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Ionic Gel Paper with Long-Term Bendable Electrical Robustness for Use in Flexible Electroluminescent Devices

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Supporting Information

ABSTRACT: Conductive paper has low-cost, lightweight, sustainability, easy scale-up, and tailorable advantages, allowing for its promising potential in flexible electronics, such as bendable supercapacitors, solar cells, electromagnetic shields, and actuators. Ionic gels, exhibiting a lower Young's modulus together with facile manufacturing, can fully serve as the conductive component to prepare conductive paper. Herein we report a low-cost (~1.3 dollars/m^2), continuous, and high-throughput (up to ~30 m/min) fabrication of reliable and long-term (stable for more than two months) conductive paper. As-prepared conductive paper shows a high electrical durability with negligible bending−recovering signal changes over 5000 cycles. Using this ionic gel paper (IGP) as a key component, we build a variety of proof-of-principle demonstrations to show the capacity of IGP in constructing flexible electroluminescent devices with diverse patterns, including a square, an alphabetic string, and a laughing face. Our methodology has the potential to open a new powerful route to fabricate bendable conductive paper for a myriad of applications in future flexible electronics.

KEYWORDS: *conductive paper, coating, ionic gel, flexible, electroluminescent*

INTRODUCTION

Paper is an ancient yet still widely used material that can trace its history back to early second century (around 2200 years ago).[1] Generally, paper is prepared by dewatering a dilute suspension of natural cellulose fibers, leading to a hierarchically porous structure as well as a hydrophilic nature.[2] This rough structure, together with the rich surface chemistry, enables the paper to swell inks and serve as the most important medium to record and expand information and knowledge during the human civilization. In recent decades, paper has attracted increasing interests in diverse fields beyond the information industry, such as microfluidics,[3−5] early stage diagnostics,[6] 3D scaffolds for cell growth,[7] and especially for flexible electronics.[8−11]

Flexible electronic devices commonly utilize lightweight polymeric thin films as the conductive substrates.[12] Compared with the plastic counterpart, paper is low-cost (1/20 price compared with that of polyethylene terephthalate), renewable, recyclable, biocompatible, biodegradable, easily scaled up, and tailorable,[13−15] allowing for a rapid development of paper-based flexible electronics. Since the intrinsic conductivity of paper is poor (around 10^{11}−10^{15} Ω sq^{-1}),[9] there have been intensive efforts in developing conductive paper. Directly depositing metals onto the paper has been prominent in this field. However, the requirement of high temperature and vacuum during the fabrication process prevents its practical application.[16,17] Consequently, room-temperature solution-processed strategies have been proposed such as drop-casting,[17,18] ink-jetting,[19] spraying,[20] or filtrating[21] a suspension of conductive polymers,[18,22] metallic particles,[17] nanowires,[23−25] microplates,[26] carbon colloids,[27] nanotubes,[21,28−31] graphene nanosheets,[20,32] or their mixtures[33] onto the paper. The hierarchically structural cellulose fibers were covered by active nanomaterials, leading to conductive paper that can be used in flexible supercapacitors,[29,32] solar cells,[30] electromagnetic shields,[21] actuators,[33,34] and medical fields.[35,36]

In spite of intensive efforts invested in developing conductive paper, two issues have not been targeted until now: The first is the lack of continuous and high-throughput fabrication of conductive paper through the roll-to-plate (R2P) process. An available R2P technique can uniformly and rapidly (up to almost 30 m/min) transfer the conductive inks/suspensions onto the paper and is mature with the development of a paper-based information industry. However, most proposed nanomaterial-based inks/suspensions are not desirable for the R2P process which requires a proper viscosity and the elasticity of coating materials. Furthermore, the high price of nanomaterials is also considerable. It is expected that a fast, low-cost R2P process and the use of inexpensive conducting materials, can appear in the

