

Highly Conductive and Stretchable Nanostructured Ionogels for 3D Printing Capacitive Sensors with Superior Performance



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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

Dear editor,

The presented manuscript reports a photopolymerization-induced microphase separation strategy to prepare a bi-continuous nanostructured ionogel that simultaneously achieves high ionic conductivity, high stretchability, low degree of hysteresis, wide-temperature-range thermostability and humidity tolerance. In addition, the superior 3D printability enables facile fabrication of ionogels into high resolution microstructures, which can be utilized to fabricate high-performance ionotronic sensors and wearable pressure-sensing skin. Moreover, most of the claims made in this work were based on assumptions with enough clear evidence and principles to support them. Some of the claims made in this work need to be correctly justified and properly explained. I think this manuscript can be published after a minor revision. The comments are as follows:

1. In Fig. 1h, the authors showed a schematic illustration of a bi-continuous structure in the ionogel, which is separated into BA phase and PEGMA phase. Additionally, the evidence for this microphase separation was presented via SEM and SAXS. However, the interaction between polymers and ionic liquid is not discussed detailly, which is very important for understanding the mechanism leading to the microphase separation and bicontinuous network formation. So, the FTIR or Raman data should be added.
2. The author fabricated high-performance wearable pressure-sensing skin, however, the compressibility and compression performance of the ionogels are not discussed.
3. In Fig. 2l, the CSN ionogels exhibit good stability at humid environment and no weight change has been observed over the 7 days. But ionic liquids with dicyanamide (DCA) or BF₄ are very hygroscopic, which is different with the reported ionogels prepared with hygroscopic ionic liquids. So, the reason should be explained in detail.
4. A clear information about number of repetitions for all methods applied and statistical evaluation of the raw data is missing. This information is very important for a high-quality research work.
5. How about the size stability under different temperature? Do IL leakage occur.
6. There are some grammar and codes errors. The manuscript is in need of a major proofreading/grammatical polishing. For example, In Fig.4b, "Pressue" should be "Pressure".

Reviewer #2 (Remarks to the Author):

The authors reported a bicontinuous nanostructured ionogel with high ionic conductivity, high stretchability, and superior 3D printability by introducing a photopolymerization-induced microphase separation strategy. This work is interesting and comprehensive in terms of the design of 3D printing and the application of ionotronic sensors, but some issues need to be answered. The specific issues are as follows:

1. The authors mentioned that the ionogel without PEGMA shows macroscopic phase separation (Fig. 1f), so the SAXS experiment of the ionogel without PEGMA should also have a scattering peak (Fig. 1k). Similarly, the SEM image of ionogel without PEGMA should have a macroscopic phase-separated morphology (Fig. 1l).
2. In Fig. 2a-f, the content of PEGDA in the CSN ionogels is 0.2 wt.%. However, the study of the effect of PEGDA content on residual strain and elongation-at-break of the CSN ionogel was tested from 0.5 wt.% (Fig. 2g). The hysteresis of the CSN ionogel with 0.2 wt.% PEGDA should also be tested.
3. The composition of the CSN ionogels tested is too complex and contextually inconsistent. For example, the ionogel in Fig. 2c has the highest conductivity with [EMIm][DCA] content of 70 wt.%, but the ionogel with [EMIm][DCA] content of 40 wt.% was chosen for hysteresis testing in Fig. 2g. In addition, the PEGDA content of the ionogels selected for the 3D printing section is not mentioned. It is recommended that the composition of the other components of the ionogels, except for the test component, be kept consistent and that the optimal ratio be selected for subsequent characterization.
4. The 3D printed ionogel sample in Fig. 3 has a porous structure, does it have an effect on its conductivity?
5. The 3D printed sample in the manuscript is too simple and more complex samples should be shown
6. Minor issue: The explanation of ΔU_{mix} on page 4 is repeated twice.

Reviewer #3 (Remarks to the Author):

Overall this paper reflecting significant amounts of well-executed experiments and demonstrations work and the subject matter is of scientific and technological interest. However, there are issues that should be addressed

Although there is a discussion of the ionogel synthesis and structure, largely based on previously published work, a significant fraction of this paper covers interesting demonstrations and environmental tests accompanied by significant numbers of figures. These demonstrations and the larger amount of data are outside what this reviewer would normally associate with Nature Communications and may be better placed in engineering and design journals.

Focusing on the background, ionogel synthesis, structure and characterization sections there are some general issues:

1. There is confusion over the terminology and use of microstructure, nanostructure and microphase
 2. In the second paragraph of the introduction and in the SI, the authors claim that "the currently printed ionogel sensors exhibit neither high resolution nor remarkable sensing capabilities (Table S1). The author's should consider additional work on 3D printed ionogels here. There are reports that demonstrate significantly higher dR/R than in the experiments outline in the paper, high elongation and good stability using BMIM/BF4 base dmaterials: DOI 10.1088/1361-6528/ab2440
 3. There is some apparent contradiction between claims of homogenous structure versus diagrams and micrographs of micron scale heterogeneity in the gel structure as seen in Figure 1.
as well there appears to be a mismatch or attribution of lengthscales in SAXS versus SEM as shown in Figures j,k and l. The SAXS shows a length scale of 10 nm while the phase separation of the samples with PGMEA show a much larger microstructure in the SEM. Additional explanation would improve this.
 4. the use of PEO-containing salt or ionic liquid based gels is well known and the observation of higher conductivity, as observed here, with the introduction of a material like PEGMEA could be attributed to basic solvation and not a special microstructure. It is unclear that the claims made for the improved performance reported here are not novel.
 5. The author's state in the 'Thermomechanical and electrical properties of the CSN ionogel' section "To demonstrate the high conductivity of the ionogel with [EMIm][DCA], as shown in Fig. 2e, only 4 V voltage can light up a light-emitting diode (LED) bulb in the circuit where the ionogel with [EMIm][DCA] is used as conductor. In comparison, the 4 V circuit with the LiTFSI-based conductor fails to light the LED bulb due to its low conductivity."
- Ionogels are often not used in DC biasing applications such as an LED which is a rectifying diode, as there is a finite amount of charge carrying capability with ion motion, double layer formation and/or electrochemistry takes place at the ionogel interface with the electrodes. Differences in running an LED in DC current mode could be due to other factors and AC biasing with symmetric electrodes is more relevant and the conclusions claimed here by the authors may not be appropriate.
6. In the first paragraph of the 'Working mechanism of the 3D printed capacitive sensor with CSN ionogels,' The length scales in the functional description are confusing and not substantiated in this work. In any case, EC mechanisms are well known and do not need to be repeated here. Citations of appropriate sources could better achieve the descriptive aims of the author's here.

Overall this paper presents one principle ionogel synthesis and properties section and some of these conclusions in that section may need significant revision with regards to the issues discussed above.

Also, although demonstrations can contribute to the impact and conclusions of the paper, the amount of demonstrations here is large and not all add significantly to the scientific aspect of a Nature Communication article.

The authors might consider breaking this up into multiple journal articles and potentially a journal where the implementation demonstrations may be a better fit.

Reviewer #4 (Remarks to the Author):

The authors have done a great job on the development of highly conductive and stretchable nanostructured ionogels using DLP 3D printing. They further apply the printed sensor to various applications (pressure sensors, monitoring real-time physiological signals, robotic gripper) to demonstrate the superior sensing performance of the newly proposed ionogels.

This study represents a significant contribution to the field of ionogels and ionotronics. Through its rigorous experimentation, insightful analysis, and clear presentation of findings, the study advances our understanding of ionogel materials and their potential applications, paving the way for further innovation in this research field. However, the manuscript could benefit from minor changes before publication. Please consider the following comments:

1. In Figure 2, the properties of the ionogels are analyzed based on the IL content. However, the TGA curves of the ionogels fabricated with 50%, 60%, and 70% of the ionic liquid [EMIm][DCA] are absent (Fig. 2k). No rationale is provided to explain the omission of these results.

2. As shown in Fig. 2l, the ionogel and the LiTFSI-based conductor were placed in a humid environment and their weight variations are compared. The results obtained are somehow expected because an ionic liquid ([EMIm][DCA]) and a very hygroscopic salt (LiTFSI) are being compared. This discussion could benefit by including the results for the ionogel composed of [Emim][Otf], an ionic liquid that also allows the preparation of ionogel materials with good conductivity properties.

3. The authors state that the prepared ionogels achieved high ionic conductivity (over 3 S m^{-1}) and high stretchability (over 1500 %), as those are the values shown by the ionogel with circa 70 % IL (maximum IL amount used to optimize the ionogel materials before the 3D printing study). However, in the end, the printed ionogel sensor is prepared with 40 %IL and this ionogel does not have $3.23 \text{ (S m}^{-1}\text{)}$ or 1500% elongation-at-break as described in Table S2 and in some parts of the manuscript text.

4. I have observed that upon comparing the "Abstract" and "Conclusion" sections, a considerable portion, approximately 45%, of the content in the conclusion appears to be a repetition or variation of the text used in the Abstract. This redundancy signifies a notable overlap between the two sections, implying a substantial similarity that is not recommended.

Reviewer #5 (Remarks to the Author):

In this manuscript, the authors report a photopolymerization-induced microphase separation strategy to prepare a bicontinuous nanostructured ionogel that simultaneously achieves high ionic conductivity, high stretchability, low degree of hysteresis, and other excellent properties.

Moreover, the developed ionogel exhibits high compatibility with DLP 3D printing that allows the authors to fabricate EDL - based capacitive sensors with superior sensing performances. The authors present a few applications to demonstrate these superior sensing performances of the 3D printed ionogel sensors. It is a well written manuscript that reports a high performance ionogel for 3D printing flexible electronic sensors. Therefore, it is recommended for publication in Nature Communications after addressing the following minor issues.

1. In this manuscript, the authors have studied the effect of PEGMA content on the transmittance and conductivity of ionogels. What is the effect of PEGMA content on the ionogel mechanical properties?
2. For capacitive sensor with ionogels, the thickness of the ionogel layers should be given.
3. The last sentence in abstract sounds misleading. Please revise this sentence.
4. On page 2 line 50-52, in the definition of ionic liquid, the last “, and liquid” seems redundant, or does not appear at the right place.
5. On page 4 line 120, ΔU_{mix} is introduced twice but ΔS_{mix} is not introduced.
6. On page 6 line 159, unit of molecular weight should be written.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The presented manuscript reports a photopolymerization-induced microphase separation strategy to prepare a bi-continuous nanostructured ionogel that simultaneously achieves high ionic conductivity, high stretchability, low degree of hysteresis, wide-temperature-range thermostability and humidity tolerance. In addition, the superior 3D printability enables facile fabrication of ionogels into high resolution microstructures, which can be utilized to fabricate high-performance ionotronic sensors and wearable pressure-sensing skin. Moreover, most of the claims made in this work were based on assumptions with enough clear evidence and principles to support them. Some of the claims made in this work need to be correctly justified and properly explained. I think this manuscript can be published after a minor revision. The comments are as follows:

Response: We thank the reviewer for taking precious time to review our paper and giving us the constructive comments and suggestions.

Comment 1.1. In Fig. 1h, the authors showed a schematic illustration of a bi-continuous structure in the ionogel, which is separated into BA phase and PEGMA phase. Additionally, the evidence for this microphase separation was presented via SEM and SAXS. However, the interaction between polymers and ionic liquid is not discussed detailly, which is very important for understanding the mechanism leading to the microphase separation and bicontinuous network formation. So, the FTIR or Raman data should be added.

Response: Thanks for the constructive suggestions to improve our manuscript. In the revision, we have added the Fourier transform infrared (FTIR) spectroscopy results to validate the interaction between polymers and ionic liquid. As shown in **Figure R1 (Supplementary Figure 4)**, the increase in the PEGMA content shifts the C≡N group stretching and C-N group stretching of [EMIm][DCA] to a lower wavenumber indicating the existence of the interaction between PEO side chains of PEGMA and IL.

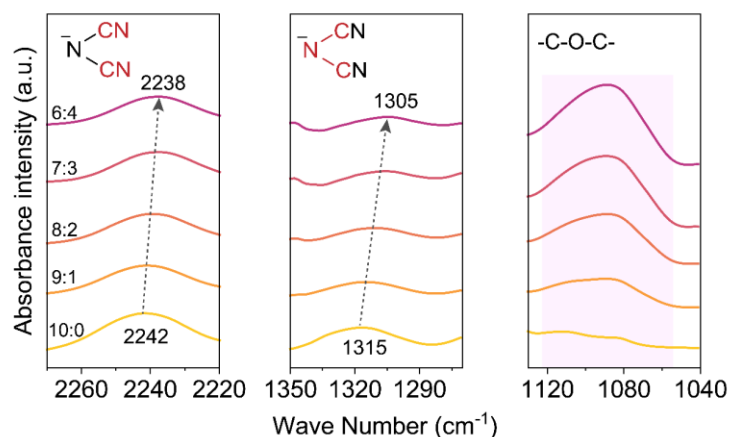


Figure R1 (Supplementary Figure 4). FTIR spectrum of the ionogels with different PEGMA contents.

