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ADVANCED MATERIALS

Electroluminescence of Giant Stretchability

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Displays and solid-state lighting rely on electroluminescence of various kinds. For example, subject to a voltage, a phosphor generates in its interior mobile electrons and holes, which then combine and produce light. As another example, when an electric current is injected into a light-emitting diode, electrons and holes combine at the p–n junction and produce light. A device of phosphors requires a transparent conductor (e.g., indium tin oxide) to apply voltage and let light out. A device of light-emitting diodes uses metallic conductors to inject electric current. These electroluminescent devices are stiff and brittle, struggling to satisfy the fast growing demands for mobile and wearable applications.[1–3] Intense research has been taking place to develop stretchable (and sometimes transparent) conductors, such as patterned metallic lines, carbon nanotubes, and silver nanowires.[4–11]

The conductors mentioned so far carry electricity using electrons. The electronic conductors are much less stretchable and transparent than ionic conductors such as hydrogels and ionogels.[12,13] These ionic conductors maintain their conductivity and transparency under large deformation. A gel aggregates a cross-linked network of polymer and a liquid (e.g., saline water for a hydrogel and ionic liquid for an ionogel). The network makes the gel an elastic solid, and the liquid makes the gel an ionic conductor. For example, polyacrylamide hydrogels can dissolve over 10 M of lithium chloride and achieve conductivity ≈ 10 S m^{-1}.[14] Ionogels made of polyacrylic acid and ionic liquid [C_2mim][$EtSO_4$] give conductivity ≈ 1 S m^{-1}.[13] Gels can be as soft as tissues, and as stretchable as elastomers.[15–17] We have shown recently that humectants enable hydrogels to retain water in low-humidity environment.[14] Furthermore, polymer networks swollen with ionic liquids (i.e., ionogels) are nonvolatile even in vacuum.[13]

Recent works have shown that gels readily function as stretchable and transparent conductors to enable artificial muscles, skins, and axons.[12,18,19] Such devices integrate ionic and electronic components, and are called ionotronics.[18] These demonstrations pose a question. Can gels enable other unusual devices? Here we use ionic conductors to realize electroluminescence of giant stretchability by using phosphors.

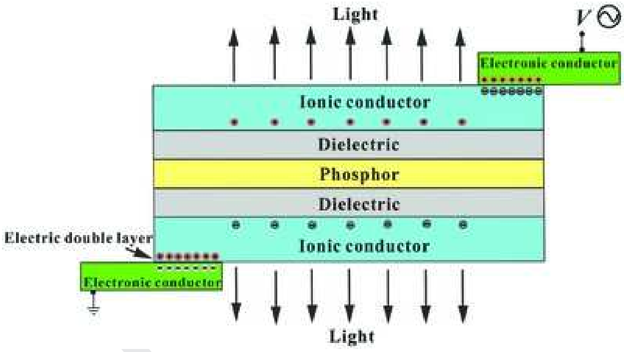

Figure 1. Principle of ionotronic luminescence. Phosphor particles are sandwiched between two layers of dielectric, and then between two layers of ionic conductor. Both the dielectric and the ionic conductor are stretchable and transparent. Outside the active area, the ionic conductors connect through electronic conductors to a cyclic power source.

We sandwich phosphor particles between two layers of dielectric and two layers of ionic conductor (**Figure 1**). Both the dielectric and the ionic conductor are transparent and stretchable, allowing the light produced by the phosphor particles to come out, and the overall structure to deform. The phosphor particles do not limit the stretchability of the ionic conductor and the dielectric. The ionic conductors connect to a power source through electronic conductors. The electronic conductors are placed outside the active area of the device, and need not to be transparent or stretchable; ordinary metallic conductors serve the function.

Our design of the structure resolves a fundamental issue: the electroluminescence of the phosphors requires an alternating electric field of high amplitude, but high voltage may electrolyze the gel. For a suitably chosen electronic conductor and ionic conductor, their interface forms a stable electric double layer (EDL)—that is, electrons and ions do not continuously cross the interface to engender electrolysis. So long as the applied voltage across the interface is within a range, e.g., between −1 and +1 V, the EDL will remain stable, and behave like a capacitor.[20] When the power source applies a voltage between the two electronic conductors, the two ionic conductors spread ions of opposite polarities on the interfaces between the ionic conductors and the dielectrics. The EDL separates charges of opposite polarities at the nanometer scale, whereas the dielectric layer separates changes of opposite po-