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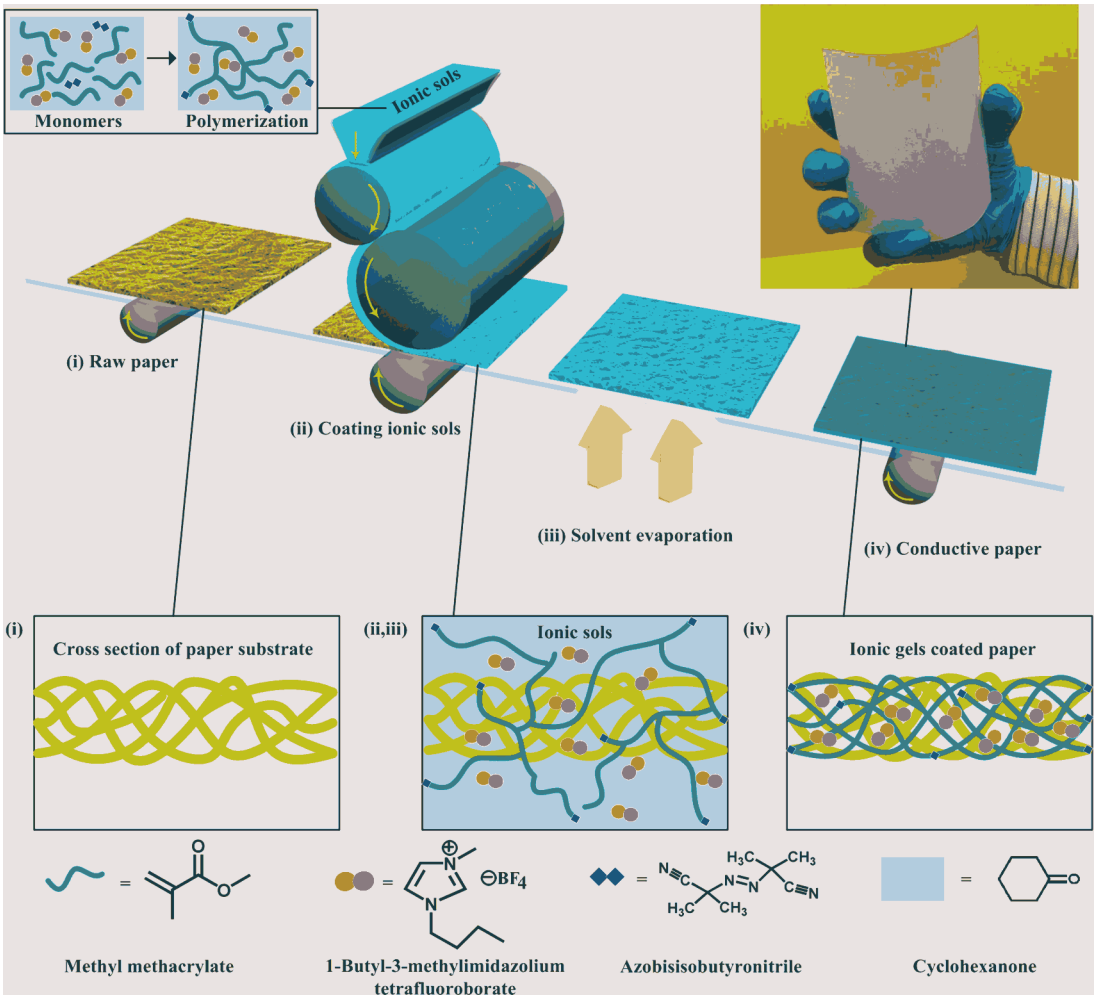

Figure 1. Fabrication of reliable and uniform conductive ionic gel paper (IGP). Fabrication procedure of IGP by a roll-based coating includes: (i) continuous transport of original paper through the bottom coating table; (ii) uniform coating of a thin layer of the ionic gel ink onto the original paper; (iii) heating process to remove volatile solvent from the IGP; and (iv) completed IGP. The ionic gel ink was prepared by the polymerization of vinyl monomer in the presence of ionic liquid, initiator, and organic solvent. The right inset image is the digital photograph of one piece of uniform IGP held by hand, showing its bendability.

fabrication of conductive paper. Second, mismatched Young's modulus differences, ~100 times, exists between the soft cellulose fibers and rigid metallic conductors. Generally, the Young's modulus values of cellulose fibers are ~10^9 Pa,[37] while those of carbons or metals are higher than ~10^{11} Pa.[38] The concept of using a conductor with a high Young's modulus to prepare conductive paper will lead to material delamination and/or local fracturing when bending the composite paper. Thus, a new strategy to fabricate bendable conductive paper with simultaneous mechanical and electronic robustness is a prerequisite.

Herein we demonstrated a low-cost (~1.3 dollars/m^2), reliable, and long-term (stable for more than two months) ionic gel paper (IGP). Soft ionic gels were used as the coating ink to prepare conductive paper. Ionic gels contributed two significant advantages: (1) A lower Young's modulus compared with that of cellulose fibers and facile manufacturing. (2) As a result, IGP show a high electrical durability with negligible bending−recovering signal changes over 5000 cycles. Using this IGP as a key component, we built a variety of proof-of-principle demonstrations to show its capacity in constructing flexible electroluminescent devices. Since the paper was tailorable, different electroluminescent patterns, such as a square, an alphabetic string, or a laughing face, could be achieved by carefully designing the paper shapes. Our methodology has the potential to open up a new powerful route to fabricate bendable conductive paper for a myriad of applications in future flexible electronics.