Comment 1.2. The author fabricated high-performance wearable pressure-sensing skin, however, the compressibility and compression performance of the ionogels are not discussed.

Response: We thank the reviewer for raising this suggestion. We performed compressive tests to investigate the stress–strain behavior of the ionogels with different [EMIm][DCA] contents. As shown in **Figure R2 (Supplementary Figure 6)**, all the ionogel samples exhibit excellent compressibility and can be compressed by 90% without breaking. The stiffness of ionogel decreases with the increase in [EMIm][DCA] content.

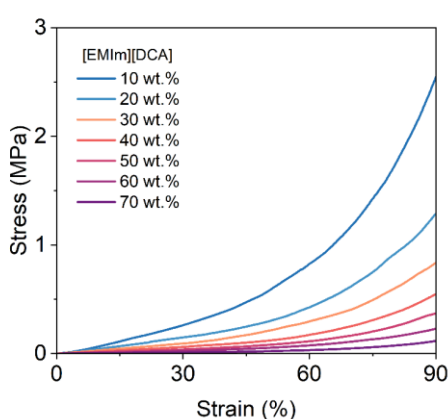


Figure R2 (Supplementary Figure 6). Compressive test of the ionogels with different [EMIm][DCA] contents.

Comment 1.3. In Fig. 21, the CSN ionogels exhibit good stability at humid environment

and no weight change has been observed over the 7 days. But ionic liquids with dicyanamide (DCA) or BF₄ are very hygroscopic, which is different with the reported ionogels prepared with hygroscopic ionic liquids. So, the reason should be explained in detail.

Response: We thank the reviewer for raising this suggestion. Based on our experimental observation and previous reports (Cao Y. et al, Physical Chemistry Chemical Physics, 2012; Cao Y. et al., Industrial & Engineering Chemistry Research, 2013), in fact, ionic liquids with DCA⁻ or BF₄⁻ are not very hygroscopic. As shown in **Figure R3a and R3b**, we tested the weight change of the different ionic liquids and LiTFSI in a humid environment (humidity: 80%). Due to its strong hygroscopicity, LiTFSI salt quickly becomes a solution (Figure R3a). Compared with LiTFSI, the moisture absorption capacity of the five ionic liquids is very weak (Figure R3b).

More importantly, according to the previous reported ionogel systems, the introduction of hydrophobic groups can keep the ionogels stable in the water environment and avoid the interference of water molecules (Du D. et al., Chemical Engineering Journal, 2023; Zhao Y. et al., ACS Applied Materials & Interfaces, 2023). In bicontinuous nanostructured ionogel developed in this work, the domains of BA phase possess hydrophobic groups that can ensure the stability of the ionic liquid in the PEGMA phase in humid environments. As shown in **Figure R3c (Supplementary Figure 12)**, we tested the weight change of the P(BA-co-PEGMA) samples with different ionic liquid in humid environments. No weight change has been observed on the ionogel sample over the 7 days.

In the revision, we have added a short explanation on the stability of CSN ionogels in humid environment:

“The excellent stability of CSN ionogels in humid environment can be attributed to two reasons: compared with LiTFSI, the ILs are much less hydroscopic^{42,50}; the hydrophobic domains of the BA phase further enhance the stability of the CSN ionogels in humid environment.”

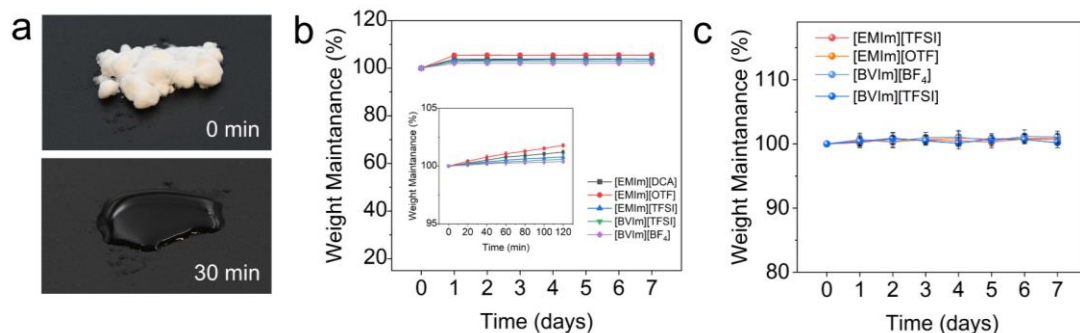


Figure R3. **a** The change of LiTFSI in humid environment. **b** The weight change of the different ionic liquids in humid environment. **c** (Supplementary Figure 12) Weight change of the P(BA-co-PEGMA) samples with different ionic conductive component in humid environments.

Reference

- Cao Y, Chen Y, Sun X, Zhang Z, Mu T. Water sorption in ionic liquids: kinetics, mechanisms and hydrophilicity. *Physical Chemistry Chemical Physics*, 14, 12252-12262 (2012).
- Cao Y, Chen Y, Lu L, Xue Z, Mu T. Water Sorption in Functionalized Ionic Liquids: Kinetics and Intermolecular Interactions. *Industrial & Engineering Chemistry Research*, 52, 2073-2083 (2013).
- Du DY, Zhou JH, Kaneko T, Dong WF, Chen MQ, Shi DJ. Stretchable and hydrophobic eutectogel for underwater human health monitoring based on hierarchical dynamic interactions. *Chemical Engineering Journal*, 474, 145704 (2023).
- Zhao Y, et al. Underwater Self-Healing and Recyclable Ionogel Sensor for Physiological Signal Monitoring. *ACS Applied Materials & Interfaces*, 15, 28664-28674 (2023).

Comment 1.4. A clear information about number of repetitions for all methods applied and statistical evaluation of the raw data is missing. This information is very important for a high-quality research work.

Response: We thank the reviewer for this suggestion. We repeated each experiment at least three times to obtain the experimental data. Based on your comments, we have added related information in the Methods section.

Comment 1.5. How about the size stability under different temperature? Do IL leakage

occur.

Response: We thank the reviewer for this question. We have conducted the experiments to measure the size variations of the CSN ionogels under different temperatures. As shown in **Figure R4 (Supplementary Figure 11)**, after 24 hours at 100 °C or -30 °C, there is no change in the weight and morphology of the ionogel sample. Due to the strong interaction between PEO side chains of PEGMA and IL, IL in ionogels does not leak out. We have added the results to the revision (**Supplementary Figure 11**).

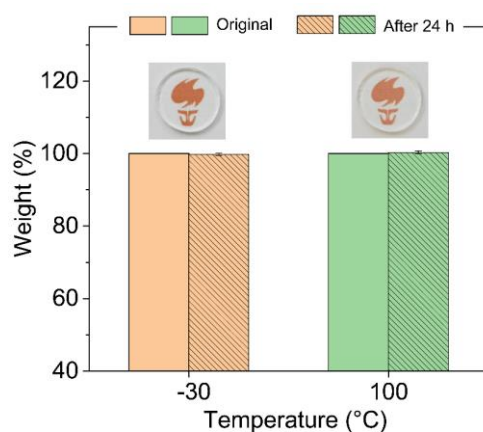


Figure R4 (Supplementary Figure 11). Weight change of ionogel samples after being stored at 100°C and -30°C for 24 h.

Comment 1.6. There are some grammar and codes errors. The manuscript is in need of a major proofreading/grammatical polishing. For example, In Fig.4b, “Pressue” should be “Pressure”.

Response: We thank the reviewer for pointing out the errors. Based on your comments, we have proofread the manuscript carefully and made corresponding corrections.

Reviewer #2 (Remarks to the Author):

The authors reported a bicontinuous nanostructured ionogel with high ionic conductivity, high stretchability, and superior 3D printability by introducing a photopolymerization-induced microphase separation strategy. This work is interesting and comprehensive in terms of the design of 3D printing and the application of ionotronic sensors, but some issues need to be answered.

Response: We thank the reviewer for taking precious time to review our paper and

giving us the constructive comments and suggestions.

The specific issues are as follows:

Comment 2.1. The authors mentioned that the ionogel without PEGMA shows macroscopic phase separation (Fig. 1f), so the SAXS experiment of the ionogel without PEGMA should also have a scattering peak (Fig. 1k). Similarly, the SEM image of ionogel without PEGMA should have a macroscopic phase-separated morphology (Fig. 1l).

Response: We thank the reviewer for raising this question. As shown in **Figure R5 (Supplementary Figure 2)**, the macroscopic phase separation occurs in the ionogel without PEGMA. It can be clearly seen that the macroscopic phase separation leads to white plaques which are the ionic liquid phase with the size at sub-millimeter scale (Figure R5a). In contrast, the ionogel with PEGMA does not show macroscopic phase separation (Figure R5b), but has bicontinuous microstructures with **nanoscale morphologies** due to photopolymerization induced microphase separation.

SAXS and SEM are the characterization tools used to observe features **at nanoscales**. For example, in Fig 1k, the scattering vector magnitude q ranges from $0.05 \sim 1 \text{ nm}^{-1}$. Thus, the feature size d of the microstructures can be observed in SAXS ranges from 6.3 to 125.7 nm based on the d - q relation $d = 2\pi/q$. Similarly, in Fig. 1k, the scale bar in the SEM images is **1 μm** . Therefore, the **sub-millimeter scale macroscopic phases** in ionogel with PEGMA **cannot be observed** in SAXS and SEM characterizations.

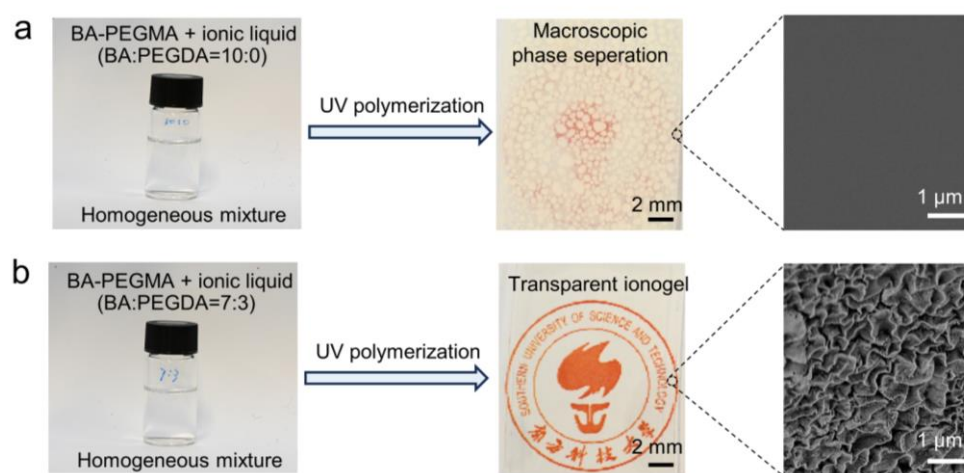


Figure R5 (Supplementary Figure 2). The photographs of the BA-PEGMA ionogel with different BA:PEGMA ratios. **a** BA:PEGMA = 10:0. **b** BA:PEGMA = 7:3.

Comment 2.2. In Fig. 2a-f, the content of PEGDA in the CSN ionogels is 0.2 wt.%. However, the study of the effect of PEGDA content on residual strain and elongation-at-break of the CSN ionogel was tested from 0.5 wt.% (Fig. 2g). The hysteresis of the CSN ionogel with 0.2 wt.% PEGDA should also be tested.

Response: We thank the reviewer for this suggestion. As shown in **Figure R6 (Supplementary Figure 8 and Fig. 2g)**, we have added the tests that investigate the residual strain and elongation-at-break for the CSN ionogel with 0.2 wt.% PEGDA. We have added the results to the revision (**Supplementary Figure 8 and Fig. 2g**).

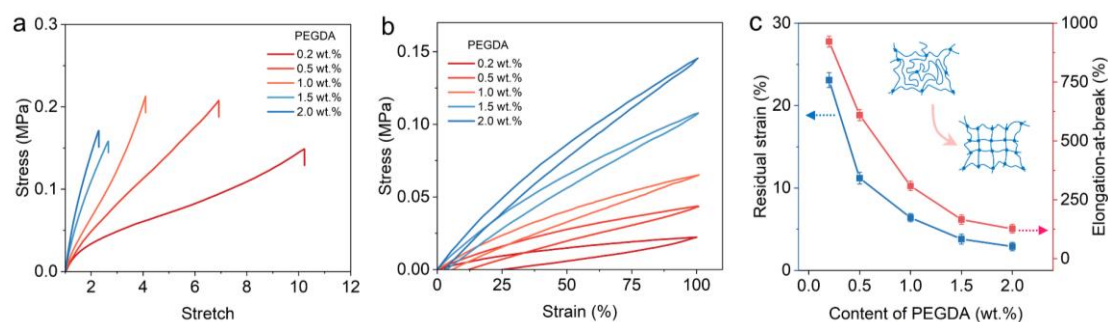


Figure R6 (Supplementary Figure 8 and Fig. 2g). **a** Stress–strain behavior of the CSN ionogel with different PEGDA content. **b** Cyclic stress-strain curves of the CSN ionogel with different PEGDA content. **c** Effect of PEGDA content on residual strain and elongation-at-break of the CSN ionogel.

