a challenge: integrate hydrogels and hydrophobic elastomers—in various manufacturing processes—with strong, stretchable, and transparent adhesion. Here, a multistep dip-coating process is described to enable hydrogel ionotronics of diverse configurations. In doing so, a hydrophobic surface is primed to let a hydrophilic precursor wet it, and then polymers of different layers are interlinked with covalent bonds. As a representative example, an ionotronic luminescent fiber that can be lengthened to ≈2.5 times its original length and keeps functioning after 10 000 cycles of stretching is fabricated. A luminescent fabric that displays movable pixels and other configurations is also demonstrated. The proposed method of fabrication expands the design space for hydrogel ionotronics.

Despite their recent origin, hydrogel ionotronics are advancing rapidly.[1] Demonstrated ionotronic devices include transparent loudspeakers,[2] ionic skins,[3,4] artificial axons,[5] ionotronic luminescence,[6] stretchable liquid crystal displays,[7] transparent touchpads,[8] ionic fish,[9] self-healing hydraulic actuators,[10] stretchable diodes,[11] and ionic spiderwebs.[12] The functions of these devices often require that hydrogels and elastomers be stretchable and transparent. Hydrogel ionotronics reported to date are commonly limited to planar architectures. Hurdles stand in the development of manufacturing processes that integrate hydrogels and hydrophobic elastomers with strong adhesion, without scarifying stretchability and transparency.

Here, we begin with an ionotronic luminescent fiber of a coaxial structure, consisting of a hydrogel core, a luminescent layer, a hydrogel layer, and an elastomer layer (**Figure** 1A). When a power source applies an alternating voltage between the hydrogel core and hydrogel layer, ions of opposite polarities periodically accumulate at the hydrogel/elastomer interfaces, produce an alternative electric field in the luminescent layer, and generate electron–hole pairs in the phosphor particles. The phosphor particles are dispersed in the dielectric elastomer, so that the electrons and holes do not migrate out of the phosphor particles, but recombine and emit light. The elastomer and hydrogel are transparent and let light out. The fiber is intact and keeps luminescing after 10 000 cycles of stretching to 1.5 times its original length. We also demonstrate a fabric that luminesces with movable pixels.

Because a hydrogel consists of a large amount of water, the hydrogel and a hydrophobic elastomer typically adhere weakly.[13] Strong adhesion requires that the two polymer networks connect through chemical bonds or topological entanglement.[14–17] Existing approaches to achieving strong, stretchable, and transparent adhesion have overlooked the requirement for wetting. In one approach, a hydrogel is pre-formed and then placed on a hydrophobic elastomer to adhere.[17,18] In another approach, the liquid precursor of a hydrogel is cast on a hydrophobic elastomer and cured in situ.[14] These approaches are difficult to apply in fabricating ionotronic luminescent fibers.

We fabricate the fiber by multistep dip coating (**Figure** 1B). We use polyacrylamide (PAAm) hydrogel containing lithium chloride as the ionic conductor, poly(dimethylsiloxane) (PDMS) dispersed with copper-doped zinc sulfide (ZnS:Cu) particles as the luminescent layer, PDMS as the dielectric layer, and silanes as the coupling agents. Lithium chloride is hygroscopic and can retain water under low humidity,[19] and a layer of PDMS further retards the loss of water.[20] ZnS has long been used as phosphor for displays and lighting.[21] Silanes have recently been used to adhere hydrogels and various materials[4,16,22] (Figure S1, Supporting Information). We mix ZnS:Cu particles with PDMS and silanes to make the precursor for the luminescent layer (Figure S2, Supporting Information) and optimize the time of dip coating (Figure S3, Supporting Information). The small ZnS:Cu particles are embedded within the PDMS matrix and affect the adhesion between PAAm hydrogel and PDMS negligibly (Figure S4, Supporting Information). The cross-sectional view of a fiber shows a coaxial structure with a luminescent layer of thickness ≈150 µm (Figure 1C). Scanning electron microscopy (SEM) imaging shows the dispersed