EXPERIMENTAL SECTION

Materials. 1-Butyl-3-methylimidazolium tetrafluoroborate ([C_4mim][BF_4], >99%, Guangzhou Howei Chemical Co., Ltd., China), methyl methacrylate (MMA, >99%, Evonik Degussa Industries AG), cyclohexanone (Guangzhou Qishuo Chemical Co., Ltd., China), and azobis(isobutyronitrile) (AIBN, 98%, Guangzhou Zuhao Chemical Co., Ltd., China) were used as received; 184 silicone elastomer from Dow Corning SYLGARD was used to prepare polydimethylsiloxane (PDMS) rubber. Electroluminescent ZnS:Cu powders were purchased from Shanghai KPT company.

Fabrication of Original Paper. The original paper was made according to TAPPI (Technical Association of the Pulp and Paper Industry) standard method T205. First, eucalyptus dry pulp was wetted in deionized water and then torn into pieces (about 30 mm^2). After being soaked for 24 h, the pulp was diluted to 2000 mL with deionized water and then disintegrated by Lorentzen & Wettre Pulp Disintegrator for 70 000 revolutions. Next, the pulp solution was diluted from 2000 mL to 8 L and ready for making paper. By properly mixing the stock

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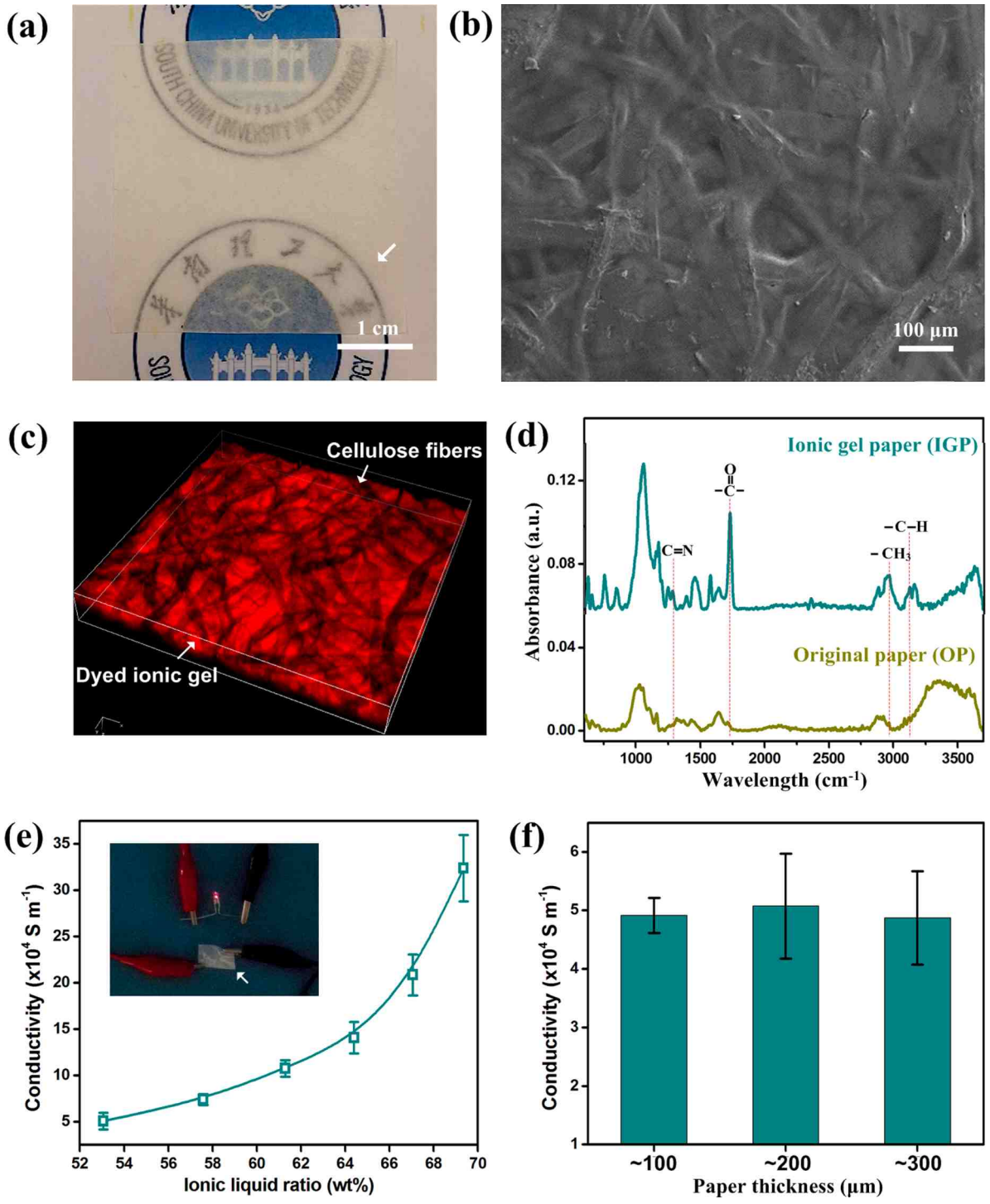