Comment 2.2. The composition of the CSN ionogels tested is too complex and contextually inconsistent. For example, the ionogel in Fig. 2c has the highest conductivity with [EMIm][DCA] content of 70 wt.%, but the ionogel with [EMIm][DCA] content of 40 wt.% was chosen for hysteresis testing in Fig. 2g. In addition, the PEGDA content of the ionogels selected for the 3D printing section is not mentioned. It is recommended that the composition of the other components of the ionogels, except for the test component, be kept consistent and that the optimal ratio be selected for subsequent characterization.

Response: We thank the reviewer for this suggestion. The ionogels developed in this work are eventually used for 3D printing capacitive pressure sensors. Therefore, besides conductivity, the mechanical properties such as Young’s modulus and residual strain, and printability also other key factors that determine the performance of the 3D printed sensors.

Compared with the ionogel with 70 wt.% ionic liquid (conductivity: $3.23 \text{ S}\cdot\text{m}^{-1}$), the ionogel with 40 wt.% ionic liquid has relative lower conductivity (conductivity: $0.86 \text{ S}\cdot\text{m}^{-1}$, still higher than that of all the previously reported ionogels), but higher Young’s

modulus and lower residual strain (**Figure R7a (Fig. 2b)**). Therefore, in Figure 2g-i, we selected the ionogel with 40 wt.% ionic liquid to investigate the effect of PEGDA on residual strain and hysteresis. Based on the investigation, we conclude that the ionogel with 40 wt.% ionic liquid and 2 wt.% PEGDA has the lowest residual strain, and still can be stretched by 120%. In addition, as shown in **Figure R7b (Fig. 3c)**, compared with the ionogel with 70 wt.% ionic liquid, the one with 40 wt.% ionic liquid is more photo-reactive which ensures high-resolution microstructures from 3D printing. Thus, in the following of this work, we used the ionogel with 40 wt.% ionic liquid and 2 wt. % PEGDA to print all the sensors.

In the revision, we have added discussions on the reason of using the ionogel with 40 wt.% ionic liquid to investigate the effect of residual strain:

“For making high-performance ionic sensors, the ionogels are also required to have high elasticity and low hysteresis to ensure good stability and repeatability of detected signals. As shown in Fig. 2b and c, compared with the CSN ionogel with 70 wt.% [EMIm][DCA], the one with 40 wt.% [EMIm][DCA] has higher Young’s modulus (63 kPa) and reasonable high ionic conductivity ($0.86\text{ S}\cdot\text{m}^{-1}$) which are both favorable properties for ionic sensors. Thus, in the following work, we tune the stiffness and hysteresis by changing the PEGDA crosslinker content in the CSN ionogel with 40 wt.% [EMIm][DCA].”

We have added one sentence to emphasize that all the sensors are printed with the ionogel with 40 wt.% ionic liquid and 2 wt. % PEGDA:

“In the following work, we print ionic conductive structures and sensors by using the CSN ionogel precursor solution with 40 wt.% [EMIm][DCA] and 2 wt.% PEGDA which ensures high printability and conductivity.”

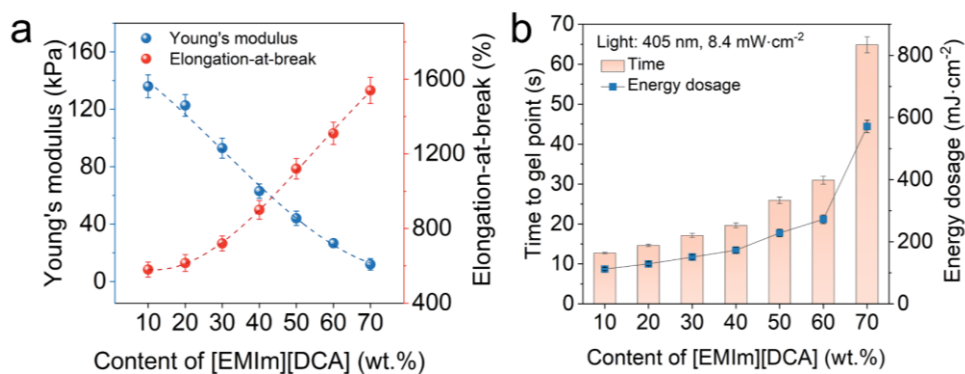


Figure R7 (Fig.2b and Fig.3c). **a** Effect of [EMIm][DCA] content on Young’s modulus and elongation-at-break of the CSN ionogels. **b** Effect of [EMIm][DCA]

content on time and energy dosage to gel point of the CSN ionogel.

Comment 2.4. The 3D printed ionogel sample in Fig. 3 has a porous structure, does it have an effect on its conductivity?

Response: We thank the reviewer for this question. If the conductivity refers to the intrinsic material property of the ability to conduct electric current, it does not change when the ionogel changes from bulk material to porous structure. If the conductivity refers to the ability of an ionogel structure to conduct electric current, it may change when the ionogel structure is different. As shown in **Figure R8**, we tested the resistance of ionogel with Gyroid structure and solid cubic structure. The resistance of ionogel with Gyroid structure is higher than that of the solid cubic one. This is because the relative density of the hollow structure is smaller than that of the solid structure.

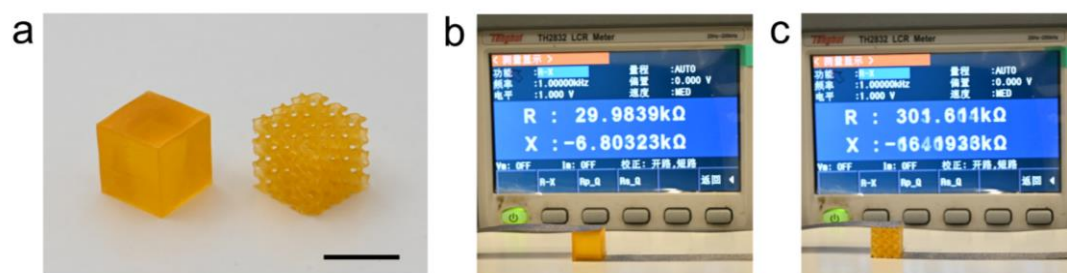


Figure R8. **a** Photograph of 3D printed solid cube structure and Gyroid structure with CSN ionogel. Scale bar: 10 mm. **b** The resistance of ionogel with cube structure. **c** The resistance of ionogel with Gyroid structure.

Comment 2.5. The 3D printed sample in the manuscript is too simple and more complex samples should be shown.

Response: We thank the reviewer for this suggestion. As shown in **Figure R9** (**Fig. 3e** and **Supplementary Figure 15**), a Gyroid structure, a Kelvin foam structure, and an Octet truss structure have been 3D printed.

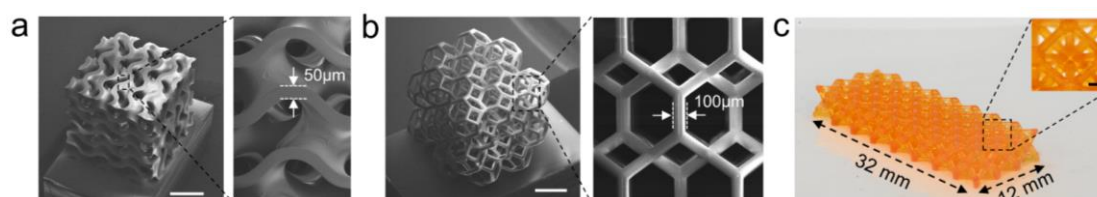


Figure R9 (**Fig. 3e** and **Supplementary Figure 15**). **a** SEM image of a Gyroid structure. Scale bar: 500 μm. **b** SEM image of a Kelvin foam structure. Scale bar: 1 mm. **c** An Octet truss structure. Scale bar: 1 mm.

Comment 2.6. Minor issue: The explanation of ΔU_{mix} on page 4 is repeated twice.

Response: We thank the reviewer for pointing out this mistake. We have revised the sentence accordingly.

Reviewer #3 (Remarks to the Author):

Overall this paper reflecting significant amounts of well-executed experiments and demonstrations work and the subject matter is of scientific and technological interest. However, there are issues that should be addressed.

Although there is a discussion of the ionogel synthesis and structure, largely based on previously published work, a significant fraction of this paper covers interesting demonstrations and environmental tests accompanied by significant numbers of figures. These demonstrations and the larger amount of data are outside what this reviewer would normally associate with Nature Communications and may be better placed in engineering and design journals.

Focusing on the background, ionogel synthesis, structure and characterization sections there are some general issues:

Response: We thank the reviewer for taking precious time to review our paper and giving us the constructive comments and suggestions.

Comment 3.1. There is confusion over the terminology and use of microstructure, nanostructure and microphase

Response: we thank the reviewer for this comment. **Microstructure** refers to the structure realized by DLP 3D printing. The feature size of the microstructure is about ~ 10 to $100 \mu\text{m}$. In the context, microstructure appears in Fig.3 and Fig. 4 along with the words “3D printing”, “manufacturing”, “fabrication”. **Nanostructure** refers to the bicontinuous nanostructure resulted from photopolymerization induced microphase separation. Nanostructure is discussed in Fig. 1h-i. The feature size of the nanostructure is $\sim 10 \text{ nm}$. **Microphase** appears in the context of **Polymerization induced microphase separation** which has been well studied by Timothy P. Lodge and his co-workers (Schulze M W et al., Nano Letters, 2014; Chopade S A et al., ACS Applied Materials & Interfaces, 2016, 2017). In this work, the microphases are formed during photopolymerization process, and construct the nanostructures in Fig. 1h-i.

Reference:

Schulze M W, McIntosh L D, Hillmyer M A, et al. High-modulus, high-conductivity nanostructured polymer electrolyte membranes via polymerization-induced phase separation. *Nano letters*, **14**, 122-126 (2014).

Chopade S A, So S, Hillmyer M A, et al. Anhydrous proton conducting polymer electrolyte membranes via polymerization-induced microphase separation. *ACS Applied Materials & Interfaces*, **8**, 6200-6210 (2016).

Chopade S A, Au J G, Li Z, et al. Robust polymer electrolyte membranes with high ambient-temperature lithium-ion conductivity via polymerization-induced microphase separation. *ACS applied materials & interfaces*, **9**, 14561-14565 (2017).

Comment 3.2. In the second paragraph of the introduction and in the SI, the authors claim that "the currently printed ionogel sensors exhibit neither high resolution nor remarkable sensing capabilities (Table S1). The author's should consider additional work on 3D printed ionogels here. There are reports that demonstrate significantly higher dR/R than in the experiments outline in the paper, high elongation and good stability using BMIM/BF₄ base dmaterials: DOI 10.1088/1361-6528/ab2440

Response: We thank the reviewer for the comment. The claim that "the currently printed ionogel sensors exhibit neither high resolution nor remarkable sensing capabilities" appears in the context, "However, despite a few recent explorations on developing UV curable ionogels for **DLP 3D printing**, the currently printed ionogel sensors exhibit neither high resolution nor remarkable sensing capabilities (Table S1)". Thus, the discussion is limited to the ionogel sensors printed by DLP 3D printing.

We thank the reviewer for suggesting us the paper published in *Nanotechnology* (2019). However, after carefully reading the paper, we found that the sensors in that work were formed by using direct ink writing (DIW) to write ionogel lines in the partially cured PDMS. Since the printing technology is not DLP, we decide to not include this paper for comparison.

Comment 3.3. There is some apparent contradiction between claims of homogenous structure versus diagrams and micrographs of micron scale heterogeneity in the gel structure as seen in Figure 1. as well there appears to be a mismatch or attribution of lengthscales in SAXS versus SEM as shown in Figures j,k and l. The SAXS shows a lengthsh scale of 10 nm while the phase separation of the samples with PGMEA show a

much larger microstructure in the SEM. Additional explanation would improve this.

Response: We thank the reviewer for the comment. We use Figure 1e to demonstrate the role of PEGMA to facilitate a homogeneous mixture between polymer network and ionic liquid (IL) after photopolymerization.

