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(54) Title: ELASTOMERIC COMPOSITE FOAM MATERIAL FOR SENSING APPLICATIONS AND SENSOR DEVICE

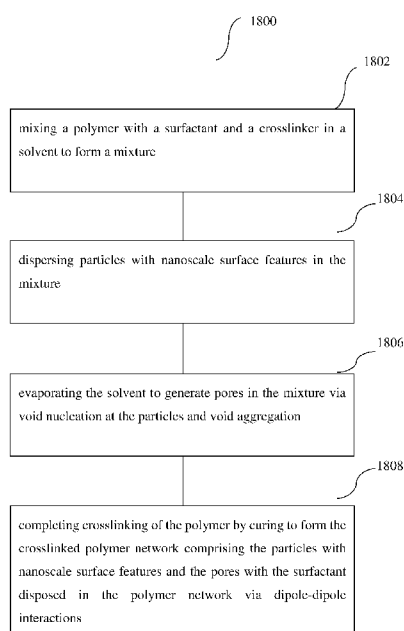


Fig. 18

(57) Abstract: A structure comprising a carrier, a crosslinked polymer network, and an array of electrodes extending from the carrier at least partially through a thickness of the crosslinked polymer network, wherein the electrodes are electrically contactable for detecting changes in electrical characteristics between pairs of electrodes; a method of fabricating a sensor device comprising the structure; and a method of fabricating the crosslinked polymer network. The method of fabricating the crosslinked polymer network comprises the steps of mixing a polymer with a surfactant and a crosslinker in a solvent to form a mixture; dispersing particles with nanoscale surface features in the mixture; evaporating the solvent to generate pores in the mixture via void nucleation at the particles and void aggregation; and completing crosslinking of the polymer by curing to form the crosslinked polymer network comprising the particles with nanoscale surface features and the pores with the surfactant disposed in the polymer network via dipole-dipole interactions.

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ELASTOMERIC COMPOSITE FOAM MATERIAL FOR SENSING APPLICATIONS AND SENSOR DEVICE

FIELD OF INVENTION

- 5 The present invention relates broadly to a structure comprising a crosslinked polymer network, to a method of fabricating a sensor device and to a method of fabricating a crosslinked polymer network, in particular to artificially innervated self-healing foams as synthetic piezo-impedance sensor skins.

10 BACKGROUND

Any mention and/or discussion of prior art throughout the specification should not be considered, in any way, as an admission that this prior art is well known or forms part of common general knowledge in the field.

- 15 Human skin has remarkable self-healing abilities while being innervated by a wide variety of sensory neuron subtypes known as mechanoreceptors. These mechanoreceptors buried beneath the skin extending into the epidermis convey the tactile stimuli to the nerves and enable us to use the sense of touch to manipulate objects, perform social communication, and react to unstructured external environments. To mimic human skins, electronic skin (e-skins) has progressed swiftly from purely fictional imaginations to increasingly sophisticated
20 embodiments over the last decade. Such synthetic skins have great potential in a large variety of applications including health care, human-machine interactions, and robotics. Although many different tactile sensing e-skins have been demonstrated, an integrated e-skin sensor material that is self-healing, detects proximal pre-contact events and senses force directions simultaneously have yet to be demonstrated. There are efforts to use ionic gels as artificial
25 nerves in e-skins with organic transistors, but the ionic gels based nerves did not show tactile sensitivity.

- Furthermore, current e-skin tactile sensors have also relied heavily on either piezocapacitive or piezoresistive materials sandwiched between planar two-dimensional (2D) electrode patterns. The use of planar patterns with a sandwiched dielectric or conductive material could add
30 complexity in the encapsulation assembly arising from potential air gaps or delamination. Moreover, the use of such 2D electrode patterns typically detects normal forces only. While there are reports on e-skins that detect both normal and shear forces, most of them require encapsulation with sandwiched structures to work.

Embodiments of the present invention seek to address at least one of the above problems.

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SUMMARY

In accordance with a first aspect of the present invention, there is provided a structure comprising:

a crosslinked polymer network; and

- 5 a surfactant disposed in the polymer network via dipole-dipole interactions;

wherein the polymer network further comprises particles with nanoscale surface features and pores.

In accordance with a second aspect of the present invention, there is provided a method of fabricating a sensor device comprising the steps of:

- 10 providing a carrier;

disposing a crosslinked polymer network on the carrier, the foam material exhibiting a piezoimpedance property;

providing an array of electrodes extending from the carrier at least partially through a thickness of the crosslinked polymer network; and

- 15 providing interconnections for electrically contacting the electrodes for detecting changes in electrical characteristics between pairs of electrodes.

In accordance with a third aspect of the present invention, there is provided a method of fabricating a crosslinked polymer network, the method comprising:

mixing a polymer with a surfactant and a crosslinker in a solvent to form a mixture;

- 20 dispersing particles with nanoscale surface features in the mixture;

evaporating the solvent to generate pores in the mixture via void nucleation at the particles and void aggregation; and

completing crosslinking of the polymer by curing to form the crosslinked polymer network comprising the particles with nanoscale surface features and the pores with the surfactant

- 25 disposed in the polymer network via dipole-dipole interactions.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the invention will be better understood and readily apparent to one of ordinary skill in the art from the following written description, by way of example only, and in conjunction with the drawings, in which:

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Fig. 1 shows schematic drawings illustrating an artificially innervated pressure sensor that is low-modulus, elastic and self-healing, according to an example embodiment.

Fig. 2a shows SEM images of foam sensor with 3D electrodes according to an example embodiment, revealing the original state, normal-force loading state and shear-force loading state, respectively.