Figure 2. Semitransparent, uniform, and conductive IGP with tunable electrical performances. (a) Digital photograph of one piece of IGP placed horizontally. This IGP exhibits a semitransparent property. The filling of ionic gels inside the pores of cellulose fiber networks enables more light to transport through the IGP. (b) Top view scanning electron microscope (SEM) image of the IGP. A continuous layer of ionic gel covered the cellulose fiber network. (c) 3D laser scanning confocal microscope observations of IGP. Rhodamine B was dissolved inside the inks to enable it show red fluorescence when exposed to the laser irradiation. Ionic gels, represented by red fluorescence, appeared inside pores of cross-linked cellulose fibers. (d) Attenuated total reflection infrared spectra (ATR-IR) of IGP and original paper. (e) Dependence of conductivity on the weight ratio of ionic liquid in the ionic gel ink. Inset image is the digital photograph of an IGP in series with a light-emitting diode (LED) light. (f) Values of conductivity of IGP prepared by original paper with diverse thicknesses.

solution, 400 mL of stock was transferred into the handsheet machine to form 1 paper sheet. All original paper was then dried in a conditioned atmosphere with 23 °C and 50% relative humidity (RH) for further use. The thickness of paper was tunable by changing the basis weight of paper during the fabrication process.

Fabrication of Ionic Gel Paper. The ionic gel ink was fabricated by using a radical cross-linked polymerization in the presence of vinyl monomer, ionic liquid, and initiator. Mixtures with 44.2 g of MMA, 50–100 g of [C_4mim][BF4], 100 g of cyclohexanone, and 1.45 g of azobis(isobutyronitrile) (AIBN) were bubbled with nitrogen for at least

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30 min. Then, radical cross-linked polymerization was carried out at 80 °C for 6 h to yield ionic gel ink. For diverse species of ionic liquids, the weight ratios of each components and the fabrication process were similar to that by using [C_4mim][BF4]. Uniform IGP can be fabricated by drop-casting, spin-coating, doctor-blade, or a conventional R2P process. In this study, we demonstrated the R2P technique as an example to show the fabrication process of IGP. A scalable R2P process for fabricating conductive paper was designed based on the innovative use of a continuous gluing machine, which has been widely used in packaging industry. A modified gluing machine is available for handling paper sheets with basis weight below 3000 gsm, and coating them with ionic gel ink at the speed of up to 30 m/min. The prices of MMA, ionic liquid, cyclohexanone, and AIBN were 1.9, 62.3, 1.6, and 6.4 dollars/kg, respectively. The amount of ionic gels needed to prepare IGP was around 50 g/m^2. Thus, the final price of IGP was around 1.3 dollar/m^2 and could be further reduced when produced in a large scale.

Fabrication of Flexible Electroluminescent Devices. The flexible electroluminescent device was assembled by three layers: two IGP on the top/bottom parts and an emissive layer in the middle part. The fabrication of the middle emissive layer can be found as follows:[39] PDMS 184 liquid (Dow Corning 10:1) and ZnS:Cu microparticles (purchased from Shanghai KPT company) were mixed in a weight ratio of 1:1. Then, the opaque solution was spin-coated onto a polystyrene dics with a speed of 1000 r/s for 60 s. The PDMS/ZnS:Cu gel was fully solidified under 80 °C for 2 h. Finally, it was peeled off and used. Copper tapes were used to electrically connect IGP layers. The input power of this flexible electroluminescent device was purchased from the Shanghai KPT company. The power device can transfer the direct current (dc) field of two commercial batteries to an alternating current (ac) field with increased voltage.