As shown in **Figure R10a (Figure 1e and Supplementary Figure 2)**, when the polymer network without PEGMA, photopolymerization leads to **macroscopic** phase separation. The ionogel to be translucent with low transmittance where the submillimeter IL (white plaques) which can be clearly seen through naked eye. Fig. 1f illustrates this **macroscopic** phase separation which clearly states the BA:PEGMA mass ratio is 10:0.

As shown in **Figure R10b (Figure 1e and Supplementary Figure 2)**, the addition of PEGMA to facilitate a homogeneous mixture between polymer network and ionic liquid after photopolymerization, and a transparent ionogel is achieved. Figure 1g illustrates this homogeneous ionogel when BA:PEGMA is 7:3.

Regarding to the SEM and SAXS characterizations in Fig. 1j, k and l, we use them to verify the existence of the bicontinuous nanostructure resulted from photopolymerization induced **microphase separation** with the introduction of PEGMA. Different from **macroscopic phase separation** which forms the BA phase and IL phase at **sub-millimeter scale**, the photopolymerization induced **microphase separation** generates the nanostructures formed by the BA phase and the PEGMA-IL phase **at the scale of ~ 10 nm** which can only be observed by SEM and SAXS. In Fig. 1k, the SAXS scattering intensity profile of the BA-PEGMA ionogel shows a single broad scattering peak (q from 0.041 to 1.22 nm with $q^* = 0.1 \text{ nm}^{-1}$) indicating the nanostructured morphology resulted from the microphase separation. Based on the d - q relation ($d = 2\pi/q$), the feature size of nanostructure ranges from 5 to 153 nm, which agrees well with the feature size of the nanostructure observed in SEM in Figure 1l.

In the revision, we have modified the discussion part for SAXS results:

“In Fig. 1k, the SAXS scattering intensity profile of the BA-PEGMA ionogel shows a single broad scattering peak (the magnitude of the scattering vector q ranging from 0.041 to 1.22 nm with the peak point $q^ = 0.1 \text{ nm}^{-1}$) indicating the nanostructured morphology resulted from the microphase separation. Based on d - q relation ($d = 2\pi/q$)^{35, 37}, the feature size d of nanostructure ranges from 5 to 153 nm. In contrast, the SAXS profile of the BA ionogel shows no peak indicating no nanostructure existing in the BA ionogel.”*

In addition, we use the Flory-Huggins model to explain the role of PEGMA to facilitate a homogeneous mixture between polymer network and ionic liquid (IL) after photopolymerization. The detailed explanations are highlighted in the revision and Eq. S1-S2 of Supplementary Materials.

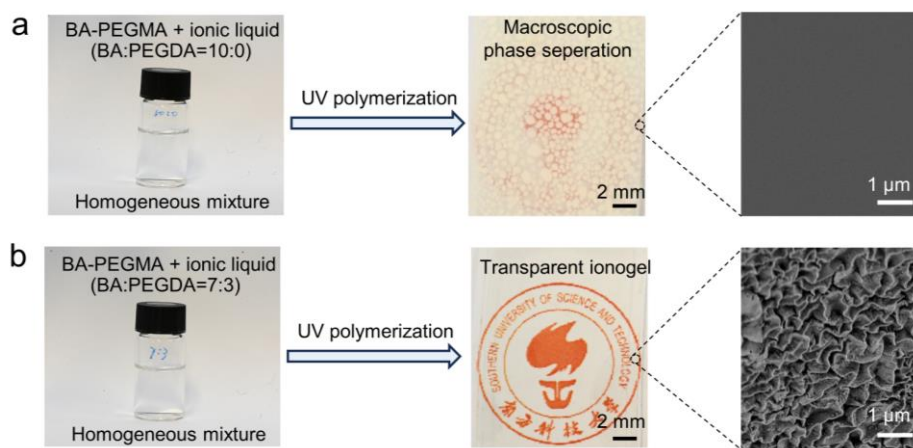


Figure R10 (Supplementary Figure 2). The photographs of the BA-PEGMA ionogel with different BA:PEGMA ratios before and after UV polymerization. a BA:PEGMA = 10:0. b BA:PEGMA = 7:3.

Comment 3.4. the use of PEO-containing salt or ionic liquid based gels is well known and the observation of higher conductivity, as observed here, with the introduction of a material like PEGMEA could be attributed to basic solvation and not a special microstructure. It is unclear that the claims made for the improved performance reported here are not novel.

Response: We thank the reviewer for this comment. **The goal of this work is to develop a highly conductive, stretchable, UV curable ionogels for 3D printing capacitive sensors with superior performance. To achieve high conductivity without sacrificing its printability and mechanical properties,** we propose a photopolymerization-induced microphase separation strategy to prepare BA-PEGMA homogeneous ionogel where PEGMA plays the key role to form continuous microchannels that percolate in the polymer network to facilitate ion transportation for achieving high conductivity.

Compared with previous reports, this work advances stretchable and UV curable ionogel and resulted high-performance capacitive sensors by 3D printing the CSN ionogels in the following four aspects:

(i) **Excellent Property and Printability.** As summarized in **Figure R11a**, the CSN

ionogel developed in this work exhibit excellent physical properties including high ionic conductivity (over $3 \text{ S}\cdot\text{m}^{-1}$, which is highest among all the ionic conductors), high stretchability (over 1500%), low degree of hysteresis (degree of hysteresis: 0.4% at 50% strain), wide-temperature-range thermostability ($-72 \sim 250^\circ\text{C}$), and humidity tolerance. Moreover, its high compatibility with DLP 3D printing allows us to fabricate ionogel structures with extremely high resolution (up to $5 \mu\text{m}$ demonstrated in **Figure R11b**). The excellent physical properties and printability allow us to print CNS ionogel structure which can work under extreme conditions. For example, the 3D printed CNS lattice structure can be twisted at -40°C (**Figure R11c**) and still conductive at -30°C (**Figure R11d**).

(ii) **Bicontinuous Nanostructures for High Conductivity.** We propose a photopolymerization-induced microphase separation strategy to prepare BA-PEGMA homogeneous ionogel where PEGMA plays the key role to form continuous microchannels (**Figure R11e and f**) that percolate in the polymer network to facilitate ion transportation (**Figure R11g**) for achieving high conductivity. To verify the existence of the bicontinuous morphology resulted from the introduction of PEGMA, we perform SAXS (**Figure R11h**) and SEM experiments (**Figure R11i**) on the ionogel samples with and without PEGDMA.

(iii) **High-performance Capacitive Sensors with 3D Printed Microstructures.** Exploiting such high conductivity and printability, we can manufacture electron double layer (EDL) - based capacitive sensors (**Figure R11j**) where the geometries of the CSN ionogel layers (**Figure R11k**) can be rationally designed to achieve superior sensing performances such as high sensitivity, high linearity, fast dynamic response, and excellent cyclic stability (**Figure R11l and m**).

(iv) **3D Printed Capacitive Sensors for Real-time Robotic Sensing.** Integrated with 3D printed sensors, robotic hands can realize the tactile perception as humans and interact with the environment. As shown in **Figure R11n**, a robotic gripper is equipped with an array of printed sensors which response differently when the grippers grab different objects (**Figure R11o**). We can also fabricate a pressure sensor array composed of 4×4 sensing units which can be attached to a glove and responses instantaneously to displace the corresponding contact pressure distributions (**Figure R11p**).

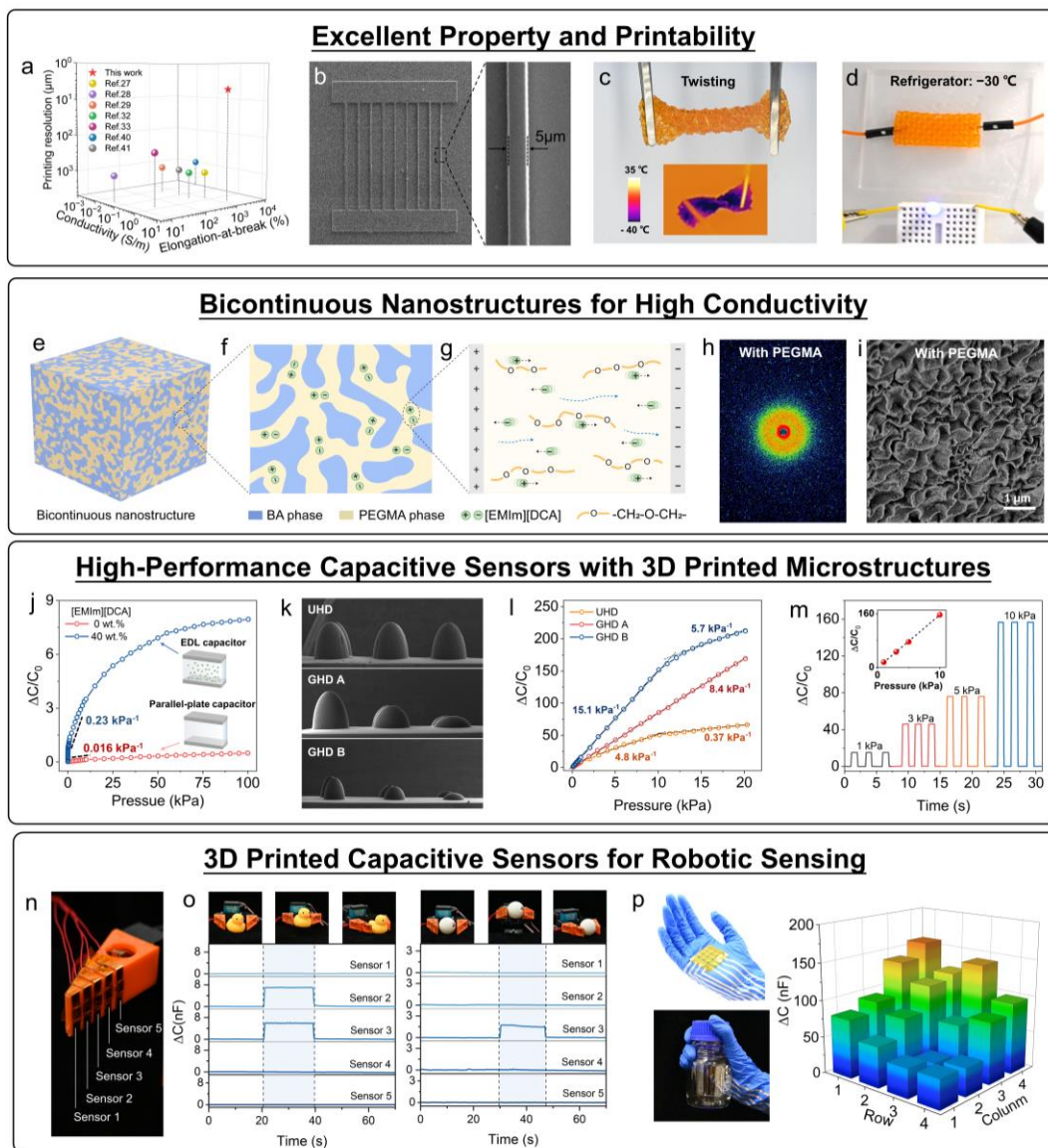


Figure R11. Properties, mechanisms, applications of the 3D printable CNS ionogels developed in this work. **a** Comparisons on printing resolution, conductivity, and elongation-at-break between the CSN ionogel in this work and other reported 3D printing ionogels. **b** SEM image of a 3D printed ionogel sample with ultra-thin horizontal width. **c** The CSN ionogel lattice structure is highly deformable at $-30\text{ }^{\circ}\text{C}$. **d** The lattice structure exhibiting good electrical conductivity at $-30\text{ }^{\circ}\text{C}$. **e** Illustration of the bicontinuous nanostructures. **f** Illustration of the microphase-separated structure within the CSN ionogel. **g** Schematic presentation of ionic pathway along the PEGMA phase. **h** 2D SAXS scattering patterns for ionogel with PEGMA. **i** SEM image for the ionogel with PEGMA. **j** Comparison on the $\Delta C/C_0 - P$ relation between the parallel-plate capacitor and the CSN ionogel-based EDL capacitor. **k** SEM images of the dome shaped CSN ionogels with different geometries. **l** Comparison on the $\Delta C/C_0 - P$ relation of the CSN ionogel capacitive sensors with the corresponding microstructures from **g**. **m** Capacitance response of the printed CSN ionogel sensor. **n** Robotic hand integrated

with an array of five CSN ionogel sensors. **o** Singal variations of the CSN ionogel sensor array when the gripper grabbing different objects. **p** The pressure distribution of a multiplex pressure sensor array on the glove when grabbing a bottle.

Comment 3.5. The author's state in the 'Thermomechanical and electrical properties of the CSN ionogel' section "To demonstrate the high conductivity of the ionogel with [EMIm][DCA], as shown in Fig. 2e, only 4 V voltage can light up a light-emitting diode (LED) bulb in the circuit where the ionogel with [EMIm][DCA] is used as conductor. In comparison, the 4 V circuit with the LiTFSI-based conductor fails to light the LED bulb due to its low conductivity."