5 Fig. 2b shows resistance responses on applying normal force of 15N to an Aifoam sensors according to an example embodiment and control with 2D planar electrodes.

Fig. 2c shows resistance change on applying a shear force to the foam sensor according to an example embodiment and control with 2D planar electrodes.

Fig. 2d shows capacitance change responses on applying normal force of 15N to Aifoam sensors according to an example embodiment and control with 2D planar electrodes.

10 Fig. 2e shows capacitance change on applying a shear force to the foam sensor according to an example embodiment and control with 2D planar electrodes.

Fig. 3a shows DMA result of the base polymer showing its viscoelasticity. Left insets show the flowability of the material before crosslink. Right insets show the solid-state material after crosslink.

15 Fig. 3b shows typical stress-strain curves of original and healed base elastomer material. Inset: Photographs of a self-healed sample being stretched.

Fig. 3c shows stress-strain curves of base elastomer and foam materials with different μNi loadings, according to example embodiment. Inset: An image of the foam structure. Scale bar: 1 mm.

20 Fig. 3d is a graph showing the self-healing of piezoresistive and piezocapacitive behaviours of foam for use in example embodiments.

Fig. 3e shows cross-sectional SEM images revealing the self-healing performance of foam material for use in example embodiments; left, Bifurcated; right, Self-healed at 70 °C for 4 days. Scale bar: 50 μm .

25 Fig. 4a shows Nyquist plots of foam materials with different μNi loadings according to example embodiments. Inset is the equivalent circuit of the foam materials.

Fig. 4b, shows permittivity of foam materials with different μNi loadings according to example embodiments and control sample under the frequency range of 1 – 10⁵ Hz.

30 Fig. 4c shows resistance responses of foam with different μNi loadings, according to example embodiments.

Fig. 4d shows capacitance responses of foam with different μNi loadings, according to example embodiments.

Fig. 5a shows a schematic of foam sensor for direction identification, according to an example embodiment.

Fig. 5b shows a photograph of foam sensor for direction identification, according to an example embodiment.

5 Fig. 5c shows schematics and results of foam sensor (30 vol% μNi) in detecting the direction and force distribution, according to an example embodiment. Top, Illustration of the deformation of a pixelated foam sensor under external force loading; bottom, Resistance change response to the external force loadings.

Fig. 5d shows measured and predicted forces along different directions based on results of Fig 5c. Top, Shear force components along x and y directions; bottom, Normal force components along z direction.

10 Fig. 6a shows Photographs showing both proximity sensing and pressure sensing of foam sensor according to an example embodiment.

Fig. 6b shows the capacitance change responses on the distance between the finger and the foam sensor according to an example embodiment.

15 Fig. 6c shows the resistance change responses on external pressure, according to an example embodiment.

Fig. 7a shows a photograph of 3D electrodes inside the foam sensor according to an example embodiment.

Fig. 7b, shows a photograph illustrating the 3D electrodes array holds the foam materials to the electrode tightly like skewers, according to an example embodiment.

20 Fig. 7c is a graph showing that the foam material does not detach from the electrodes even if delamination occurs between the foam materials and the bottom substrate due to wear-and-tear in an foam sensor according to an example embodiment.

25 Fig. 7d is a graph showing that this is in sharp contrast with a planar electrode sensor (Foam-2D), where the contact between the electrode and the foam could not be retained after delamination occurs.

Fig. 8a shows typical resistance changes of foam sensor during loading-unloading, according to an example embodiment.

Fig. 8b shows typical capacitance changes of foam sensor during loading-unloading, according to an example embodiment.

30 Fig. 8c shows typical absolute impedance changes of foam sensor during loading-unloading, according to an example embodiment.

Fig. 8d shows typical phase changes of foam sensor during loading-unloading, according to an example embodiment.

Fig. 9a shows photographs of a, PVDF-HFP-fluorosurfactant [mass ratio of PVDF-HFP: fluorosurfactant was 49: 50], heated at 70 °C.

- 5 Fig. 9b shows photographs of crosslinked PVDF-HFP-fluorosurfactant-DAP [mass ratio of PVDF-HFP: fluorosurfactant: DAP was 49: 50: 1], heated at 70 °C, for use in an example embodiment.

- 10 Fig. 10 illustrates the crosslinking process contains the dehydrofluorination of PVDF-HFP and the formation of C=N bonds between the PVDF-HFP chain and DAP molecular, for use in an example embodiment.

Fig. 11a shows FTIR spectra for PVDF-HFP, fluorosurfactant (Zonyl FS-300), PVDF-HFP-fluorosurfactant, PVDF-HFP-fluorosurfactant-DAP, and PVDF-HFP-DAP.

- 15 Fig. 11b shows details of a new peak appeared at 1651 cm^{-1} in the FTIR spectrum of the crosslinked PVDF-HFP-fluorosurfactant-DAP polymer reflected the vibration of C=N bonds, proving the crosslinking by DAP.

Fig. 11c shows details of the peak located at 882 cm^{-1} indicates the amorphous phase of PVDF-HFP, and the peaks at 833 and 840 cm^{-1} corresponds to the β -phase of PVDF.

Fig. 12a shows TGA result of PVDF-HFP-fluorosurfactant-DAP.

Fig. 12b shows TGA result of PVDF-HFP.

- 20 Fig. 12c shows TGA result of fluorosurfactant Zonyl FS300.

Fig. 12d shows DSC spectrum of PVDF-HFP and PVDF-HFP-fluorosurfactant-DAP.