Measuring the Conductivity of IGP. Since IGP is ionic conductor, we measured the conductivity of IGP through an ac impedance method. The measuring system and the instrument was PARSTAT 2273 (Princeton Applied Research; Figure S1). Current ranging was 200 mA, and the frequency range was from 1 Hz to 1 MHz. The sample was cut into pieces 5 mm (width) × 5 mm (length) × 0.2 mm (thickness) and sandwiched by copper tapes (Figure S1b,c). The testing condition was room temperature (25 °C) and 30−35% RH. The values of conductivity were calculated from the impedance curves.

Characterizations. Scanning electron microscope (SEM) images were obtained by using the HITACHI TM3030 Tabletop SEM. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded on a Bruker Equinox 55 spectrometer. The bending−unbending cycles were manipulated with the assistance of a translation stage (Model LTS150/M, Thorlabs). Confocal images were obtained using a Nikon A1Rsi laser scanning confocal microscope with the excitation wavelength of 561.3 nm. Optical images and demonstration videos were taken by a Nikon Digital Sight DS-Fil camera. The transmittance of samples was measured by a solar film transmission meter (Linshang Tech Co., Ltd., China). The topographical features of IGP were measured by an optical profilometer (Bruker ContourGT-I 3D Optical Microscope, Karlsruhe, Germany).

RESULTS AND DISCUSSION

Figure 1 illustrates the fabrication procedure of IGP. Uniform IGP based on a thin layer of conductive gel can be fabricated on flat original paper sheets by drop-casting, spin-coating, doctor-blade or a conventional R2P process. In this study, we take the R2P technique (Figure S2) as an example to show the fabrication process of IGP. At the beginning, methyl methacrylate was mixed with [C_4mim][BF_4] and cyclohexanone and polymerized in the presence of AIBN as the initiator. Optimized polymerization control, combined with a suitable amount of solvent, allowed the resulting ink to reach the engineering standard of R2P technique (10−50 Pa·s). Then, original paper sheets were continuously transported through the bottom coating table (step (i)), and uniformly coated by a thin layer of the ionic gel ink under the assistant of the application roller and impression roller (step (ii)). Rough structure, together with rich surface chemistry, enables the original paper sheets to absorb ionic gel ink quickly and completely. The volatile solvent, cyclohexanone, was removed through a rapid heating process, around 80 °C (step (iii)), or exposed to the air for a longer time. Rapid evaporation of organic solvent at a high temperature led to increased wrinkles upon the IGP, indicating increased surface roughness (Figure S3). However, slower evaporation at room temperature could cause more smooth surfaces of IGP. Finally, poly(methyl methacrylate) in the gel closed their molecular chains and restricted the ionic liquid inside the cellulose fiber network, allowing for a rapid fabrication of uniform IGP (step (iv)).

The physical morphologies, as well as tunable electrical properties of IGP were investigated, as shown in Figure. 2. Traditional paper is opaque because it consists of randomly dispersive cellulose microfibers, indicating considerable light scattering upon their surfaces. When coated by active nanomaterials, such as metals or carbons, the conductive paper would block more light to show a metallic reflection/absorption. In contrast to existing conductive paper,[17,23−31] our IGP became more transparent (Figures 2a and S4). This result is attributed to the filling of ionic gel inside the pores of cellulose fiber matrix of the conductive paper, allowing a ∼68% increase of transmission rate (3.2 ± 0.2%) when compared with that of original paper (1.9 ± 0.2%). Although ionic liquids can endow the paper with conductivity, they easily flow,[40] yielding contamination problems when contacted with other matters (Figure S5). In contrast, ionic gels, rather than ionic liquids, were used as the conductive component in the IGP, showing residual-free advantage. As-prepared IGP was uniform and nonadherent whether it was being bent (inset image in Figure 1) or horizontally placed (Figure 2a). The microstructures of IGP were observed by the scanning electron microscope (SEM). Figure 2b shows the top view SEM image of the IGP. Compared with the original paper (Figure S4b), a continuous layer of ionic gel covered the cellulose fiber network of IGP. From the cross-sectional SEM image (Figure S6), we can find that the ionic gel not only covered the top but also permeated inside the ∼200 μm thick paper which was in accordance with the result of laser scanning confocal microscope (LSCM). Rhodamine B (λ_{ex} = 590 nm) was used to stain ionic gels for easy observation (Figure 2c). Ionic gels, represented by the red fluorescence, appeared inside pores of among cellulose fibers (with the fibers themselves showed little fluorescence; black wires), indicating the ionic gels have fully permeated the paper. Attenuated total reflection infrared spectra of IGP and original paper are shown in Figure 2d. The peaks at 1726 cm^{-1} (carbonyl stretching absorption) and 2948 cm^{-1} (C−H stretching of $-CH_3$) were assigned for poly(methyl methacrylate) while those at 1299 cm^{-1} (C−N stretching) and 3179 cm^{-1} (C−H stretching of heterocycle) attributed to the [C_4mim][BF_4].