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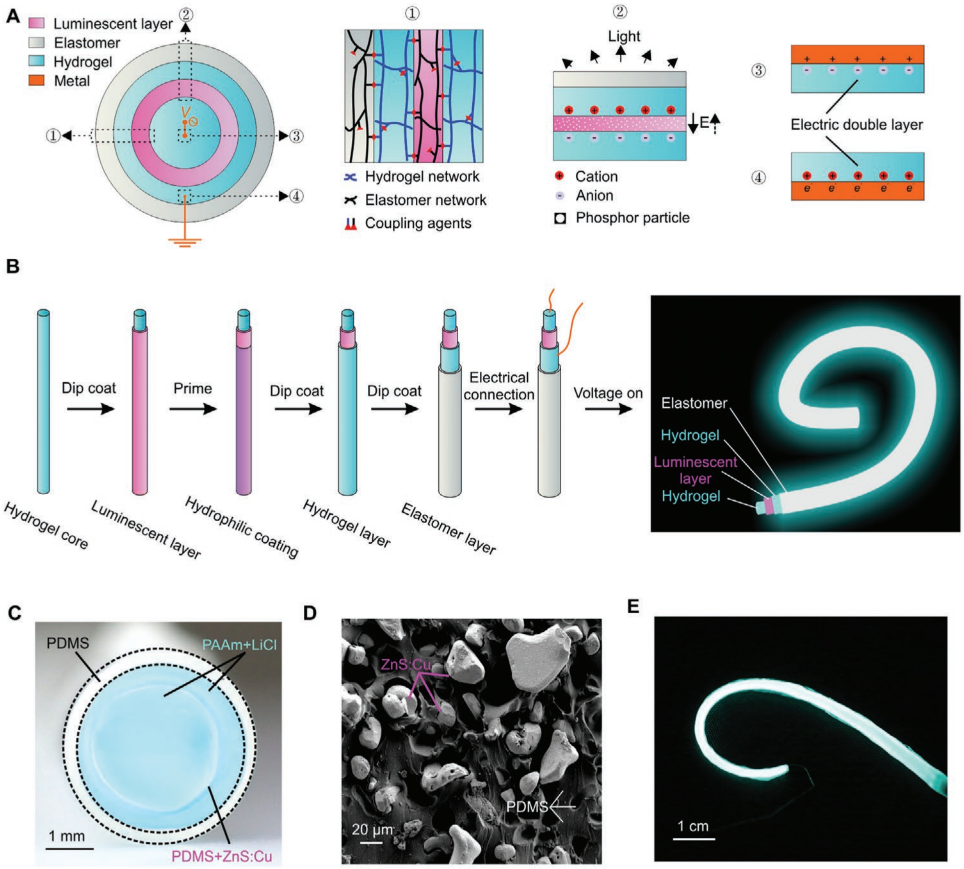

Figure 1. Ionotronic luminescent fiber. A) The fiber consists of a hydrogel core, a luminescent layer, a hydrogel layer, and an elastomer layer. Coupling agents crosslink polymers in hydrogels and interlink polymers between different layers. The two hydrogels connect to metallic wires. When the two metallic wires are subjected to an alternating voltage, the luminescent layer lights up. Electrons in a metal and ions in a hydrogel meet at the interface and form an electric double layer, which behaves like a capacitor. B) Multistep dip coating. C) Photograph of cross section of an ionotronic luminescent fiber with hydrogels colored by blue dye. D) SEM image of the luminescent layer. E) Photograph of a bent fiber under an alternating electric field of amplitude 3 V µm^{-1} and frequency 1 kHz.

ZnS:Cu particles of size ranging from several microns to tens of microns (Figure 1D). When an electric field of 3 V µm^{-1} and frequency 1 kHz is applied, the fiber lights up (Figure 1E). The fiber luminesces without electrolyzing the hydrogels (Figure S5, Supporting Information).