Fig. 13 shows photographs of self-healing performance of left: PVDF-HFP-fluorosurfactant-DAP and right: PVDF-HFP-hydrocarbon surfactant-DAP.

- 25 Fig. 14a schematically shows the Fabrication process of the resistive foam material according to an example embodiment.

Fig. 14b shows SEM images of Foam 25 μNi according to an example embodiment.

Fig. 15a shows optical microscope images of Left: Foam 20 μNi . Middle: Foam 25 μNi . Right: Foam 30 μNi , according to example embodiments.

Fig. 15b, shows the pore size distributions of the images in Fig. 15a.

- 30 Fig. 16a schematically shows that voids nucleate at the μNi particles/polymer solution and electrode/polymer solution interfaces when the solvent evaporates, according to an example embodiment.

Fig. 16b shows SEM images of Left: base elastomer without μNi , Middle: 25 μNi with no pores, and Right: Foam 25 μNi , according to an example embodiment.

Fig. 17a, shows porosity of foam with different μNi loadings according to example embodiments.

- 5 Fig. 17b shows a graph illustrating consistency of sensor performance across 3 different batches, according to example embodiments.

Fig. 18 shows a flowchart illustrating a method of fabricating a crosslinked polymer network, according to an example embodiment. Fig. 18d shows schematics to explain the effects of DAP on the self-healing ability of polymer.

- 10 Fig. 19a shows a graph illustrating self-healing of the resistance of Foam 25 μNi upon bifurcation and contact.

Fig. 19b shows a graph illustrating self-healing of the pressure sensing of Foam 25 μNi after bifurcation and self-heal.

- 15 Fig. 19c shows a graph illustrating resistance change vs normal pressure on Foam 30 μNi after self-healing.

Fig. 19d shows a graph illustrating capacitance change vs normal pressure on Foam 30 μNi after self-healing.

Fig. 20 shows Bode plots of foam materials with different μNi loadings, according to example embodiments.

- 20 Fig. 21a shows I-V curves of Foam 20 μNi under different loadings ($F = 0-15\text{ N}$), according to an example embodiment.

Fig. 21b shows I-V curves of Foam 25 μNi under different loadings ($F = 0-15\text{ N}$), according to an example embodiment.

- 25 Fig. 21c shows I-V curves of Foam 30 μNi under different loadings ($F = 0-15\text{ N}$), according to an example embodiment.

Fig. 22a shows SEM image of μNi particles.

Fig. 22b shows a zoom-in SEM view of μNi particles.

Fig. 22c shows an SEM image of μNi particles buried in the foam polymer.

Fig. 22d shows COMSOL simulations urchin-like μNi particles, and spherical μNi particles.

- 30 Fig. 23 shows the equivalent circuit for the PVDF-HFP-fluorosurfactant-DAP- μNi materials, according to an example embodiment.

Fig. 24a shows Nyquist plot of Foam 25 μNi with no addition of fluorosurfactant.

Fig. 24b shows Bode plot of Foam 25 μNi with no addition of fluorosurfactant.

Fig. 24c shows Nyquist plot for samples with different fluorosurfactant concentrations, according to example embodiments.

5 Fig. 24d shows Bode plots for samples with different fluorosurfactant concentrations, according to example embodiments.

Fig. 24e shows Nyquist plot for the sample without μNi .

Fig. 24f shows, Bode plot for the sample without μNi .

Fig. 25a shows Nyquist plots for foam samples with different μNi , according to example embodiments.

10 Fig. 25b shows Bode plots for foam samples with different μNi , according to example embodiments.

Fig. 25c shows Nyquist plot for nonfoam samples different μNi , according to example embodiments.

15 Fig. 25d shows Bode plots for nonfoam samples different μNi , according to example embodiments.

Fig. 26a shows EDS mapping of base elastomer.

Fig. 26b shows EDS mapping of base elastomer without fluorosurfactant.

Fig. 26c shows EDS mapping of Foam 25 μNi , according to an example embodiment.

20 Fig. 27a shows permittivity of materials with different μNi concentration, according to example embodiments.

Fig. 27b shows loss tangent of materials with different μNi concentration, according to example embodiments.

Fig. 28a shows resistance change vs normal pressure, according to an example embodiment.

Fig. 28b shows capacitance change vs normal pressure, according to an example embodiment.

25 Fig. 29a shows pressure sensing response time according to example embodiments.

Fig. 29b shows the response time for foam as proximity sensor with a slow moving hand, according to an example embodiment.

Fig. 29c shows the response time for foam as proximity sensor with a fast moving hand, according to an example embodiment.

30 Fig. 30a shows absolute impedance response to temperature (constant relative humidity at 60 %), according to an example embodiment.

Fig. 30b resistance response to temperature (constant relative humidity at 60 %), according to an example embodiment.

Fig. 30c shows capacitance response to temperature (constant relative humidity at 60 %), according to an example embodiment.

- 5 Fig. 30d shows absolute impedance response to temperature (constant relative humidity at 60 %), according to an example embodiment.

Fig. 30e shows resistance response to temperature (constant relative humidity at 60 %), according to an example embodiment.

- 10 Fig. 30f shows capacitance response to temperature (constant relative humidity at 60 %), according to an example embodiment.

Fig. 31a shows absolute impedance response to humidity (temperature maintained at 70 °C at all the tested humidity levels), according to an example embodiment.

Fig. 31b shows resistance response to humidity (temperature maintained at 70 °C at all the tested humidity levels). , according to an example embodiment

- 15 Fig. 31c shows capacitance response to humidity (temperature maintained at 70 °C at all the tested humidity levels), according to an example embodiment.