Uniform dispersion of ionic gels inside cellulose fiber matrix leads to functional paper with tunable conductivities. The electrical performances of IGP have been studied by changing the amount of ionic liquid in the gel (Figure 2e). Since IGP is an ionic conductor, we measured the conductivity of IGP through an ac impedance method. The conductivity of IGP could rise from 0.5 to 3.2 mS m^{-1} by increasing the weight ratio of ionic liquids, enabling the illumination of a light-emitting diode (LED) light in series with IGP (see inset image in Figure 2e). A smaller amount of ionic liquid (<52 wt %) led to nonconductive paper, while a value larger than 68 wt % resulted in a dilute ink that was difficult to coat due to a reduced viscosity. The IGP could keep its stable

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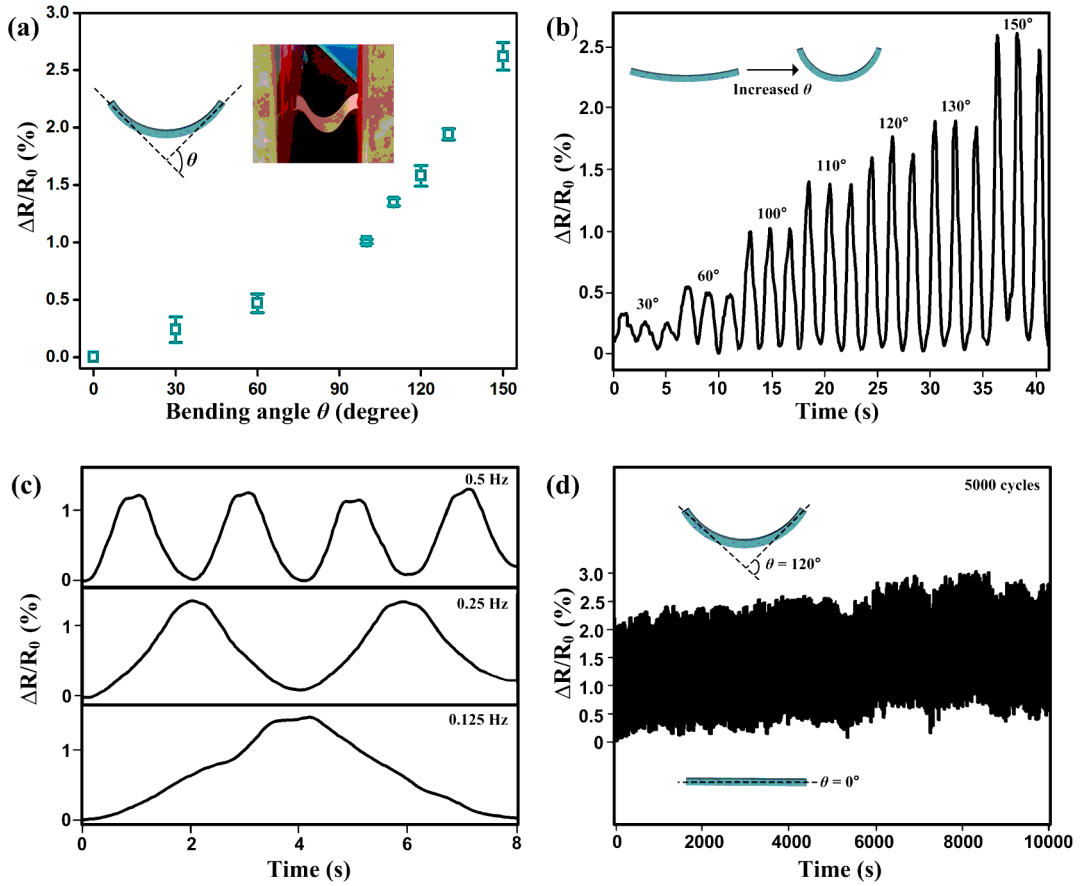

Figure 3. Stable electrical performances of IGP after bending for 5000 cycles. (a) Bending−response plots for IGP. The inset image is a schematic illustration (left) and a digital photograph of a bended IGP. (b) Plots of resistance change of IGP as a function of time (input frequency: 0.5 Hz) for the bending angle in the range of 30−150°. (c) Plots of resistance change for IGP as a function of time (bending angle: 120°) for diverse frequencies including 0.125, 0.25, and 0.5 Hz. (d) Lfetime test at a bending angle of 120° and a frequency of 0.5 Hz. The resistance change curves were recorded for 5000 cycles. The applied voltage in the electrical tests was 1 V, the relative humidity was 35%, and the temperature was 25 °C.