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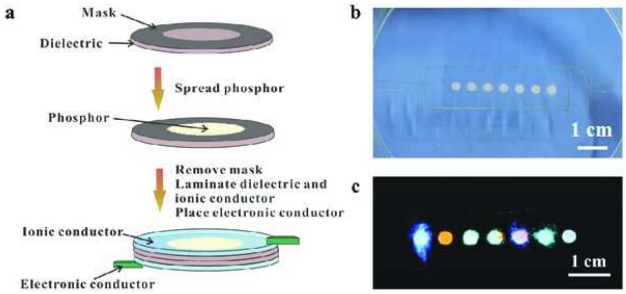

Figure 2. a) Steps of fabrication of the stretchable electroluminescent device. b) Image of the fabricated device in daylight. c) Image of the luminescent device in darkroom. Subject to a cyclic voltage, amplitude 3 kV and frequency 1000 Hz, phosphor particles doped with different metallic elements luminesce in several colors.

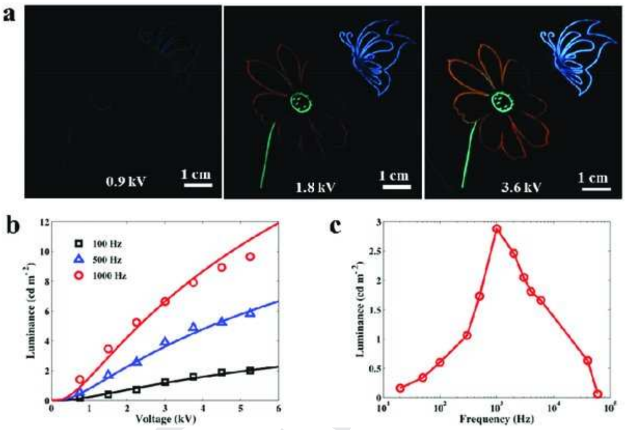

Figure 3. Luminescent performance of ionotronic luminescence. a) A display luminesces at a cyclic voltage of frequency 1000 Hz. The brightness increases as the applied voltage increases. b) Luminance versus the amplitude of the applied voltage at several frequencies. c) Luminance versus frequency of applied voltage of amplitude 3 kV.

larities at the millimeter scale. Consequently, the capacitance of the EDL is much larger than that of the dielectric and the phosphor. The voltage applied between the two electronic conductors drops negligibly across the EDL, and drops mainly across the dielectric and phosphor. The low voltage across the EDL does not electrolyze the gel. The high electric field in the phosphor generates mobile electrons and holes, which then combines to produce light.[21]

We fabricate the device as follows (**Figure 2**a). We attach a mask on a sheet of dielectric and spread phosphor subsequently. After removing the mask, we laminate another sheet of dielectric and then two ionic conductors on the top and bottom sides. Finally, electronic conductors are placed outside the active area to connect the device to a power source.

In this design, each component—the electronic conductor, ionic conductor, dielectric, and phosphor—can be chosen among many materials. The phosphor can be an inorganic compound,[22] an organic compound,[23] or a polymer.[24] The ionic conductor can be a hydrogel of a variety of polymers and salts, or an ionogel of a variety of polymers and ionic liquids. This diversity in the choice of materials opens an enormous space to design devices to satisfy multifarious needs.

We demonstrate ionotronic luminescence using a widely available phosphor, zinc sulfide (ZnS), doped with Cu, Mo, or Cl to luminesce in several colors.[21] ZnS-based phosphors, either thin films or powders, have been developed for displays and solid-state lighting for decades.[25–27] Here, to make the device stretchable, we use ZnS in the form of powders (Science and Technology Ltd., Shenzhen, China). We use a transparent, 1 mm thick, acrylic elastomer (VHB 4910, 3M) as the dielectric, a polyacrylamide hydrogel containing lithium chloride as the ionic conductor,[14,28,29] and aluminum as the electronic conductor. The device is transparent except for parts covered with phosphor (Figure 2b). Subject to a cyclic voltage, the device luminesces in several colors (Figure 2c and Movie 1, Supporting Information).