Fig. 31d shows absolute impedance response to humidity (temperature maintained at 70 °C at all the tested humidity levels), according to an example embodiment.

- 20 Fig. 31e shows resistance response to humidity (temperature maintained at 70 °C at all the tested humidity levels), according to an example embodiment.

Fig. 31f shows capacitance response to humidity (temperature maintained at 70 °C at all the tested humidity levels), according to an example embodiment.

Fig. 32a shows a photograph of foam sensor with 4 zones for force distribution and direction identification test, according to an example embodiment.

- 25 Fig. 32b shows schematics of foam sensor (25 vol% μNi) in detecting the direction and force distribution, according to an example embodiment.

Fig. 33a shows resistance change response of material with 25 vol% Ag nanoflakes (Ag Nfs) and 25 vol% μNi , according to an example embodiment, under 100 kPa.

- 30 Fig. 33b shows capacitance change response of material with 25 vol% Ag nanoflakes and 25 vol% μNi , according to an example embodiment, under 100 kPa.

Fig. 33c shows resistance response of material with 25 vol% Ag Nfs under 100 kPa.

Fig. 33d shows Capacitance response of material with 25 vol% Ag Nfs under 100 kPa.

Fig. 34 shows a proximity test graph of the foam sensor according to an example embodiment. Inset: cross-section of foam sensor (3D electrodes was buried inside the Foam 25 μ Ni), according to an example embodiment.

5 Fig. 35a shows capacitance response of foam sensors as a proximity sensor, according to example embodiments.

Fig. 35b shows resistance response of the foam sensors as a proximity sensor, according to example embodiments.

Fig. 36 shows the electrical circuit for proximity and pressure LED demonstration, according to an example embodiment.

10 Fig. 37a shows a photo of shear force test of foam sensor before shear force applied, according to an example embodiment.

Fig. 37b shows a photo of shear force test of foam sensor after the shear force applied, according to an example embodiment.

15 Fig. 38 is a schematic of the calibration setup for force vector estimation, according to an example embodiment.

Fig. 39 shows a flowchart illustrating a method of fabricating a sensor device, according to an example embodiment.

DETAILED DESCRIPTION

20 Inspired by the architecture of the human mechanosensory innervations, an example embodiment of the present invention provides a structure 100 that uses three-dimensional (3D) metal wire electrodes e.g. 102 as ‘nerves’ embedded with a low-modulus yet elastic self-healing foam 104 foam(**Fig. 1**). Compared with other foam-based sensors, the synthesized self-healing foam material used according to an example embodiment has a low-modulus of 600
25 kPa and is relatively elastic to provide a restoring force for contact forces sensing. The 3D electrodes e.g. 102 in the foam 104 according to an example embodiment enable the structure 100 to be sensitive to both normal and shear forces. By embedding the 3D electrodes e.g. 102 within the near-percolation metal particle foam composite 104 according to an example embodiment, a sensor according to an example embodiment based on the structure 100 can
30 operate in both piezoresistive and piezocapacitive modes. For example, an foam e-skin according to an example embodiment can detect tactile contact and proximity of the human touch.

Artificial innervation with 3D electrodes according to an example embodiment

Figure 2a shows the images of a foam sensor 200 according to an example embodiment with 3D electrodes e.g. 202 (and as outlined by the dotted line boxes) embedded. When a normal force 201a or shear force 201b is applied, the foam material 203 will be deformed in shape relative to the 3D electrodes e.g. 202. This deformation causes a measurable electrical impedance change. The 3D electrodes e.g. 202 are flexible copper wires with a radius of 75 μm soldered on a flexible printed circuit board (PCB) 204, in an example embodiment. A polymer was then cast on the flexible PCB 204, inducing self-foaming by evaporation-induced phase inversion. The 3D electrodes e.g. 202 hold the foam material 201 in place, even if the foam sensor 200 is delaminated from the PCB due to wear-and-tear (**Fig. 7**).

Specifically, **Fig. 7a** shows a photograph of 3D electrodes (partly exposed) inside the foam sensor 200 according to an example embodiment. The foam material is elastic. **Fig. 7b** shows a photograph illustrating that the 3D electrodes array holds the foam material to the electrode tightly like skewers. **Fig. 7c** shows a graph illustrating that the foam material does not detach from the electrodes even if delamination occurs between the foam material and the bottom substrate due to wear-and-tear. The contact between the foam material and 3D electrodes is always intact. **Fig. 1d** shows, for comparison, that this is in sharp contrast with a planar electrode sensor (Foam-2D), where the contact between the electrode and the foam could not be retained after delamination occurs. This highlights that the foam sensor according to an example embodiment can still be held together, even if delamination from the PCB would occur.

Returning to Fig. 2, the foam sensor 200 with 3D electrodes e.g. 202 according to an example embodiment was tested, as well as a similarly prepared control foam sensor except with planar electrodes (Foam-2D), by applying normal and shear forces. The piezoresistance effect decreases electrical resistance of both electrode configurations when an external pressure was applied (**Fig. 2b**), but the foam sensor 200 exhibited lower initial resistance because of the larger contact areas of the 3D electrodes to the foam compared to the Foam-2D version. The extension of the 3D electrodes e.g. 202 into the foam material 203 enables more sensitive deformation sensing compared to the planar electrodes, in particular for applied shear force. One can see the height of the 3D electrode e.g. 202, relative to the thickness of the foam material 203 in the foam sensor 200 according to an example embodiment, in **Fig. 2a**. When pressed, the top surface of the foam sensor 200 was near the top of the electrodes e.g. 202. The difference of foam sensor 200 with 3D electrodes e.g. 202 according to an example embodiment and planar electrodes is also presented schematically in the insets of **Figs. 2b & c**. The bottom schematic of the insets have 3D electrodes e.g. 206, while the top have planar electrodes 208. Hence, when a shear force was applied to the top surface, the foam sensor 200 according to an example embodiment showed obvious resistance drop (**Fig. 2c**) but the Foam-2D device did not show consistently detectable resistance change. Thus, the foam sensor 200 according to an example embodiment can capture and respond to small changes in surface deformations from an external mechanical stimulus.