conductive robustness for more than 2 months (Figure S7). The conductivity of IGP has been further investigated by replacing the species of ionic liquids (Figure S8) or the paper thickness (Figure S9). Following the increase of carbochains in the cation segment of ionic liquids, the activity of ions for transporting electrical signal was reduced, yielding a decreased conductivity. The change of paper thickness showed a negligible effect on the conductivity (Figure 2f).

Bendability is a basic property of paper materials. The dependence of electrical performances of IGP on the bending parameters, including bending angles, frequencies, and cycles, were investigated. Bending the ionic liquids/gels can increase the spacing among the ions,[40,41] allowing for a rapid change in resistance of the IGP. Figure 4a shows the relationship between the resistance change of IGP and the bending angle. The greater the bending angle θ (defined in Figure. 3a), the higher the resistance. The fiber matrix of paper provides the mechanical strength to IGP. Figure S10 shows the comparison of electrical robustness between IGP and an ionic gel film. Without the support of cellulose fiber matrix, the resistance change of ionic gel film was considerably unstable. The responses of IGP to dynamic mechanical bending were determined. As shown in Figure 3b, the resistance change of IGP was noise-free, stable, and continuous when bent at an angle ranging from 30 to 150°. Besides different bending angles, the response of IGP toward diverse frequencies was also investigated (Figure 3c). The thickness of paper could cause diverse electrical responses (Figure S11). When coated with the same amount of ionic gel, the resistance change of thinner IGP was much larger than that of thicker counterpart. This result can be attributed to the dispersion states of ionic gel in the cellulose fiber matrix. Thinner paper indicates that cellulose fibers were immersed inside the ionic gel. In this case, the stretching of fibers can cause a greater physical deformation of ionic gel and consequent resistance change. However, thicker paper provided a increased fiber matrix to hold the ionic gel on the fiber surfaces. Stretching IGP caused limited deformation of ionic gel. Thus, their electrical response was reduced. Stable output electrical signals appeared without obvious change in amplitude at typical frequencies of 0.125, 0.25, and 0.5 Hz. The cycling stability, one of the most critical parameters in the flexible substrates, was tested under a 120° bending angle strain at a frequency of 0.5 Hz (Figure 3d). The response of resistance change with the bending applied on IGP could be maintained after 5000 loading−unloading cycles, implying a long working life and reliability of the IGP.

Conductive, bendable, and tailorable advances of IGP enable this soft material to find promising application in flexible electronics. We show a variety of proof-of-principle demonstrations by using IGP as the key building block to form flexible electroluminescent devices (Figure 4). Although the conductivity of our IGP was lower than those of traditionally metal coated paper,[17−32] the application of conductive paper in electro-

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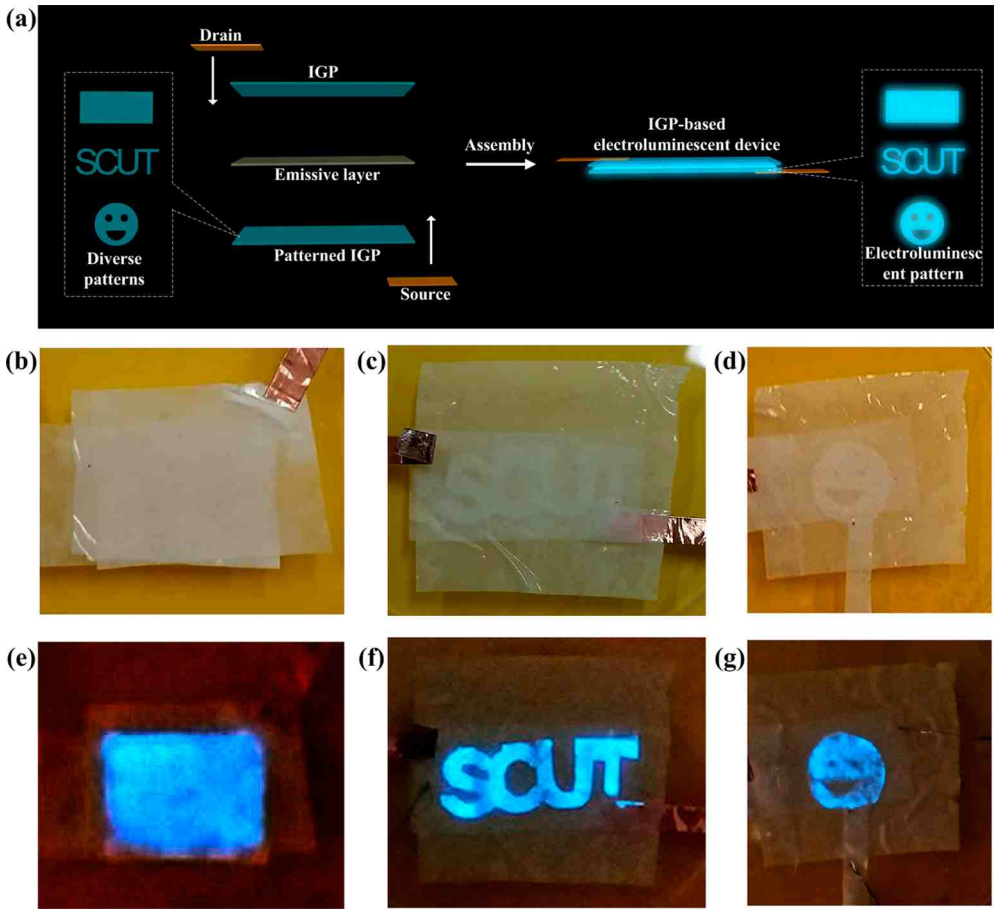