Ionogels are often not used in DC biasing applications such as an LED which is a rectifying diode, as there is a finite amount of charge carrying capability with ion motion, could be layer formation and/or electrochemistry takes place at the ionogel interface with the electrodes. Differences in running an LED in DC current mode could be due to other factors and AC biasing with symmetric electrodes is more rellevant and the conclusions claimed here by the authors may not be appropriate.

Response: We thank the reviewer for this comment. We agree with the reviewer that "Ionogels are often not used in DC biasing applications". In fact, in the capacitive sensor applications in Figures 4-6, **all the capacitive signals** are achieved through **AC electric field** with the testing frequency of 1 kHz. The details on the signal collection are highlighted in the Characterizations of Methods section:

"The capacitance and resistance were measured by using an LCR meter in a frequency of 1 kHz with a 1 V AC signal..."

The goal of Fig. 2e is to demonstrate the high conductivity of the developed CSN ionogel with [EMIm][DCA]. From our observation, a 4 V DC does light up a LED bulk in the circuit where the ionogel with [EMIm][DCA] is used as conductor.

Based on the reviewer's suggestion, as shown in **Figure R12**, we conduct the conductivity between the ionogel and LiTFSI-based conductor in an AC electric field. However, to light up the three LED mini dots in the circuit with [EMIm][DCA] ionogel requires a 150 V AC which fails to light up the three LED mini dots in the circuit with LiTFSI conductor.

Considering the goal of Fig. 2e is to demonstrate the high conductivity of developed [EMIm][DCA] ionogel, we decide to keep the demonstration where a 4V DC is applied to the two circuits.

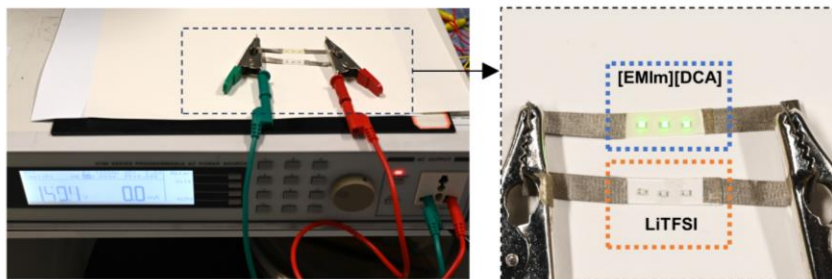


Figure R12. Demonstration to compare the conductivity between the CSN ionogel with [EMIm][DCA] and the ionic conductor with LiTFSI.

Comment 3.6. In the first paragraph of the 'Working mechanism of the 3D printed capacitive sensor with CSN ionogels,' The length scales in the functional description are confusing and not substantiated in this work. In any case, EC mechanisms are well known and do not need to be repeated here. Citations of appropriate sources could better achieve the descriptive aims of the author's here.

Response: We thank the reviewer for the suggestion. Here, we have to emphasize that the printed sensors with CSN ionogel are capacitive sensors. There is only a voltage applied to the two electrodes, but **neither current running through the sensor nor electrochemical (EC) taking place inside the sensor**. Since there is no EC taking place inside the sensor, we respectfully disagree with the reviewer's statement "EC mechanisms are well known and do not need to be repeated here".

The purpose of the first paragraph of the "Working mechanism of the 3D printed capacitive sensor with CSN ionogels" is to tell the readers that the mechanism of capacitive sensor in this work is electron double layer (EDL) which has 1000 times higher capacitance than that of the traditional parallel-plate capacitive sensor, and explain the reasons why EDL capacitive sensor has much higher capacitance. According to the reviewer's comment, we have revised the paragraph and reduced its length.

Comment 3.7. Overall this paper presents one principle ionogel synthesis and properties section and some of these conclusions in that section may need significant revision with regards to the issues discussed above.

Response: we thank the review for this comment. According to the comments from all the reviewers, we have revised the manuscript significantly.

We want to emphasize that this paper is **much more than a paper of ionogel synthesis**

and material property characterization. This work develops the stretchable and UV curable ionogels that are used to 3D print capacitive sensors with high performance. The detailed contributions of this work have been summarized in the response to **Comment 3.4.**

Comment 3.8. Also, although demonstrations can contribute to the impact and conclusions of the paper, the amount of demonstrations here is large and not all add significantly to the scientific aspect of a Nature Communication article.

The authors might consider breaking this up into multiple journal articles and potentially a journal where the implementation demonstrations may be a better fit.

Response: we thank the review for this comment. To goal of this work is to develop the stretchable and UV curable ionogels for 3D printing capacitive sensors with high performance. The demonstrations in Figure 5 and Figure 6 are **all real-time monitoring of pressure signals** (Movie S1 - S5), which well reflect the high performances of the printed sensors including high sensitivity, high linearity, fast dynamic response, excellent cyclic stability, and wide operating temperature range.

Reviewer #4 (Remarks to the Author):

The authors have done a great job on the development of highly conductive and stretchable nanostructured ionogels using DLP 3D printing. They further apply the printed sensor to various applications (pressure sensors, monitoring real-time physiological signals, robotic gripper) to demonstrate the superior sensing performance of the newly proposed ionogels.

This study represents a significant contribution to the field of ionogels and ionotronics. Through its rigorous experimentation, insightful analysis, and clear presentation of findings, the study advances our understanding of ionogel materials and their potential applications, paving the way for further innovation in this research field. However, the manuscript could benefit from minor changes before publication. Please consider the following comments:

Response: We thank the reviewer for taking precious time to review our paper and giving us the constructive comments and suggestions.

Comment 4.1. In Figure 2, the properties of the ionogels are analyzed based on the IL content. However, the TGA curves of the ionogels fabricated with 50%, 60%, and 70% of the ionic liquid [EMIm][DCA] are absent (Fig. 2k). No rationale is provided to explain the omission of these results.

Response: We thank the reviewer for this suggestion. In the revision, as shown in **Figure R13 (Fig. 2k)**, we have added the TGA curves of the ionogels fabricated with 50%, 60%, and 70% of the ionic liquid [EMIm][DCA].

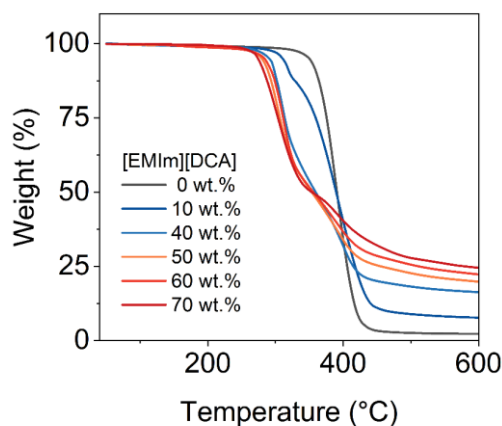


Figure R13 (Fig. 2k). Thermogravimetric curves of the CSN ionogel with different [EMIm][DCA] contents.

Comment 4.2. As shown in Fig. 2l, the ionogel and the LiTFSI-based conductor were placed in a humid environment and their weight variations are compared. The results obtained are somehow expected because an ionic liquid ([EMIm][DCA]) and a very hygroscopic salt (LiTFSI) are being compared. This discussion could benefit by including the results for the ionogel composed of [Emim][Otf], an ionic liquid that also allows the preparation of ionogel materials with good conductivity properties.

Response: We thank the reviewer for this suggestion. In the revision, as shown in **Figure R14 (Supplementary Figure 7 and Supplementary Figure 12)**, we have tested the weight change of the P(BA-co-PEGMA) samples with different ionic liquid including [EMIm][OTF], [EMIm][TFSI], [BVIIm][BF₄], [BVIIm][TFSI] in humid environment. No weight change has been observed on the ionogel sample over the 7 days.

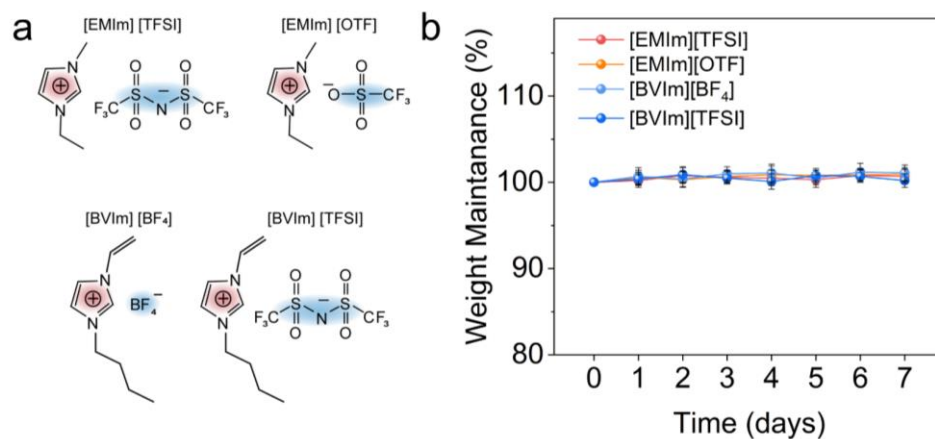


Figure R14 (Supplementary Figure 7 and Supplementary Figure 12). **a** Detailed chemical structure of [EMIm][TFSI], [EMIm][OTF], [BVIIm][BF₄] and [BVIIm][TFSI]. **b** Weight change of the P(BA-co-PEGMA) samples with different ionic conductive component in humid environments.

Comment 4.3. The authors state that the prepared ionogels achieved high ionic conductivity (over 3 S m⁻¹) and high stretchability (over 1500 %), as those are the values shown by the ionogel with circa 70 % IL (maximum IL amount used to optimize the ionogel materials before the 3D printing study). However, in the end, the printed ionogel sensor is prepared with 40 %IL and this ionogel does not have 3.23 (S m⁻¹) or 1500% elongation-at-break as described in Table S2 and in some parts of the manuscript text.

Response: We thank the reviewer for this question. The ionogels developed in this work are eventually used for 3D printing capacitive pressure sensors. Therefore, besides conductivity, the mechanical properties (Young's modulus and residual strain) and printability are the other key factors that determine the performance of the 3D printed sensors.

Compared with the ionogel with 70 wt.% ionic liquid (conductivity: 3.23 S·m⁻¹), the ionogel with 40 wt.% ionic liquid has relative lower conductivity (conductivity: 0.86 S·m⁻¹, higher than that of the previously reported ionogels), but higher Young's modulus and lower residual strain. Therefore, in Figure 2g-i, we optimize the residual strain and hysteresis based on the ionogel with 40 wt.% ionic liquid. In addition, as shown in **Figure R15 (Fig. 3b, Supplementary Figure 13 and Fig. 3c)**, we performed in-situ photo-rheological characterizations to investigate the photo-reactivity of the ionogel precursor solutions. We identify the time to gel point (gelation time) when the storage modulus curve intersects to the loss modulus curve. The time to gel point increases with the increase of ionic liquid content. Compared with the ionogel with 70 wt.% ionic

liquid, the one with 40 wt.% ionic liquid is more photo-reactive which ensures high-resolution microstructures from 3D printing.

Based on above considerations, we used the ionogel with 40 wt.% ionic liquid and 2 wt. % PEGDA to print all the sensors.

In the revision, we have added discussions on the reason of using the ionogel with 40 wt.% ionic liquid to investigate the effect of residual strain:

“For making high-performance ionic sensors, the ionogels are also required to have high elasticity and low hysteresis to ensure good stability and repeatability of detected signals. As shown in Fig. 2b and c, compared with the CSN ionogel with 70 wt.% [EMIm][DCA], the one with 40 wt.% [EMIm][DCA] has higher Young’s modulus (63 kPa) and reasonable high ionic conductivity ($0.86\text{ S}\cdot\text{m}^{-1}$) which are both favorable properties for ionic sensors. Thus, in the following work, we tune the stiffness and hysteresis by changing the PEGDA crosslinker content in the CSN ionogel with 40 wt.% [EMIm][DCA].”

We have added one sentence to emphasize that all the sensors are printed with the ionogel with 40 wt.% ionic liquid and 2 wt. % PEGDA:

“In the following work, we print ionic conductive structures and sensors by using the CSN ionogel precursor solution with 40 wt.% [EMIm][DCA] and 2 wt.% PEGDA which ensures high printability and conductivity.”