It was found that the foam sensor 200 according to an example embodiment can be operated in both piezoresistive and piezocapacitive modes simultaneously due to the interfacial impedance of the foam material (**Fig. 8**), which is partly capacitive as well as resistive in nature. That is, the foam sensor 200 according to an example embodiment can also detect normal and shear forces by monitoring capacitance changes. In piezocapacitive mode, the capacitance change increases when an external force was applied (**Fig. 2d**). The capacitance of the sensor also increased with the shear forces (**Fig. 2e**).

More specifically, **Fig. 8** shows typical impedance changes of a foam sensor according to an example embodiment during loading-unloading, which includes resistance (**Fig. 8a**), capacitance (**Fig. 8b**), absolute impedance (**Fig. 8c**) and phase changes (**Fig. 8d**) simultaneously.

Impedance is a complex number defined as:

$$Z = R + jX,$$

Where the real part R is resistance and imaginary part X is reactance. As $X = |Z| \sin \theta$, where θ is phase angle, X is a negative value here as θ is within $0^\circ \sim -90^\circ$, indicating X here is capacitive reactance, or capacitance.

Low-modulus, elastic and self-healing foam according to an example embodiment

The base elastomer of the foam according to an example embodiment is synthesized by mixing a fluoropolymer (in one example embodiment PVDF-HFP and a fluorosurfactant (in one example embodiments Zonyl FS-300)), followed by partial crosslinking of the mixture using 1,3-diaminopropane (DAP)] (see also "Methods according to an example embodiment", below). Mixing at a mass ratio of 49:50 (polymer:fluorosurfactant) at 70 °C resulted in a flowable, gel-like polymer solution (**Fig. 3a** inset and **Fig. 9a**) because the fluorosurfactant is a polar solvent of PVDF-HFP. When DAP was added and the crosslinking process completed, the polymer solution becomes the base elastomer (**Fig. 3a** inset and **Fig. 9b**).

More specifically, **Fig. 9a** shows photographs of PVDF-HFP-fluorosurfactant [mass ratio of PVDF-HFP: fluorosurfactant was 49: 50] and **Fig. 9b**, of crosslinked PVDF-HFP-fluorosurfactant-DAP [mass ratio of PVDF-HFP: fluorosurfactant: DAP was 49: 50: 1], both heated at 70 °C. Fluorosurfactant is a polar solvent for PVDF-HFP. Without crosslinking, the PVDF-HFP-fluorosurfactant is flowable. After adding DAP into the mixture and crosslink at 120 °C, the mixture turned into a soft elastomer.

It is noted that any polymers that can be dissolved in solvents can form the foam materials according to various example embodiments. For self-healing, PVDF-HFP is a fluorine-rich polymer that can form dipole-dipole interaction among polymer chains, which is helpful for self-healing. Meanwhile, it can be dissolved in various organic solvent with low boiling point(b.p.) like acetone, DMF, etc., for the solvent-evaporation method to obtain the foam structure according to the example embodiment described in detail herein. That is, any polymer

that can form high dipole-dipole interaction and can be dissolved in low b.p. organic solvent can be used in different embodiments, such as, but not limited to, PVDF-TrFE.

Also, Zonyl used in the example embodiment described in detail herein is a fluorine-rich surfactant that can form dipole-dipole interaction between polymer chains and surfactant
 5 moleculars, which is helpful for self-healing. Meanwhile, it is also a plasticizer that can soften the polymer and make it easier for polymer chains to move and self-heal. However, it is noted that any surfactants that can form high intermolecular force between polymer chains and surfactant moleculars and can work as plasticizer can be used in different embodiments, such as, but not limited to, 3M fluorosurfactant FC-4434.

10 Using DAP to crosslink PVDF-based polymer in the example embodiment described in detail herein is a well-developed method. However, it is noted that any binucleophiles such as, but not limited to, diamines (e.g di-n-butylamine) can be used for crosslinking fluoropolymer in different example embodiments.

Dynamic Mechanical Analysis (DMA) was applied on the cross-linked base elastomer
 15 according to an example embodiment to determine its mechanical properties. The cross-linked base elastomer according to an example embodiment shows a higher storage modulus than loss modulus, indicating that the base elastomer is viscoelastic with a loss factor of 15° to 19° within a frequency range of 1-200 Hz at ambient temperature. The viscoelasticity can be attributed to the DAP molecules that bridge the PVDF-HFP polymer chains (**Fig. 10 and 11**).