The luminance of the device depends on the amplitude and frequency of the applied voltage (**Figure 3**). For example, subject to voltage of frequency 1000 Hz, the device starts to luminesce at a voltage about 0.9 kV and becomes much brighter at a voltage of 3.6 kV (Figure 3a). The measured luminance as a function of amplitude of the applied voltage fits a commonly used expression $L = L_0 \exp(-\beta/V^{1/2})$,[21] where L is the luminance, V is the voltage, and L_0 and β are the fitting parameters (Figure 3b). We also measure the luminance as a function of the frequency with an applied voltage of amplitude 3 kV (Figure 3c). A maximum is obtained at an intermediate frequency at 1000 Hz. When the frequency is low, the power is too small. When the frequency is too high, the electrons and holes cannot respond. The luminescence flickers at low frequency but gradually becomes stable at high frequency (Movie 2, Supporting Information).

Our design enables electroluminescence of giant stretchability (**Figure 4**). The stretchability refers to not only the overall device, but also the light-emitting area itself. This high stretchability is achieved by integrating stretchable dielectrics and ionic conductors, as well as electroluminescent materials in the form of powders. Polyacrylamide hydrogel can be stretched 20 times its original length (Figure S1, Supporting Information), and VHB can be stretched nine times its original length.[18] To ensure that the ZnS powder densely covers the active area of the dielectric in the stretched state, we prestretch the dielectric by an area strain of 1500%, spread the phosphor powder, and then release the dielectric (Figure S2, Supporting Information). The resulting device achieves, in the released state and in the stretched state of area strain up to 1500%, with comparable luminance of 9.4 and 9.3 cd m^{-2}, respectively. Electroluminescent devices of such large stretchability should be compared with existing ones that use transparent electronic conductors, where damage of the conductors limits area strain within 55%.[27,30–32]

We estimate the theoretical limit of the area of the phosphor layer. As discussed above, in the absence of electrolysis, the EDL behaves like a capacitor, in series with the capacitor due

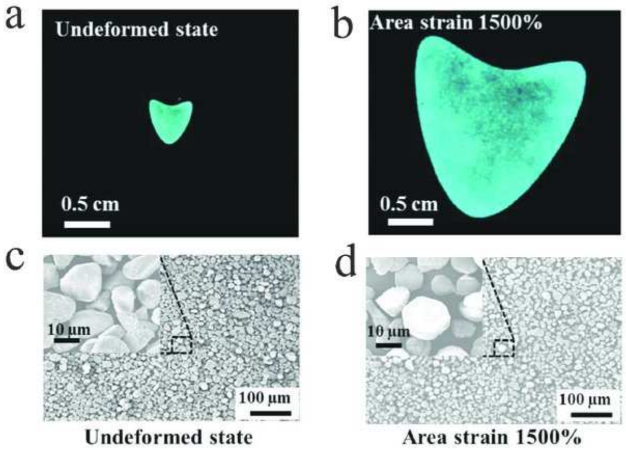

Figure 4. Giant stretchability of ionotronic luminescence. The device luminesces a) in undeformed state, and b) in a state of an areal strain of 1500%. In both undeformed and stretched states, the device is subject to a cyclic voltage of amplitude 5 kV and frequency 1000 Hz. Images of scanning electron microscope of ZnS particles on VHB in c) undeformed state and in d) stretched state.

to the phosphor layer. The balance of electric charge requires that $c_{\mathrm{EDL}}A_{\mathrm{EDL}}V_{\mathrm{EDL}} = c_{\mathrm{P}}A_{\mathrm{P}}V_{\mathrm{P}}$, where c_{EDL} is the capacitance per unit area, A_{EDL} the area and V_{EDL} the voltage of the EDL, and c_{P}, A_{P}, are V_{P} are corresponding quantities of the dielectric. We estimate the capacitance of the EDL by $c_{\mathrm{EDL}} = \varepsilon_{\mathrm{EDL}}\varepsilon_0/d_{\mathrm{EDL}}$, where $\varepsilon_{\mathrm{EDL}}$ and d_{EDL} are the effective dielectric constant and the effective thickness of the EDL. Assume that $\varepsilon_{\mathrm{P}} \approx \varepsilon_{\mathrm{EDL}}$ and $d_{\mathrm{EDL}} \approx 10^{-9}$m. Further assume that the phosphor luminesces at $E_{\mathrm{p}} = 10$ MV m^{-1}. To avoid electrolysis at the EDL, V_{EDL} is restricted to be lower than 1 V, so that $A_{\mathrm{P}} \leq 10^2 A_{\mathrm{EDL}}$. For an EDL of area $A_{\mathrm{EDL}} = 10^{-3}$ m^2, the maximum area of the phosphor can reach $A_{\mathrm{P}} = 10^{-1}$m^2. It is possible to increase the area of the interface between the ionic conductor and electronic conductor by using porous electrodes similar to those used in supercapacitors.