Figure 4. Proof-of-principle demonstrations by using IGP as the key building block to form flexible, patterned electroluminescent devices. (a) Schematic illustration of IGP-based flexible electroluminescent devices. The device was composed of the bottom pattern and top IGP sandwiched with a ∼56 μm ZnS:Cu/Ecoflex emissive layer. The electroluminescent region only appeared when the ZnS:Cu emissive layer was sandwiched between top/bottom IGP layers. Photographs of flexible electroluminescent devices showing (b, e) square, (c, f) alphabetic string and (d, g) laughing face shaped patterns in the (b−d) off and (e−g) on states. The relative humidity was ∼35%, and the temperature was 25 °C.

luminescent display does not require a high conductivity, which has been proved by our demonstration (Figure. 4) and recent reports by Frisbie et al.[42] The flexible device was composed of the bottom and top IGP with sandwiched a ∼56 μm ZnS:Cu/Ecoflex emissive layer (Figure S12). Suo and co-workers have reported the working mechanism of ionic conductors.[43] When a high-frequency alternating voltage was applied, the emissive layer afforded most of the voltage and emitted a blue luminescent light. The electroluminescent region only appeared when the ZnS:Cu emissive layer was sandwiched between top/bottom IGP layers (Figure 4a). Since IGP could be cut into diverse shapes via scissors, different electroluminescent patterns including a square (Figure 4b,e), an alphabetic string (Figure 4c,f), and a laughing face (Figure 4d,g) could be fabricated accordingly.

CONCLUSION

This work demonstrates a new design strategy for fabricating conductive paper that can combine important properties such as long-term robustness in both mechanical and electrical fields, low-cost by using ionic gels as the conductive component. Admittedly, the employment of ionic conductor might bring possible electrochemical reactions when applied by a dc field. However, the possibility of this problem could be reduced in this study when using an applied voltage as low as 1 V (Figure 3) or an ac field (Figure 4). This conductive paper exhibits the virtue of electrical durability. Our results show that there were negligible signal changes even over 5000 bending−recovering cycles. On the basis of the ionic gel paper, flexible electroluminescent devices with different patterns were successfully integrated and demonstrated. We believe that the current method may soon find industrial applications such as functional printing and intelligent packaging in which paper-based flexible electronics with low cost, rapid fabrication, recyclability, easy scalability, and bendability is required. We also look forward to further steps of the related techniques and broader applications of this approach.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b02433.

Electrical study of IGP, schematic illustration of cross-sectional structure of the roller-to-plate (R2P) process to prepare stable and uniform IGP, heating-temperature-dependent surface roughness of IGP, physical morphologies of original paper and IGP, residual-free advantage of IGP, cross-sectional morphology of IGP, long-term electrical robustness of IGP, increase of carbochains in the cation segment of ionic liquids led to the decrease of conductivity of IGP, morphologies of IGP prepared by original paper with diverse thicknesses, comparison of

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electrical robustness between IG and IGP, electrical response of IGP with diverse paper thicknesses, and cross-sectional SEM image of the ZnS:Cu emissive layer (PDF)

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Notes

The authors declare no competing financial interest.

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