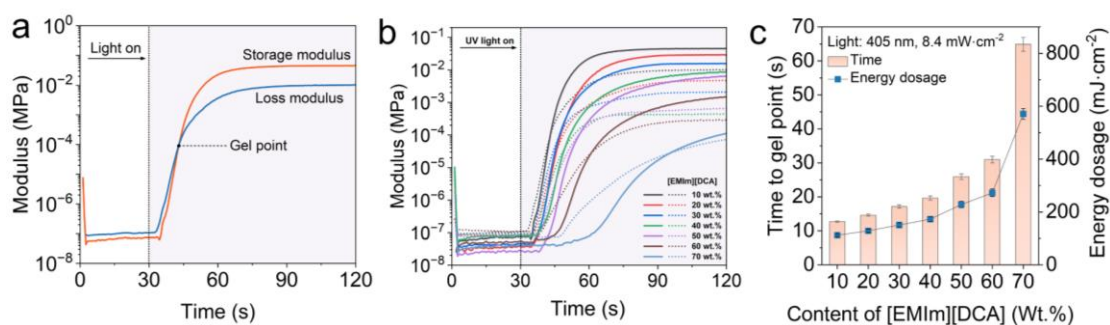


Figure R15 (Fig. 3b, Supplementary Figure 13 and Fig. 3c). **a** Photophysical test to identify the gel point of the CSN ionogel. **b** Photophysical test during light exposures of CSN ionogel precursor solution with different content of [EMIm][DCA]. (Solid curve: storage modulus, Dotted curve: loss modulus). **c** Effect of [EMIm][DCA] content on time and energy dosage to gel point of the CSN ionogel.

Comment 4.4. have observed that upon comparing the "Abstract" and "Conclusion" sections, a considerable portion, approximately 45%, of the content in the conclusion appears to be a repetition or variation of the text used in the Abstract. This redundancy signifies a notable overlap between the two sections, implying a substantial similarity that is not recommended.

Response: we thank the reviewer for this comment. In the revision, we have significantly revised both abstract and conclusion to avoid the repetition between them.

Abstract:

“Ionogels are promising material candidates for ionotronics due to their excellent ionic conductivity, stretchability, and thermal stability. However, it is challenging to develop 3D printable ionogels with both excellent electrical and mechanical properties. Here, we report a highly conductive and stretchable nanostructured (CSN) for 3D printing ionotronic sensors. We propose the photopolymerization-induced microphase separation strategy to prepare the CSN ionogels comprising continuous conducting nanochannels intertwined with cross-linked polymeric framework. The resultant CSN ionogels simultaneously achieves high ionic conductivity (over $3\text{ S}\cdot\text{m}^{-1}$), high stretchability (over 1500%), low degree of hysteresis (0.4% at 50% strain), wide-temperature-range thermostability ($-72 \sim 250\text{ }^{\circ}\text{C}$). Moreover, its high compatible with DLP 3D printing enables the fabrication of complex ionogel microstructures with high resolution (up to $5\text{ }\mu\text{m}$), which allows us to manufacture capacitive sensors with superior sensing performances. The proposed CSN ionogel paves a new efficient way to manufacture the next-generation capacitive sensors with enhanced performance.”

Conclusion:

“In this work, we develop the CSN ionogels for 3D printing capacitive sensors. We propose a photopolymerization-induced microphase separation strategy to prepare BA-PEGMA homogeneous ionogel where PEGMA moieties form continuous microchannels that percolate in the polymer network to facilitate ion transportation. This strategy allows us to endow ionogels with high conductivity without sacrificing the printability and mechanical properties. The developed CSN ionogels exhibit high ionic conductivity, high stretchability, low degree of hysteresis, wide-temperature-range thermostability, and humidity tolerance. More importantly, due to the high compatible with DLP 3D printing, we can fabricate complex CSN ionogel microstructures with high resolution.

We 3D print EDL capacitive sensors with superior sensing performances such as high sensitivity, high linearity, fast dynamic response, excellent cyclic stability, and wide operating temperature range. We make several demonstrations to exhibit the superior sensing performance of the 3D printed sensors. We use the printed sensor to monitor the real-time human deep breath and swallow, as well as pulsation. We integrate the printed sensors onto a robotic gripper which can sense grasping signals in a wide temperature range from -30 °C to 150 °C, and collect different combination of signals while grasping various objects. We further build a pressure sensor array composed of 4 × 4 printed sensors for real-time high resolution pressure mapping. The proposed CSN ionogels pave a new efficient way to manufacture ionogel-based capacitive sensors with enhanced performances.”

Reviewer #5 (Remarks to the Author):

In this manuscript, the authors report a photopolymerization-induced microphase separation strategy to prepare a bicontinuous nanostructured ionogel that simultaneously achieves high ionic conductivity, high stretchability, low degree of hysteresis, and other excellent properties. Moreover, the developed ionogel exhibits high compatible of with DLP 3D printing that allows the authors to fabricate EDL - based capacitive sensors with superior sensing performances. The authors present a few applications to demonstrate these superior sensing performances of the 3D printed ionogel sensors. It is a well written manuscript that reports a high performance ionogel for 3D printing flexible electronic sensors. Therefore, it is recommended for publication in Nature Communications after addressing the following minor issues.

Response: We thank the reviewer for taking precious time to review our paper and giving us the constructive comments and suggestions.

Comment 5.1. In this manuscript, the authors have studied the effect of PEGMA content on the transmittance and conductivity of ionogels. What is the effect of PEGMA content on the ionogel mechanical properties?

Response: We thank the reviewer for this suggestion. In the revision (**Figure R16, Supplementary Figure 1**), we have added the experimental results that studies the effect of PEGMA content on the ionogel mechanical properties.

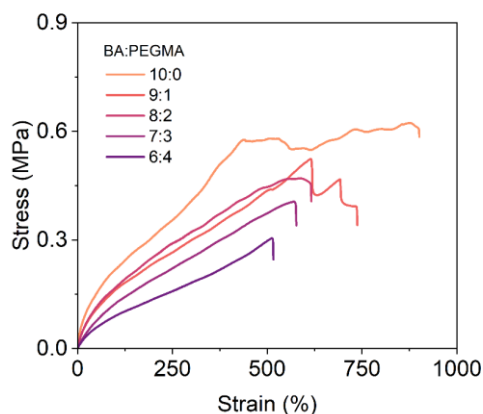


Figure R16 (Supplementary Figure 1). Stress-strain behavior of the CSN ionogel with different PEGMA contents.

Comment 5.2. For capacitive sensor with ionogels, the thickness of the ionogel layers should be given.

Response: We thank the reviewer for this suggestion. The thickness of the ionogel layers is 700 μm . In the revision, we have had the details on the thickness in Methods section.

Comment 5.3. The last sentence in abstract sounds misleading. Please revise this sentence.

Response: We thank the reviewer for this suggestion. We have thoroughly revised the abstract.

Comment 5.4. On page 2 line 50-52, in the definition of ionic liquid, the last “, and liquid” seems redundant, or does not appear at the right place.

Response: We thank the reviewer for this suggestion. We have revised the sentence accordingly.

Comment 5.5. On page 4 line 120, ΔU_{mix} is introduced twice but ΔS_{mix} is not introduced.

Response: We thank the reviewer for pointing out this mistake. We have revised this mistake.

Comment 5.6. On page 6 line 159, unit of molecular weight should be written.

Response: We thank the reviewer for pointing out this mistake. We have added the corresponding unit.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The authors addressed all the issues properly. The manuscript can be accepted now.

Reviewer #2 (Remarks to the Author):

It has been well revised, and can be accepted

Reviewer #3 (Remarks to the Author):

Comment 3.1.

The authors reiterated the issues in the original text without sufficient proposed changes. The term 'Microstructure' should not be used to describe a digitally printed designed or mechanical structure of a printed part. "Microstructure" is a well-used and recognized term across materials-related fields that refers to structure within the material itself ie. Crystalline phases, morphology and texture, compositional variations, etc. Even within the 3D printing of materials field 'microstructure' is understood as such. An internet search of the term 'microstructure' clearly shows what is meant by the term. A recent example is the nuanced distinctions between what is known as microstructure (materials substructure) and printed structure definition here in this Nature Comms article:

Gao, S., Li, Z., Van Petegem, S. et al. Additive manufacturing of alloys with programmable microstructure and properties. Nat Commun 14, 6752 (2023).
: <https://www.nature.com/articles/s41467-023-42326-y>

Comment 3.2.

"the currently printed ionogel sensors exhibit neither high resolution nor remarkable sensing capabilities" appears in the context, "However, despite a few recent explorations on developing UV curable ionogels for DLP 3D printing, the currently printed ionogel sensors exhibit neither high resolution nor remarkable sensing capabilities (Table S1)".

This is still unclear and could be misleading. If the author's wish to make negative claims about the specific prior art around DLP 3D printed sensors, they should do that more clearly with the scope of their comments made clear. One way to do this would be to revise the last quote sentence above to read:

However, despite a few recent explorations on developing UV curable ionogels, currently, DLP 3D printed ionogel sensors exhibit neither high resolution nor remarkable sensing capabilities (Table S1)".

Comment 3.3

As shown in Figure R10b (Figure 1e and Supplementary Figure 2), the addition of PEGMA to facilitate a homogeneous mixture between polymer network and ionic liquid after photopolymerization, and a transparent ionogel is achieved. Figure 1g illustrates this homogeneous ionogel when BA:PEGMA is 7:3.

The complex bicontinuous phase structure shown in Figure 1g is very clearly not a homogenous structure but a composite structure with clearly defined inhomogeneity as pictured with very discontinuous domains of different compositions. The addition of PEMA may have reduced the lengthscale of the materials phase separation microstructure but it is clearly not a homogenous phase. The homogenous terminology should be corrected to not imply something that is not shown.

This reviewer appreciates the edits and clarifications to the manuscript around the SEM/SAXS

issues in the original Comment 3.4

Comment 3.4.

Reviewer 3: "the use of PEO-containing salt or ionic liquid based gels is well known and the observation of higher conductivity, as observed here, with the introduction of a material like PEGMEA could be attributed to basic solvation and not a special microstructure. It is unclear that the claims made for the improved performance reported here are not novel"

The authors response to questions about the basic principle underlying the properties of the capacitors developed here is insufficient. Leaning on the many nice demonstrations and devices printed does not resolve the issue. The addition of PEGMEA could result in the observed performance for reasons other than the author's claim. The incomplete or possibly incorrect description of the principle at work is not consistent, in this reviewer's opinion, consistent with the standards in the standards for publication.

Comment 3.5

Considering the goal of Fig. 2e is to demonstrate the high conductivity of developed [EMIm][DCA] ionogel, we decide to keep the demonstration where a 4V DC is applied to the two circuits.

If there is a true steady state DC current through a capacitor of any significant amount (enough current to continuously light an LED in the circuit contracted to demonstrate an effect would be 'significant'). Other sources of continuous current would be (1) electrochemical side reactions, typically at the electrode that are often irreversible and undesirable (2) some continuous conductive path through the capacitor, or (3) the authors have chosen to show this demonstration for only a short 'DC' period of time.

In all cases, the publishing of this LED demo in this context in its current form is misleading as it implies a usable DC conductivity and makes the picture less credible than just showing the ionic conductivity results.

Comment 3.6.

It may be that the authors are unfamiliar with the standard and broadly excepted meaning and principles of electrochemical capacitors and the mechanisms presented in the paper. The structures shown and the definitions implied are very much ECs . An "EC" can be generally defined as "Electrochemical capacitors (supercapacitors) consist of two electrodes separated by an ion-permeable membrane (separator), and an electrolyte ionically connecting both electrodes." Which is almost certainly happening here. The authors refer to an "EDL" mechanism. EDL or Electric Double Layer capacitors are absolutely electrochemical capacitors. The author' could refer to the literature on the subject, for example (Simon, P., Gogotsi, Y. Materials for electrochemical capacitors. Nature Mater 7, 845-854 (2008)) that correctly states "Electrochemical capacitors, also called supercapacitors, store energy using either ion adsorption (electrochemical double layer capacitors) or fast surface redox reactions (pseudo-capacitors)." Depending on the time period for the "DC" LED result presented in the paper and discussed below, the ECs demonstrated in this article are electrochemical capacitors that me be be exhibiting both double layer capacitance and redox reactions, whether intended or not.

As far as the use of AC, the vast majority of applications of capacitors are for AC signals. It would be a great surprise to the entire field of electrical engineering that there is no current in an AC circuit. At steady state there may be no DC current but to suggest there is no current flowing would be implying there is no relevance of ionic conductivity. In fact the authors own LED demonstration, shown in their own Figure 3., which has misleading implications also, actually claims powering a DC LED. It is unfortunate that the authors still appear to be choosing to present a demonstration which is inconsistent with the operating principles assumed for the operating principles in the rest of the article and that is misleading or presents unanswered questions about the mechanisms causing the observed effects.

Comment 3.8

The authors' responses did not address the expressed concern and the issues remain unresolved.

Reviewer #4 (Remarks to the Author):

The authors have addressed my comments and concerns. The revised manuscript is ready for publication.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The authors addressed all the issues properly. The manuscript can be accepted now.