20 Specifically, the crosslinking process contains Step 1 the dehydrofluorination of PVDF-HFP and the Step 2 formation of C=N bonds between the PVDF-HFP chain and DAP molecular. **Fig. 11** shows FTIR spectra proving the crosslinking of the polymer. **Fig. 11a**, FTIR spectra for PVDF-HFP, fluorosurfactant (Zonyl FS-300), PVDF-HFP-fluorosurfactant, PVDF-HFP-fluorosurfactant-DAP, and PVDF-HFP-DAP. The presence of a new peak at 2880 cm^{-1}
 25 corresponds to the CH stretching due to the presence of ether from fluorosurfactant. **Fig. 11b**, a new peak appeared at 1651 cm^{-1} in the FTIR spectrum of the crosslinked PVDF-HFP-fluorosurfactant-DAP polymer reflected the vibration of C=N bonds, proving the crosslinking by DAP. **Fig. 11c**, the peak located at 882 cm^{-1} indicates the amorphous phase of PVDF-HFP. The peaks at 833 and 840 cm^{-1} corresponds to the β -phase of PVDF. Dipole-dipole interaction
 30 between fluorosurfactant and PVDF-HFP chains can induce the rearrangement of PVDF-HFP chains, as revealed by these peaks shift in FTIR spectra.

The cross-linked elastomer according to an example embodiment was stable when tested to a temperature of 385°C (**Fig. 12a-c**). Specifically, TGA result of **Fig. 12a**, PVDF-HFP-fluorosurfactant-DAP, **Fig. 12b**, PVDF-HFP, and **Fig. 12c**, fluorosurfactant Zonyl FS300, are
 35 shown.

The strong dipole-dipole interactions between the surfactant molecules and the cross-linked polymer network according to an example embodiment trap the surfactant strongly within the base elastomer. This imbued the elastomer with self-healing properties and enhanced dielectric permittivity. When the surfactant was added, the glass transition temperature (T_g) of the base
 40 elastomer decreased to -38.5°C , while the virgin PVDF-HFP had a higher T_g of -21.8°C (**Fig.**

12d). More specifically, Both PVDF-HFP and crosslinked PVDF-HFP-fluorosurfactant-DAP show no melting peak at $\sim 140^\circ\text{C}$, which is normally the melting point of crystallized PVDF-HFP, indicating the materials are amorphous. A shift of glass transition temperature (T_g) from -21.8°C of PVDF-HFP to -38.5°C of crosslinked PVDF-HFP-fluorosurfactant-DAP was observed, confirming the plasticizer function of fluorosurfactant.

This indicated the plasticizer function of the surfactant, which lowered the mechanical modulus of the resultant elastomer. The fluorosurfactant also contributed to the self-healing behaviour of the elastomer according to an example embodiment via the dipole-dipole interaction and hydrogen bonding among the fluorinated terminals of the fluorosurfactant molecules and PVDF-HFP chains. When a non-fluorinated surfactant was used, it was found that the self-healing property of the polymer disappeared (**Fig. 13**). Specifically, **Fig. 13** shows photographs of self-healing performance of **left**: PVDF-HFP-fluorosurfactant-DAP and **right**: PVDF-HFP-hydrocarbon surfactant-DAP. The hydrocarbon surfactant (Triton X-100) did not blend well with the fluoropolymer, leaching out from the polymer as shown by the white arrows. PVDF-HFP-hydrocarbon surfactant-DAP did not self-heal from bifurcations.

The base elastomer has as low as a modulus of 310 kPa and can reach a strain of $\sim 230\%$. After bifurcation, the cut interfaces self-healed at 70°C after 4 days and recovered 76.3% of its maximum strain with a toughness healing efficiency of $63.2\% \pm 14.6\%$ (**Fig. 3b**). After self-healing, the base elastomer diment can be strained up to 180% (**Fig. 3b inset**).

To make an elastomeric composite exhibiting a piezoiimpedance property, micro-nickel (μNi) particles with nanoscale surface features were added as conductive fillers in an example embodiment. It was discovered that this addition of particles resulted in a closed-cell foam material. Fortuitously, the porous structure enabled greater deformation when mechanical stress is applied without affecting the integrity of the 3D electrodes. The pore structure, size, and distribution were consistent across batches according to example embodiments (**Figs. 14 and 15**). Pore sizes are larger ($\sim 1\text{ mm}$) near the substrate surface while smaller pores (0.13 mm) were found at the top of the foam.

Specifically, **Fig. 14a** schematically illustrates a fabrication process of the resistive foam material according to an example embodiment. PVDF-HFP was dissolved in acetone and mixed with Zonyl FS-300 and DAP in sequence. After μNi was added, the mixture was directly cast into a glass mold, then immediately heated at 70°C . When heated at 70°C , acetone solvent evaporated, leaving pores inside the polymer. After increasing the temperature to 120°C , the crosslinking process of PVDF-HFP chains by DAP was accelerated and completed. **Fig. 14b** shows SEM images of Foam 25 μNi . Zoomed-in images of foam material reveal the uniformity and consistency of μNi particles dispersing inside the elastomer matrix.

Fig. 15a shows optical microscope images of **Left**: Foam 20 μNi . **Middle**: Foam 25 μNi . **Right**: Foam 30 μNi . The images depict the pore structure in foam as bigger voids at the bottom and smaller on top. All 3 samples in each group of μNi loading show the same structure, revealing the fabrication process is repeatable. **Fig. 15b** shows pore size distributions of the images in **Fig. 14a**.

It is noted that any other particles with nanoscale surface features may be used in different embodiments to impart/promote various properties of the elastomeric composite, including, but not limited to, Ag nanoflakes, carbon nanotube (CNT), graphene, metal nanowire, etc.