We compare two steps: dip-coating a layer of elastomer on a hydrogel and dip-coating a layer of hydrogel on an elastomer. The surface energy of hydrogel precursor is similar to that of water, $\gamma_1 \approx 72$ mN m^{-1}, the surface energy of PDMS is $\gamma_2 \approx 20$ mN m^{-1}, and the interface energy between water and PDMS is $\gamma_{12} \approx 40$ mN m^{-1}.[23] Because $\gamma_2 < \gamma_1 + \gamma_{12}$, the hydrogel precursor beads up on the elastomer and cannot dip-coat a uniform layer (**Figure** 2A). By contrast, because $\gamma_1 > \gamma_2 + \gamma_{12}$, the precursor of elastomer wets the hydrogel (Figure 2B; Movie S1, Supporting Information), resembling oil spreading on water.[24]

The absence of wetting does not impede casting in a mold (Figure S6, Supporting Information), but casting in a mode becomes inapplicable to fabricate devices of geometries with sharp tips and inner surfaces. Such geometries require mold-free fabrication, for which wetting is prerequisite. To wet the precursor of hydrogel on elastomer, we prime the surface of the elastomer.[25] We formulate a primer containing silane-modified PAAm polymers and soak the silane-modified PDMS in the primer. The silanes on the surface of PDMS meet water, hydrolyze, and condensate with the silanes on the PAAm polymers.[16] The resulting PDMS has a layer of covalently anchored PAAm chains and becomes hydrophilic (Figure 2C; Movie S2, Supporting Information). The hydrophilic coating is thin and fragile,[25] and another hydrogel precursor of higher viscosity is formulated to dip-coat a thicker and more robust hydrogel layer (Figure S7 and Movie S3, Supporting Information). After dip coating an external PDMS layer, the sample is stored at 65 °C for 12 h, during which silanes condensate to crosslink PAAm chains into a network and interlink PAAm network to PDMS network. The resulting adhesion is strong and does not debond even when the fiber is stretched to rupture.

We measure the contact angle as a function of time (Figure 2D). The equilibrium contact angle of water on primed PDMS (≈26.6°) is much smaller than that on bare PDMS (≈107.1°). When a PDMS droplet drips on a PAAm hydrogel, a large contact angle (96.5°) forms initially then decreases rapidly, approximately obeying a power law.[23] Wetting nearly completes after 24 h (Figure S8, Supporting Information). The PDMS surface can also be made hydrophilic by plasma, UV/ozone, or