Response: We thank the reviewer for taking precious time to review our paper.

Reviewer #2 (Remarks to the Author):

It has been well revised, and can be accepted

Response: We thank the reviewer for taking precious time to review our paper.

Reviewer #3 (Remarks to the Author):

Response: We thank the reviewer for taking precious time to review our paper and giving us the constructive comments and suggestions.

Comment 3.1. The authors reiterated the issues in the original text without sufficient proposed changes.

The term ‘Microstructure’ should not be used to describe a digitally printed designed or mechanical structure of a printed part. “Microstructure” is a well-used and recognized term across materials-related fields that refers to structure within the material itself ie. Crystalline phases, morphology and texture, compositional variations, etc. Even within the 3D printing of materials field ‘microstructure’ is understood as such. An internet search of the term ‘microstructure’ clearly shows what is meant by the term. A recent example is the nuanced distinctions between what is known as microstructure (materials substructure) and printed structure definition here in this Nature Comms article:

Gao, S., Li, Z., Van Petegem, S. et al. Additive manufacturing of alloys with programmable microstructure and properties. Nat Commun 14, 6752 (2023).

: <https://www.nature.com/articles/s41467-023-42326-y>

Response: We thank the reviewer for this suggestion. Based on the reviewer’s suggestion, in the revision, we have changed all the “microstructure” to “micro-

architecture”.

Comment 3.2. “the currently printed ionogel sensors exhibit neither high resolution nor remarkable sensing capabilities” appears in the context, “However, despite a few recent explorations on developing UV curable ionogels for DLP 3D printing, the currently printed ionogel sensors exhibit neither high resolution nor remarkable sensing capabilities (Table S1)”.

This is still unclear and could be misleading. If the author’s wish to make negative claims about the specific prior art around DLP 3D printed sensors, they should do that more clearly with the scope of their comments made clear. One way to do this would be to revise the last quote sentence above to read:

However, despite a few recent explorations on developing UV curable ionogels, currently, DLP 3D printed ionogel sensors exhibit neither high resolution nor remarkable sensing capabilities (Table S1)”.

Response: We thank the reviewer for this suggestion, and agree with reviewer that the previous statement was misleading. Based on the reviewer’s suggestion, in the revision, we have revised the sentence as:

“However, despite a few recent explorations on developing UV curable ionogels, currently, DLP 3D printed ionogel sensors exhibit neither high resolution nor remarkable sensing capabilities (Table S1)”.

Comment 3.3. As shown in Figure R10b (Figure 1e and Supplementary Figure 2), the addition of PEGMA to facilitate a homogeneous mixture between polymer network and ionic liquid after photopolymerization, and a transparent ionogel is achieved. Figure 1g illustrates this homogeneous ionogel when BA:PEGMA is 7:3.

The complex bicontinuous phase structure shown in Figure 1g is very clearly not a homogenous structure but a composite structure with clearly defined inhomogeneity as pictured with very discontinuous domains of different compositions. The addition of PEGMA may have reduced the lengthscale of the materials phase separation microstructure but it is clearly not a homogenous phase. The homogenous terminology should be corrected to not imply something that is not shown.

This reviewer appreciates the edits and clarifications to the manuscript around the SEM/SAXS issues in the original Comment 3.4

Response: We thank the reviewer for this suggestion. Based on the reviewer's suggestion, in the revision, we have avoided to use the terminology of "homogenous" and have made following changes:

-the sentence in lines 103-106 from

"More importantly, poly(ethylene glycol) methyl ether methacrylate (PEGMA) is added to facilitate a homogenous mixture of photopolymerized network and IL."

to

*"More importantly, poly(ethylene glycol) methyl ether methacrylate (PEGMA) is added to avoid **the macroscopic phase separation between polymer network and IL during photopolymerization.**"*;

-the sentence in lines 177-179 from

"Illustration of homogenous ionogel resulted from photopolymerizing the BA-PEGMA ionogel precursor with BA:PEGMA ratio of 7:3".

to

*"Illustration of **ionogel with no macroscopic phase separation** resulted from photopolymerizing the BA-PEGMA ionogel precursor with BA:PEGMA ratio of 7:3 " ;*

-the sentence in lines 129-131 from

"Compared with the BA polymer network, the BA-PEGMA polymer network and IL could mutually dissolve each other to form a homogeneous mixture (Fig. 1g and Fig. S2b)."

to

*"Compared with the BA polymer network, **no macroscopic phase separation can be observed in the ionogel consisting of BA-PEGMA polymer network and IL** (Fig. 1g and Fig. S2b)."*

-the sentence in lines 112-113 from

“To achieve the CSN ionogel where the IL is homogeneously distributed in the polymer network, PEGMA plays the key role.”

to

*“To achieve the CSN ionogel where the IL is **uniformly** distributed in the polymer network, PEGMA plays the key role.”*

-the sentence in lines 509-512 from

“We propose a photopolymerization-induced microphase separation strategy to prepare BA-PEGMA homogeneous ionogel where PEGMA moieties form continuous microchannels that percolate in the polymer network to facilitate ion transportation.”

to

*“We propose a photopolymerization-induced microphase separation strategy to prepare BA-PEGMA **homogeneous** ionogel where PEGMA moieties form continuous microchannels that percolate in the polymer network to facilitate ion transportation.”*

-description in Figure 1f from “Phase separation” to “**Macroscopic phase separation**”;

-description in Figure 1g from “Homogeneous Ionogel” to “**No macroscopic phase separation**”.

Comment 3.4. Reviewer 3: “the use of PEO-containing salt or ionic liquid based gels is well known and the observation of higher conductivity, as observed here, with the introduction of a material like PEGMEA could be attributed to basic solvation and not a special microstructure. It is unclear that the claims made for the improved performance reported here are not novel”

The authors response to questions about the basic principle underlying the properties of the capacitors developed here is insufficient. Leaning on the many nice demonstrations and devices printed does not resolve the issue. The addition of PEGMEA could result in the observed performance for reasons other than the author’s claim. The incomplete or possibly incorrect description of the principle at work is not consistent, in this reviewer’s opinion, consistent with the standards in the standards for publication.

Response: We thank the reviewer for the comment. Here, we have to emphasize again that the goal of this work is to develop UV curable ionogels which should have high ionic conductivity, high mechanical performance, and high resolution for DLP 3D printing, so that the printed ionogel-based sensors have complex geometries and high sensing performance. However, this goal has not yet been achieved (**Table R1 (Table S1)**). Especially, this goal cannot be achieved by simply adding ionic liquid into UV curable polymers (Chen J et al., Nature Communications, 2022; Mackanic DG, et al., Nature Communications, 2019).

We agree that by using of PEO to achieve high ionic conductivity has been previously reported. In fact, in our manuscript, we have cited two pioneering works (Schulze M W et al., Nano Letters, 2014; Chopade S A et al., ACS Applied Materials & Interfaces, 2016) using this method. However, in these works, the polymers are not UV curable and thus can not be used for DLP 3D printing.

In this work, we propose a UV curable ionogel system which much higher ionic conductivity compared with previous work without sacrificing high mechanical performance (**Table R1 (Table S1)**). The developed UV curable ionogel includes PEGMA which helps to avoid macroscopic phase separation which occurs in the polymer-ionic liquid system with PEGMA. We use the Flory-Huggins theory (Supplementary Note 1) to explain the role of PEGMA that increases the Flory interaction parameter χ between the photopolymerized network and ionic liquid molecules. Moreover, the addition of PEGMA significantly increases the ionic conductivity of the polymer system with ionic liquid due to not only the strong interaction between PEO and ionic liquid, but also the bicontinuous nanostructure where the ions can quickly travel through the continuous PEO nanochannels. The bicontinuous nanostructure is resulted from photopolymerization induced microphase separation. In this work, we use SAXS and SEM to verify the existence and size of the bicontinuous nanostructure.

Since the UV curable ionogel developed in this work high ionic conductivity (over $3 \text{ S}\cdot\text{m}^{-1}$), high stretchability (over 1500%), low degree of hysteresis (0.4% at 50% cyclic strain), and is compatible with DLP 3D printing to printing high-resolution structures (up to $5 \mu\text{m}$) (**Figure R1 (Fig. 3f) and R2**), we can use the developed UV curable ionogel to fabricate capacitive sensors with high sensitivity, fast response time, high linearity, and good repeatability, which are much better than the sensors fabricated by previous ionogels (**Figure R3 and R4**).

Table R1 (Table S1). Comparison of the ionogel in this work with previously reported.

Reference No. in the main text	Elongation-at-break (%)	Ionic conductivity (S/m)	3D printability	Printing resolution (μm)	Type of Sensor
This work	1580	3.23	Yes	5	Capacitive-pressure
[11]	2000	0.1	Yes	N.R.	Capacitive-pressure
[27]	1045	0.58	Yes	~ 1000	Resistance-strain
[28]	10	0.03	Yes	~ 1000	N.A.
[29]	487	0.015	Yes	~ 1000	Resistance-strain
[30]	/	0.12	Yes	~ 1000	N.A.
[31]	7000	0.11	Yes	N.R.	Resistance-strain
[32]	500	0.3	Yes	~ 1000	Resistance-strain
[33]	28	0.54	Yes	200	N.A.
[39]	1400	0.025	Yes	N.R.	Resistance-strain
[40]	10000	0.01	Yes	~ 1000	Capacitance-strain
[41]	600	0.078	Yes	~ 1000	Resistance-strain
[42]	2580	0.042	No	N.A.	Capacitance-strain
[43]	1312	0.12	No	N.A.	Capacitive-pressure
[44]	2066	0.29	No	N.A.	Resistance-strain
[45]	1100	0.21	Yes	N.R.	Resistance-strain
[46]	6000	0.024	No	N.A.	Capacitive-strain
[47]	600	0.1	No	N.A.	N.A.
[48]	5000	0.007	No	N.A.	N.A.

N.A.: not applicable; N.R.: not reported.

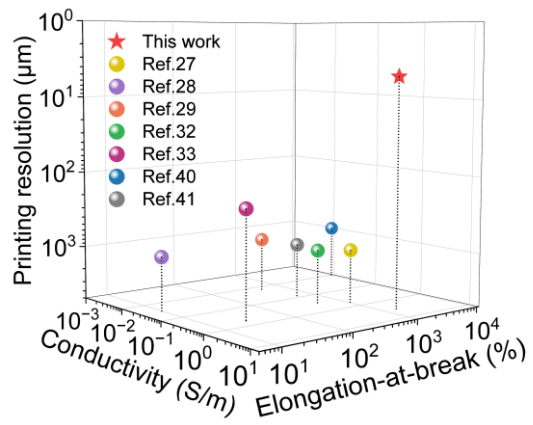


Figure R1 (Fig. 3f). Comparisons on printing resolution, conductivity, and elongation-at-break between the CSN ionogel in this work and other reported 3D printing ionogels.