The pore distribution in an example embodiment can be explained by void formation theory, similar to the swiss cheese eyes formation (**Fig. 16**). As the solvent evaporates from the polymer, the μNi particles (and Cu electrodes) served as void nucleation sites. Upon heating to 70 °C, evaporation-induced phase inversion causes greater void nucleation and aggregation, thereby generating pores within the polymer matrix. The bottom part of the polymer dries slower than the air-exposed top surface, resulting in voids aggregation that created larger pores. In contrast, when the solvents were evaporated very slowly at a low temperature, which prevented void nucleation, it was found that no pores were formed, further validating the proposed pore formation mechanism. Hence, the foam material according to an example embodiment can be synthesized in a straightforward self-foaming process. Moreover, the porosity of foam materials and the sensor performance are consistent across batches according to example embodiments (**Figs. 17**).

More specifically, **Fig. 16a** schematically illustrates that voids nucleate at the μNi particles/polymer solution and electrode/polymer solution interfaces when the solvent evaporates. The voids grow and aggregate as the solvent evaporates at 70 °C due to the evaporation-induced phase inversion. Voids at the top stop growing subsequently because the solvent evaporates more easily due to the air exposing surface. Voids at the bottom keep nucleating and growing until all the solvent escape from the polymer. Meanwhile, to make μNi samples with no pores, the polymer was formed at low temperatures for slow solvent evaporation. **Fig. 16b** shows SEM images of **Left**: base elastomer without μNi , **Middle**: 25 μNi with no pores, and **Right**: Foam 25 μNi .

Fig. 17a shows porosity of foam with different μNi loadings and **Fig. 17b**, consistency of sensor performance across 3 different batches according to example embodiments. Resistance change of foam 30 μNi samples from 3 different batches (under normal force of 1 N, 5 N and 10 N) revealed good consistency of sensor performance across batches.

From **Fig. 14** and **Fig. 15** one can see all samples have bigger pores at the bottom and smaller pores on top. This can be related to the void formation theory (see **Fig. 16**). Meanwhile, all the pore size distributions calculated by ImageJ show similar trends. For samples with 20 vol% μNi (20Ni) and 25 vol% μNi (25Ni), the most distributed pores are within the range of 100-500 μm . The range is extended to 100-700 μm for the samples with 30 vol% μNi (30Ni), indicating pore size increase with more μNi . Nevertheless, comparing with 20Ni and 25Ni samples, the 30Ni sample shows a more irregular pore shape, especially for pores with large size. This is because more void nucleation sites are provided with more μNi , these voids can grow bigger and merge when the polymer solution was heated. As the voids are growing, the polymer was solidifying slowly and confining the size and shape of the voids. Voids with different sizes and shapes merge and lead to irregular bigger shape pores at the bottom. Moreover, more μNi loading can bring more void nucleation sites and lead to porosity increase.

Porosity was calculated based on the area ratio of pores to the materials based on the cross-section of images in **Fig. 14**. With more μNi loading, the porosity increased from 52.7% (20Ni) to 60.8% (30Ni).

This self-foaming method according to an example embodiment is convenient and scalable, compared to existing processes that use sacrificial templates, such as sugar, metal foam, and PS beads, or by using multiphase reaction. Although these existing methods can produce small and uniformly distributed pores, the fabrication processes typically involve multiple steps and may still contain residues of the template materials.

Foam materials (without 3-D electrodes) with μNi concentrations of 20 volume percent (vol%), 25 vol% and 30 vol% to the base elastomer according to example embodiments (see also "Methods according to example embodiments" below) were studied further by way of example, not limitation, which are referred to herein as Foam 20 μNi , Foam 25 μNi and Foam 30 μNi , respectively. The ultimate strength of foam materials according to example embodiments decreased only slightly compared with the base elastomer, which was remarkable considering pores were introduced into the material (**Fig. 3c**).

Young's moduli of the foam material according to example embodiments increased compared to the base elastomer (**Table 1**). The addition of μNi increases the stiffness of the material while the introduction of pores decreases the ultimate strength and maximum elongation, according to example embodiments.

Sample	Modulus (MPa)
Base elastomer	0.31
Foam 20 μNi	0.60
Foam 25 μNi	0.79
Foam 30 μNi	1.1

Table 1 Young's moduli of Foam materials and base elastomer

The metal-foam composite for use according to an example embodiment also exhibited self-healing properties (**Fig. 3d-e**). Damaged parts show diminished scars over time (**Fig. 3e**). The resistance of the composite material and its pressure sensing performance recovered almost immediately upon bifurcation and contact (**Fig. 19a-b**). The piezoresistive and piezocapacitive behaviours of the foam according to an example embodiment were also characterized after bifurcation and self-healing for 4 days at 70 °C (**Fig. 3d** and **Fig. 19c-d**).

More specifically, **Fig. 19a** shows a graph illustrating self-healing of the resistance of Foam 25 μNi upon bifurcation and contact. **Fig. 19b** shows a graph illustrating self-healing of the pressure sensing of Foam 25 μNi after bifurcation and self-heal. **Fig. 19c**, shows resistance change vs normal pressure on Foam 30 μNi after self-healing. **Fig. 19d**, shows capacitance change vs normal pressure on Foam 30 μNi after self-healing.

Piezoimpedance tactile sensing according to example embodiments

The foam sensor according to an example embodiment can be operated as a piezo-impedance sensor with either capacitive or resistive changes measured. To better understand the electrical impedance characteristics of the metal-foam composites according to example embodiments, electrical impedance measurements were performed. Nyquist plots showed that Foam 20 μNi , Foam 25 μNi , and Foam 30 μNi (with 3-D electrodes) decreased in baseline electrical resistance from 0.49 MOhm, 0.35 MOhm to 0.18 MOhm, respectively (**Fig. 4a**). The lowered electrical resistance of μNi foam is due to the nanostructured μNi particles dispersed throughout the elastomer matrix. These nanostructures are known to enhance the local electric fields. As more μNi particles are incorporated into the elastomer matrix, percolation pathways for electrons emerge. This leads to a decrease in electrical resistance as more μNi particles are added (**Figs. 20-22**).