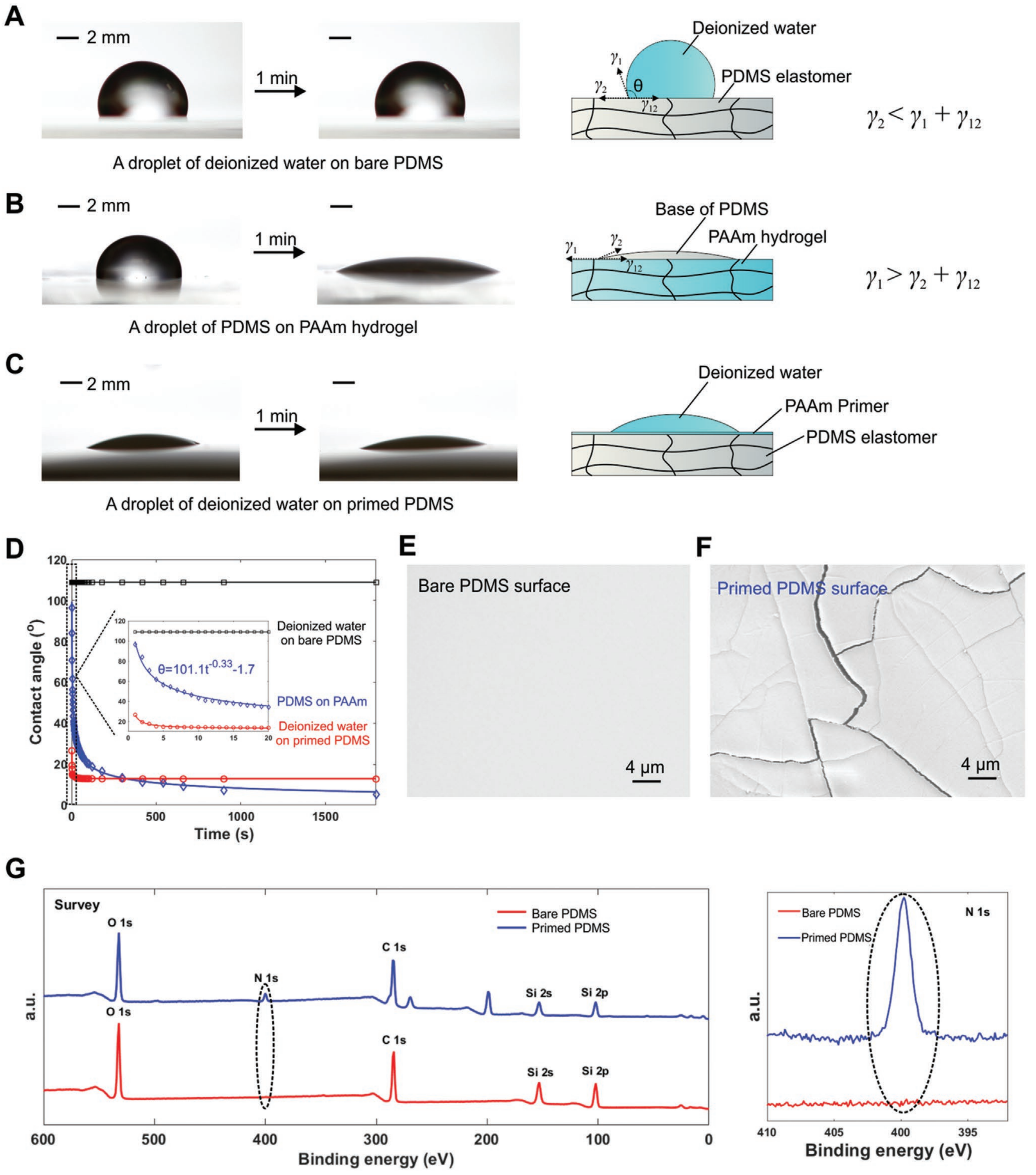

Figure 2. Surface characterization. A) Deionized water on bare PDMS. B) PDMS precursor on PAAm hydrogel. C) Deionized water on primed PDMS. D) Contact angle as a function of time. E,F) SEM images of the surface of bare PDMS (E) and primed PDMS (F). G) XPS survey of the surfaces of bare PDMS and primed PDMS.

corona discharge,[26] but the degradation of treated surface and the handling of special equipment may limit applications.

We carry out two types of surface analysis to confirm that PAAm chains stay on PDMS. The SEM image shows that a bare PDMS is smooth and clear (Figure 2E), but a primed PDMS surface is rough and even contains cracks (Figure 2F). The cracks presumably form in dried PAAm layer on the samples prepared for SEM imaging. The PDMS chains do not