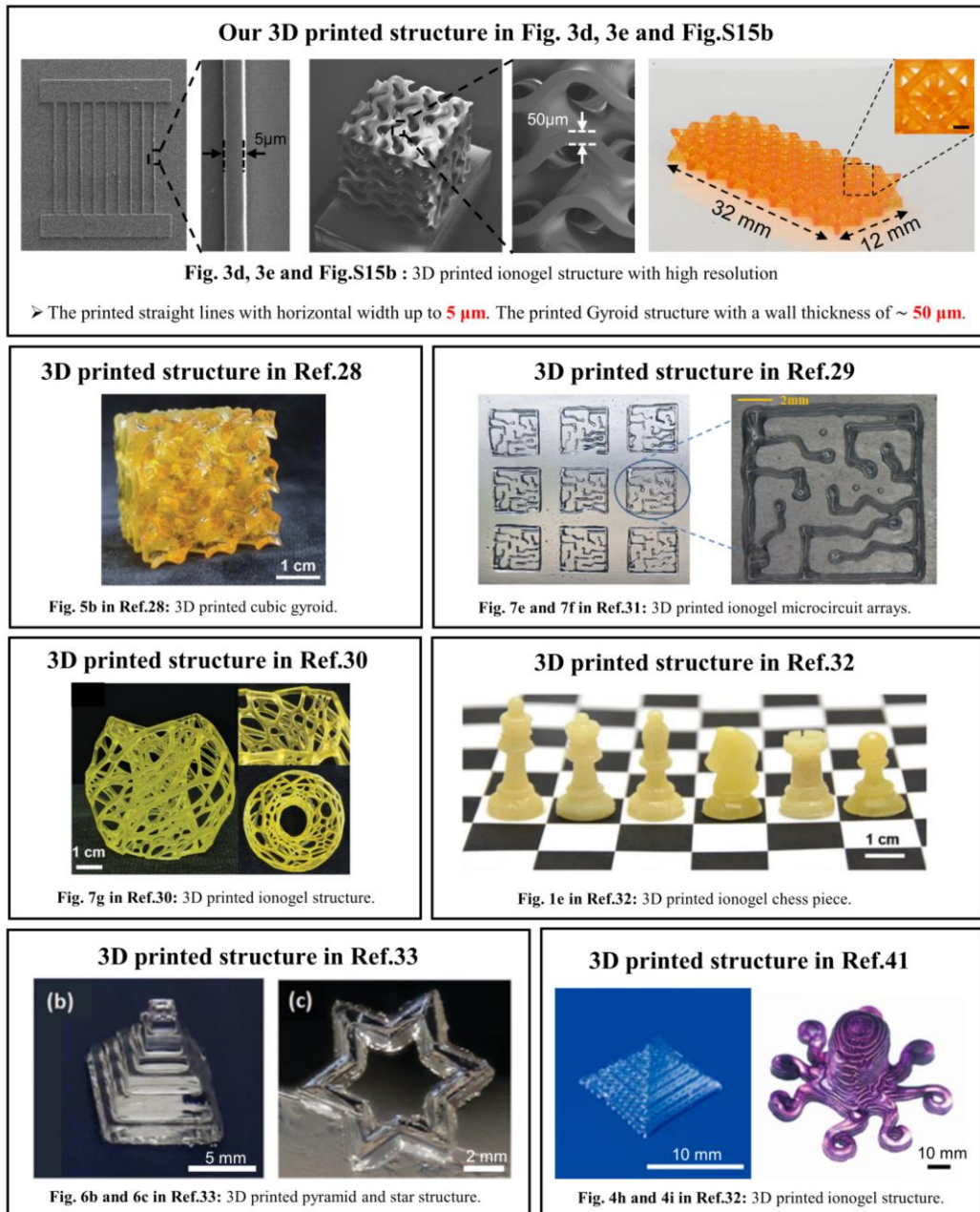


Figure R2. Comparison of the 3D printed ionogel structures in this work with the structures in previously works.

Our 3D printed sensor in Fig. 5 and Fig. 6

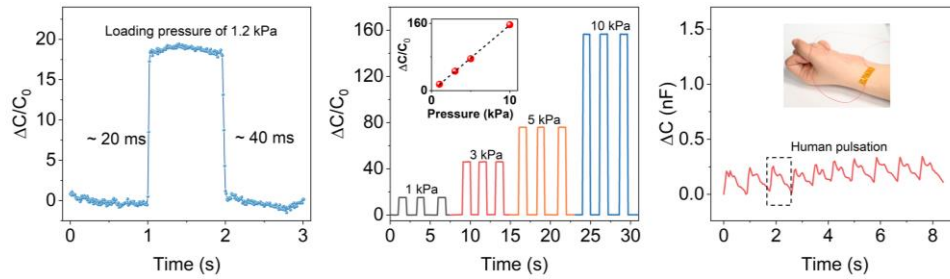


Fig. 5a, 5b and 5c: Sensing performance of the 3D printed capacitive sensor with CSN ionogels.

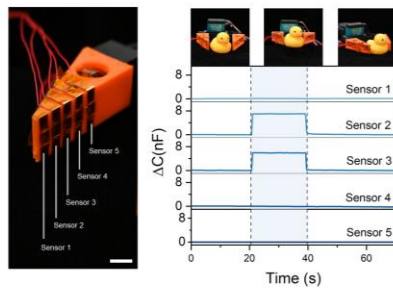


Fig. 6c and 6d: Robotic hand integrated with sensor.

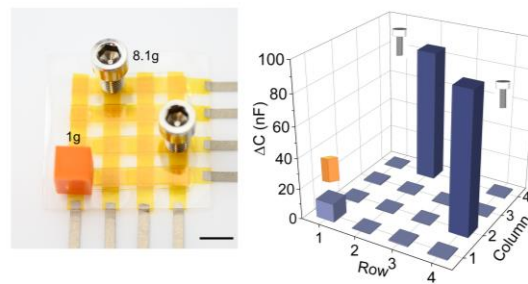


Fig. 6i and 6j: Multiplex pressure sensor array.

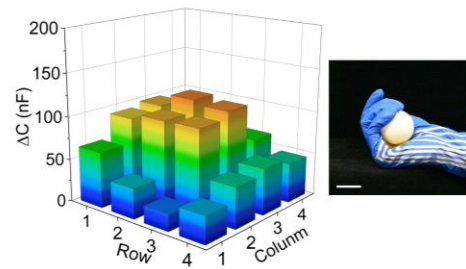
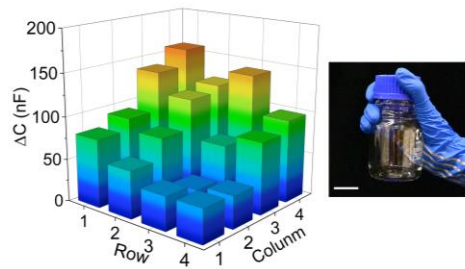


Fig. 6p and 6q: The pressure distribution of a multiplex pressure sensor array on the glove.

- **3D printed micro-architectures** endow the ionogel sensor superior sensing performances such as high sensitivity, high linearity and fast dynamic response.
- 3D printed sensor can **accurately monitor the change of weak force signals**.

Figure R3. The sensing performance of the 3D printed capacitive sensor with CSN ionogel in this work.

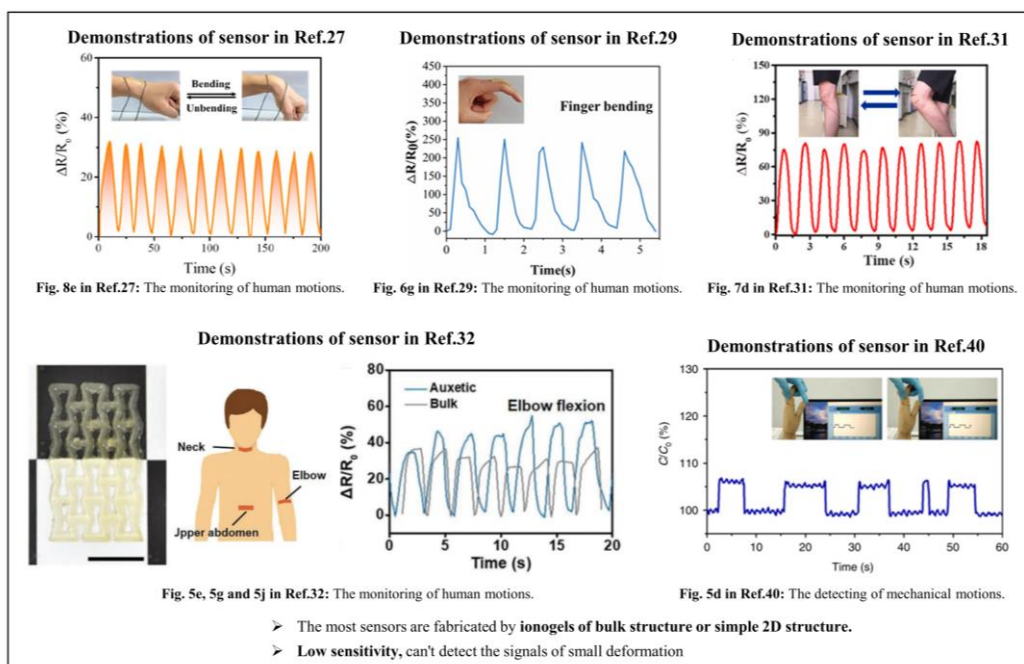


Figure R4. The sensing performances of the sensors reported in previously works.

Reference

Chen J, et al. Phase-locked constructing dynamic supramolecular ionic conductive elastomers with superior toughness, autonomous self-healing and recyclability. *Nature Communications* 13, 4868 (2022).

Mackanic DG, et al. Decoupling of mechanical properties and ionic conductivity in supramolecular lithium ion conductors. *Nature Communications* 10, 5384 (2019)

Schulze M W, McIntosh L D, Hillmyer M A, et al. High-modulus, high-conductivity nanostructured polymer electrolyte membranes via polymerization-induced phase separation. *Nano letters*, **14**, 122-126 (2014).

Chopade S A, So S, Hillmyer M A, et al. Anhydrous proton conducting polymer electrolyte membranes via polymerization-induced microphase separation. *ACS Applied Materials & Interfaces*, **8**, 6200-6210 (2016).

Comment 3.5. Considering the goal of Fig. 2e is to demonstrate the high conductivity of developed [EMIm][DCA] ionogel, we decide to keep the demonstration where a 4V DC is applied to the two circuits.

If there is a true steady state DC current through a capacitor of any significant amount

(enough current to continuously light an LED in the circuit contracted to demonstrate an effect would be ‘significant’). Other sources of continuous current would be (1) electrochemical side reactions, typically at the electrode that are often irreversible and undesirable (2) some continuous conductive path through the capacitor, or (3) the authors have chosen to show this demonstration for only a short ‘DC’ period of time.

In all cases, the publishing of this LED demo in this context in its current form is misleading as it implies a usable DC conductivity and makes the picture less credible than just showing the ionic conductivity results.

Response: We thank the reviewer for the comment, and agree with the reviewer’s concern that the LED demo in DC current demo is misleading. Therefore, as shown in **Figure R5 (Fig. 2e)**, in the revision, we use the AC current to light up the LED. We have also revised context accordingly:

“To demonstrate the high conductivity of the ionogel with [EMIm][DCA], as shown in Figure 2e, in a parallel circuit where a 150 V AC (1000 Hz) voltage is applied, three mini light-emitting diode (LED) dots can be lightened up in the component where the ionogel with [EMIm][DCA] is used as conductor; in comparison, the component with the LiTFSI-based conductor fails to light the LED dots due to its low conductivity.”

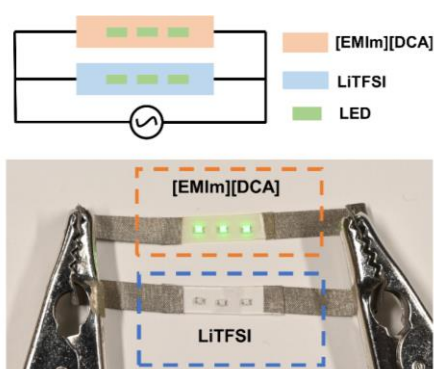


Figure R5 (Fig. 2e). The ionogel with [EMIm][DCA] and the ionic conductor with LiTFSI in an AC 150 V electric field.

Comment 3.6. It may be that the authors are unfamiliar with the standard and broadly expected meaning and principles of electrochemical capacitors and the mechanisms presented in the paper. The structures shown and the definitions implied are very much ECs. An “EC” can be generally defined as “Electrochemical capacitors (supercapacitors) consist of two electrodes separated by an ion-permeable membrane (separator), and an electrolyte ionically connecting both electrodes.” Which is almost certainly happening here. The authors refer to an “EDL” mechanism. EDL or Electric Double Layer capacitors are absolutely electrochemical capacitors. The author’ could refer to the

literature on the subject, for example (Simon, P., Gogotsi, Y. Materials for electrochemical capacitors. Nature Mater 7, 845–854 (2008)) that correctly states “Electrochemical capacitors, also called supercapacitors, store energy using either ion adsorption (electrochemical double layer capacitors) or fast surface redox reactions (pseudo-capacitors).“ Depending on the time period for the “DC” LED result presented in the paper and discussed below, the ECs demonstrated in this article are electrochemical capacitors that may be exhibiting both double layer capacitance and redox reactions, whether intended or not.

As far as the use of AC, the vast majority of applications of capacitors are for AC signals. It would be a great surprise to the entire field of electrical engineering that there is no current in an AC circuit. At steady state there may be no DC current but to suggest there is no current flowing would be implying there is no relevance of ionic conductivity. In fact the authors own LED demonstration, shown in their own Figure 3., which has misleading implications also, actually claims powering a DC LED. It is unfortunate that the authors still appear to be choosing to present a demonstration which is inconsistent with the operating principles assumed for the operating principles in the rest of the article and that is misleading or presents unanswered questions about the mechanisms causing the observed effects.

Response: We thank the reviewer for sharing the knowledge about EC. In the revision, in Figure 3, we have changed the AC circuit to replace DC circuit for the LED demonstration.

Comment 3.8. The authors’ responses did not address the expressed concern and the issues remain unresolved.

Response: we thank the review for the comment. In the revision, we have tried our best to address all the comments and concerns raised by the reviewer.

Reviewer #4 (Remarks to the Author):

The authors have addressed my comments and concerns. The revised manuscript is ready for publication.

Response: We thank the reviewer for taking precious time to review our paper.

REVIEWER COMMENTS

We thank reviewers for taking precious time to review our paper.