The two dielectric layers serve a significant electrical function: they prevent the device from electric breakdown. The dielectrics insulate the two ionic conductors from each other, and should not suffer electric breakdown when the phosphor luminesces. Prior to electroluminescence, ZnS is also a capacitor in series with the capacitors due to the dielectric layers. The balance of electric charge requires that $\varepsilon_{\mathrm{P}} E_{\mathrm{P}} = \varepsilon_{\mathrm{D}} E_{\mathrm{D}}$, where ε_{P} is the relative permittivity and E_{P} the electric field in the phospher layer, and ε_D and E_D the corresponding quantities in the dielectric. For ZnS, the relative dielectric constant is about 8.5, and the electric field to luminesce is on the order of $E_{\mathrm{p}} = 10$ MV m^{-1}.[33] For VHB, the relative dielectric constant is about 4.7, and the electric breakdown field is above 100 MV m^{-1}.[28] Consequently, VHB will not suffer electric breakdown when ZnS luminesces.

The phosphor particles used in our experiment achieve luminance ≈10 cd m^{-2}, which is lower than the best value reported in the literature, ≈10^4 cd m^{-2} for phosphors[21] and for organic light-emitting diodes.[34] In our experiment, commercially available ZnS powders are spread on VHB manually; luminance may increase by better controlled processes. The high voltage used in our experiment is due to the thickness of luminescent layer (ZnS) and dielectric layer (VHB). By reducing the thickness of luminescent layer and the dielectric layer, for instance, to 10 μm, the applied voltage can be reduced to ≈100 V.

Note that the VHB 4910 is an adequate encapsulation for ZnS, and the polyacrylamide hydrogel doped with lithium chloride can retain water under moisture as low as 11%.[29] The device performs well after being exposed in open air for more than eight months.

We have demonstrated highly stretchable electroluminescence. We use an ionic conductor as a transparent and stretchable conductor to light up phosphors. The luminescence of the phosphors is voltage-induced, and does not require the ionic conductors to inject electrons into the electroluminescent materials. Under cyclic voltage, the phosphor luminesces, but the interface between the ionic conductor and electronic conductor do not undergo electrolysis. Ionotronic luminescence provides a new strategy to replace indium tin oxide, metals and other electronic conductors by using ionic conductors. Stretchable electroluminescence opens doors to applications to wearable electronics for healthcare and entertainment.

Experimental Section

Synthesis of Polyacrylamide Hydrogel Containing Lithium Chloride: Acrylamide powders and lithium chloride grains were dissolved in deionized water with the amount of acrylamide 14.0 wt% relative to deionized water. The concentration of lithium chloride was fixed at 8.0 mol L^{-1} in the experiments. The crosslinking agent (*N,N*′-methylenebisacrylamide, MBAA), thermoinitiator (ammonium persulphate, APS) and accelerator (*N,N,N*′,*N*′-tetramethylethylenediamine, TEMED) were subsequently dissolved in the solution. The molar ratio was 0.028, 0.031, and 0.152 mol%, respectively, relative to acrylamide monomer. The mixture was then transferred into a glass mold, which was separated by a silicon spacer. The mold was put in an oven at 50 °C for 2 h to obtain the polyacrylamide hydrogel containing lithium chloride.

Fabrication of the Device: The VHB and synthesized polyacrylamide hydrogel were cut with predesigned shapes by using a laser cutter (UNIVERSAL). Then a release paper with a precut shape was used as a mask and attached on one VHB. After that, ZnS powders were deposited homogeneously on the surface of the VHB, forming the phosphor layer. After the redundant phosphor powers and the release paper were removed, another VHB was symmetrically attached, sealing the phosphor. Finally, polyacrylamide hydrogels were attached on the top and bottom surfaces. Finally, aluminum foils were attached onto the polyacrylamide hydrogels outside the active area to connect the device to power source.

Measurements: Luminance of the devices was measured by using a spectral photometer (Konica Minolta, CS-200). Measurement angle was set to be 0.2°. Movies were recorded by a digital camera (Canon Ds126321). Tensile test of polyacrylamide hydrogels were conducted by using a 500 N load cell (CMT6503, MTS). Samples were cut into dumbbell shape, with total length 35 mm, width 2 mm, and gauge length 12 mm.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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