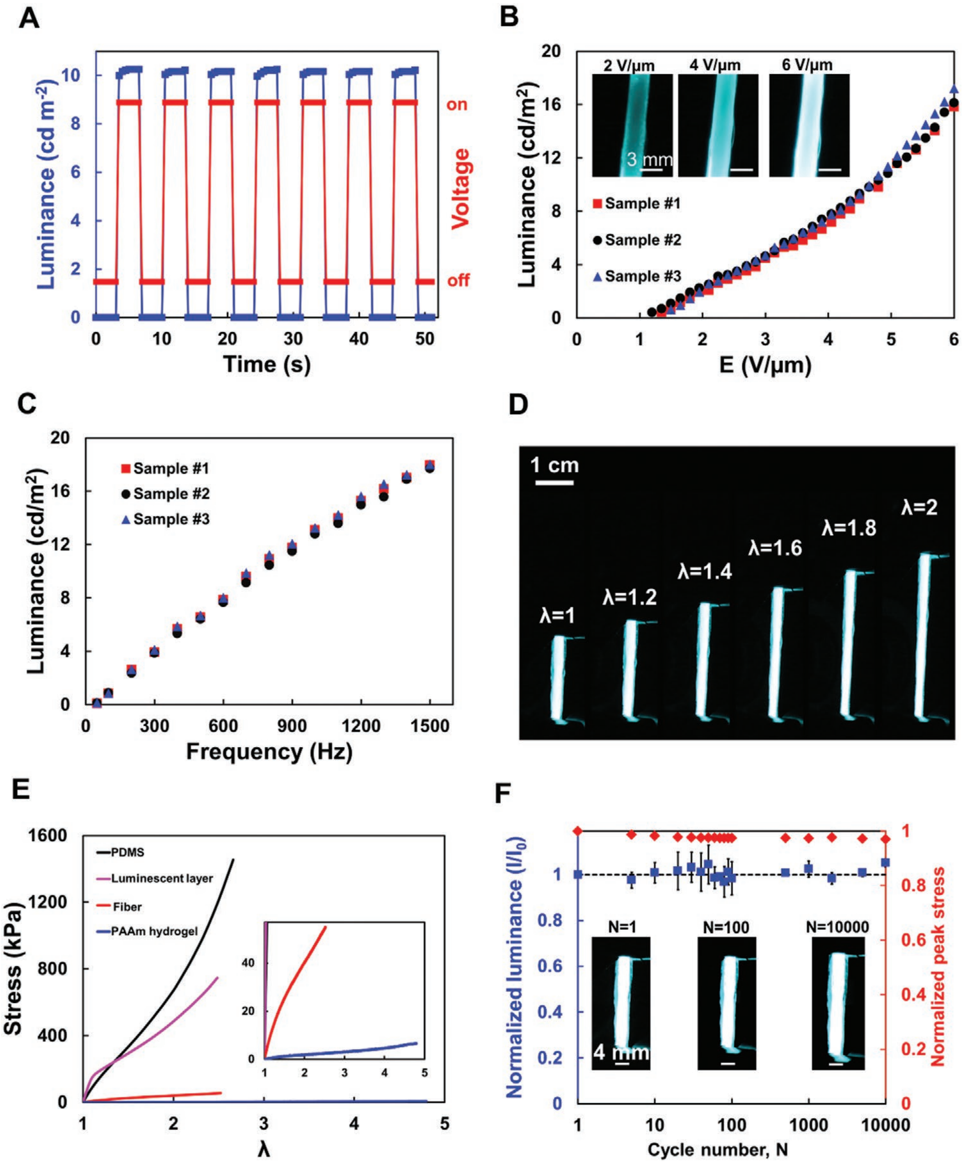

Figure 3. Performance of ionotronic luminescent fiber. A) The luminance of a fiber subject to an alternating electric field of 5 V µm^{-1} and 1 kHz. B) Luminance as a function of the amplitude of electric field. Insets: images of a fiber subject to alternating electric field of various amplitudes. C) Luminance as a function of frequency at the amplitude of electric field 6 V µm^{-1}. D) Photographs of a fiber at various stretches with an initial amplitude of electric field 5 V µm^{-1}. E) Stress–stretch curves of PDMS, luminescent layer, PAAm hydrogel, and ionotronic luminescent fiber. The inset zooms in on the curves at small stress range. F) Endurance test of a fiber cyclically stretched to 1.5 times its original length (*n* = 3). Inset: images of a fiber at different numbers of cycles.

contain nitrogen element but PAAm chains do. X-ray photoelectron spectroscopy (XPS) analysis indicates that bare PDMS surface does not show absorption for N_{1s} while primed PDMS surface does (Figure 2G).

We connect the two metallic wires to a power source. The voltage of the power source divided by the thickness of the luminescent layer defines a nominal electric field. Subject to a pulsed electric field of amplitude 5 V µm^{-1} and frequency 1 kHz, the fiber luminesces on and off (**Figure 3**A). At frequency 1 kHz, the fiber luminesces above a threshold electric field ≈1 V µm^{-1}, above which the luminance increases with the amplitude of electric field (Figure 3B). The measured luminance as a function of the amplitude of applied voltage fits well with the relation, $I = \alpha \exp(-\beta V^{-1/2})$[21] where I is the intensity of luminance, V is the voltage, and α and β are the fitting parameters (Figure S9, Supporting Information). At a fixed amplitude of the electric field 6 V µm^{-1}, the luminance increases with the frequency (Figure 3C), which fits well with a similar relation (Figure S10, Supporting Information). The fiber luminesces in all directions normal to the axis of the fiber, so that the brightness is independent of view angle (Figure S11, Supporting Information).

Ionotronic luminescent fiber is stretchable (Movie S4, Supporting Information) and maintains its luminance under deformation (Figure 3D). This behavior comes from the combination of optical, electrical, and mechanical properties

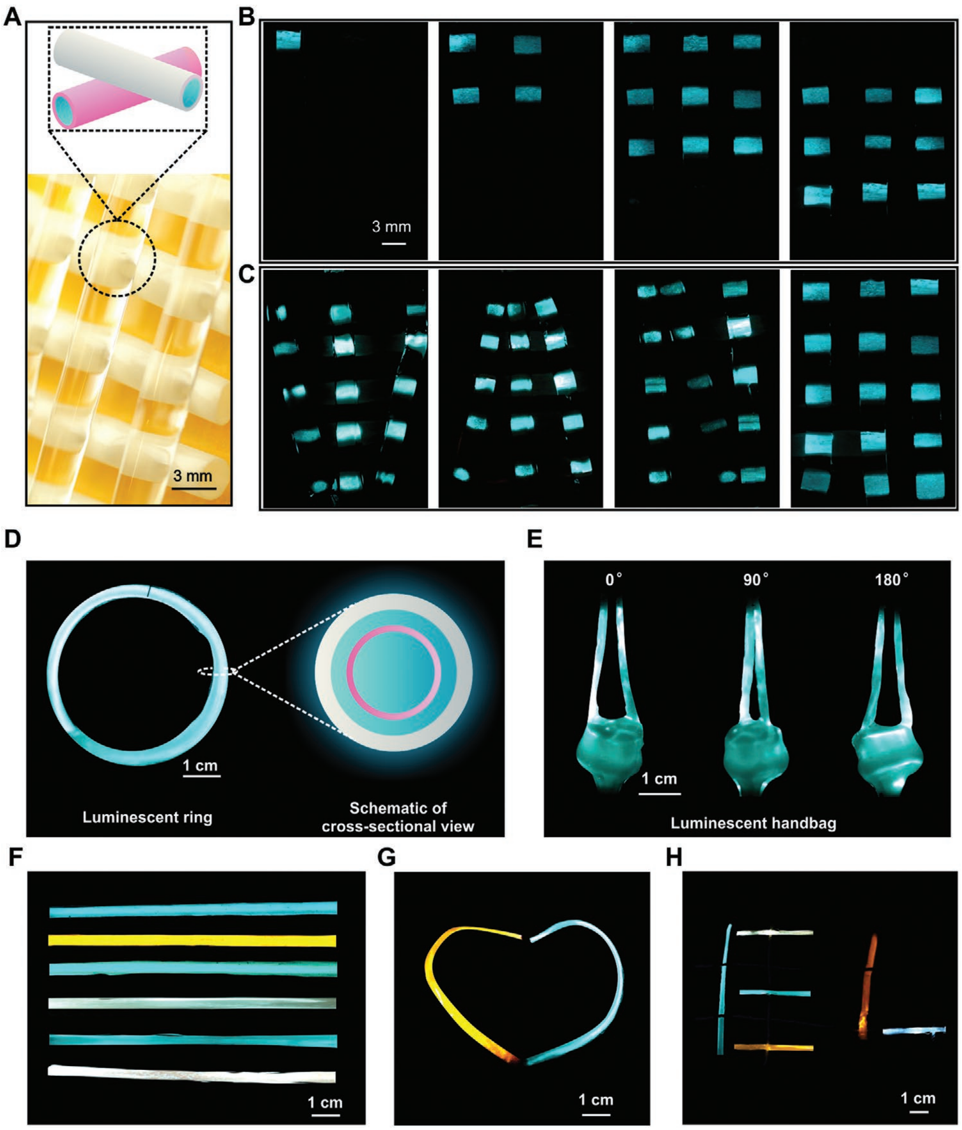

Figure 4. Hydrogel ionotronic luminescent devices of various kinds. A) A fabric display consists of two types of fibers assembled in rows and columns. B) Each junction of the display forms a pixel. When a voltage is applied, only the junctions light up. C) The movable pixels can display more information by rearranging the fibers. D) A luminescent ring containing three closed cylindrical layers: luminescent layer, PAAm layer, and PDMS layer. E) A cage-structured luminescent handbag viewed from different angles. F) Multi-color fibers. G) A luminescent "heart" made of an orange fiber and a blue fiber. H) A luminescent "EL" pattern made of multi-color fibers.

(Figure 3E; Figure S12 and S13, Supporting Information). The phosphor particles are embedded in the elastomer, isolated from the water molecules in hydrogel and ambient, which are known to degrade luminance.[27] Dissolved lithium chloride and the layer of elastomer contribute to the long-term maintenance of electrical properties of the hydrogel.[19,20] The fiber maintains its peak stress and luminance after 10 000 cycles of stretching to 1.5 times its initial length (Figure 3F; Figure S14, Supporting Information).

The softness and stretchability of the hydrogel, the strong adhesion between the hydrogel and elastomer, as well as the broad applicability of dip coating, together enable hydrogel ionotronic luminescent devices of complex geometries. We make an ionotronic luminescent fabric by assembling two types of fibers into rows and columns (**Figure** 4A). One is luminescent layer coated hydrogel fiber and the other is pure PDMS coated hydrogel fiber. Each junction of two fibers forms a pixel. Only the pixels will luminesce when a voltage is applied (Figure 4B). In a conventional display, the functional parts are built in and the positions of two rigid electrodes are fixed. By contrast, the pixels in the ionotronic luminescent fabric are soft and movable (Figure 4C). A resolution of 320 × 240 can be achieved if the device is driven by passive matrix addressing (Figure S15, Supporting Information). Both *RC* delay and response speed of ZnS:Cu particles will not limit the device performance. The *RC* delay is independent of the diameter of hydrogel fiber, allowing miniaturization of the device. Ionotronic luminescent fabrics may enable wearable displays and smart clothes.

The process can readily produce hydrogel ionotronics of many configurations. We fabricate a luminescent ring containing closed cylindrical shells of luminescent layer, PAAm hydrogel and PDMS elastomer (Figure 4D), and a luminescent handbag having a cage structure (Figure 4E). Both device configurations, with strong adhesion between the hydrogel and elastomer, are challenging for other fabrication methods. The prime, of course, is also compatible with the devices of simple configurations such as planar architecture (Figure S16, Supporting Information). Finally, we make multicolor fibers by using different ZnS particles for the luminescent layer (Figure 4F–H). We select three types of ZnS particles and mix them by certain weight ratios to achieve six colors (Figure S17 and S18, Supporting Information).

We have modified the bulk of hydrogel core with silanes, but this is unnecessary. Instead, one can preform a hydrogel of any shape using any fabrication process, and then prime the surface of the preformed hydrogel.[25] The preformed hydrogel need not have any functional group for adhesion. The prime renders a network on the surface, in topological entanglement with the preformed hydrogel network, imparting functional groups for adhesion. In addition, the prime allows one to start the fabrication process with an elastomer core. Ionotronic luminescent devices have been demonstrated by integrating hydrogel and elastomer,[6,28] but with restricted geometries. Fiber-shaped devices can be made by co-extruding hydrogel precursor and elastomer precursor,[28] but the uncrosslinked hydrogel might be squeezed out without crosslinks and interlinks. The incorporation of coupling agents and prime together open ways to create ionotronics of complex geometries. The method can be adapted to integrate not only hydrogels and elastomers, but also other materials, such as ionogels[29] and ionoelastomers.[30]

In summary, we have described a multistep dip-coating method to fabricate hydrogel ionotronics of complex geometries. The method achieves strong, stretchable, and transparent adhesion between hydrogels and hydrophobic elastomers. Ionotronic luminescent fibers, fabrics, and other configurations are demonstrated. They can potentially enable broad applications. The proposed method paves avenues for broad applications of hydrogel ionotronics.

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.

Author Contributions

C.Y. and Z.S. conceived the project. C.Y., S.C., X.Y., G.N., and Q.L. conducted experiments. C.Y. collected data, analyzed the results, and drafted the manuscript. C.Y. and Z.S. revised the manuscript and all authors commented on the manuscript.

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