More specifically, **Fig. 20** shows Bode plots of foam materials with different μNi loadings. Two peaks in the range of 10^0 to 10^2 Hz and 10^5 to 10^6 Hz, respectively, are consistent with the two semicircles shown in the Nyquist plots. The Bode plots of the samples with different μNi have similar shape and position of the peaks, although minor shifts in the phase angles were observed. This indicates that the samples with different μNi loading may be modelled and explained using the same equivalent circuit but with different parameters. The graphs reveal the ion-conductive-like behaviour of foam material.

Fig. 21 shows I-V curves of **Fig. 21a**, Foam 20 μNi , **Fig. 21b**, Foam 25 μNi , and **Fig. 21c**, Foam 30 μNi under different loadings ($F = 0-15$ N). Graphs indicate the electron-conductivity of the material, which can be related to quantum tunnelling. For example, Foam 25 Ni shows the non-linear I-V behaviour and the slope increased with increasing the loading force, which means the resistance of the material decrease with the increasing pressure. All the samples show similar behaviour. This atypical non-linear I-V phenomenon indicates that the conductivity mechanism of this foam is not pure Ohmic conduction (with linear I-V correlation). The non-linearity may also due to the additional contribution of the quantum tunnelling in the materials.

Fig. 22 shows SEM image of **Fig. 22a**, μNi particles and **Fig. 22b**, zoom-in view of μNi particles. **Fig. 22c**, SEM image of μNi particles buried in the foam polymer. **Fig. 22d** shows COMSOL simulations urchin-like μNi particles, and spherical μNi particles. Urchin-like nickel microparticles with nano-spikes on the particle surface were evenly dispersed in the polymer matrix. Compared with smooth spherical nickel particles, these nanostructures would enhance the local electric field resulting in higher conductivity. The surface charge density had an

obvious positive correlation with the curvature of the metal surface as verified by the COMSOL simulation. The electric energy density is much higher between the sharp points of particles.

The equivalent circuits (EC) of the sample were fitted from the impedance data (**Fig. 4a** inset and **Fig. 23**). More specifically, **Fig. 23** shows the equivalent circuit for the PVDF-HFP-fluorosurfactant-DAP- μ Ni materials. The R_1 represents bulk resistance, while CPE_1 and R_2 represent the double-layered capacitance and the polarization resistance of one of the constituent materials, respectively. The CPE_2 and R_3 represent the other double-layered capacitance and its polarization resistance of the other constituent material, whereas the W_1 element indicates the mass transport process inside the material. It is believed that the mass transport process correlates closely to the surfactant, which acts as both the solvent to PVDF-HFP polymer and the small molecules with charge asymmetry. Consequently, one can hypothesize that the surfactant molecules can either migrate/diffuse or assist the PVDF-HFP chains to migrate/diffuse under either an electric field or concentration gradient.

Parameters of the equivalent circuits are shown in **Tables 2-4**. It can be found that the values of R_1 show a clear correlation with Ni particle concentrations. In particular, the samples without pores showed much lower R_1 values than those with pores, as shown in Table 3 and 4. It can be also observed that the values of R_1 for composites of 30 and 35% μ Ni loading fractions without pores are indeed quite close, probably due to the percolation of the conductive fillers, which is different with the samples contains pores with the same μ Ni loading fractions. Besides, in both cases, either containing pores or not, the values of capacitance from CPE_1 are much smaller than CPE_2 , indicating a different contribution of the capacitance from the constituent materials. Given that the above-mentioned discussion is correct, the CPE_2 can be attributed to the capacitance contributed by surfactant transport, whereas the CPE_1 may originate from PVDF-HFP polymer. The values of the CPEs also show consistency with the μ Ni particles and surfactant concentrations, respectively. The values of CPE_1 increase with μ Ni particle concentration from 3.39×10^{-11} to 1.85×10^{-10} and 1.08×10^{-10} to 4.07×10^{-10} , respectively for samples with or without pores, when μ Ni particle concentration increase from 20 to 35%. This may be ascribed to the increased surface area between μ Ni particles and PVDF-HFP. On the other hand, the values of CPE_2 increase from 1.52×10^{-8} to 6.82×10^{-8} with surfactant concentrations increase from 40 to 70%, whereas the one without any μ Ni addition gave rise to a large CPE_2 of 4.67×10^{-6} .

	20 vol% Ni	25 vol% Ni	30 vol% Ni	35 vol% Ni
R_1 (Ohm)	6256	3791	3307	2146
CPE_1 (S s ⁿ)	3.3887E-11	6.0444E-11	8.1666E-11	1.8482E-10
n_1	0.91369	0.90395	0.91183	0.88672
R_2 (Ohm)	4.6281E5	3.321E5	1.3841E5	8.0993E4
W-R	87855	1.1448E5	1.6197E6	9.4493E5

W-T	0.38396	0.35555	12.67	9.495
W-P	0.59099	0.59497	0.28424	0.75116
CPE ₂ (S s ⁿ)	8.4519E-08	1.1184E-07	1.9044E-07	3.8123E-07
n ₂	0.58789	0.55675	0.57786	0.49675
R ₃ (Ohm)	1.635E6	2.2326E6	1.5975E6	1.1391E6
χ^2	1.756E-4	1.58E-4	1.33E-4	2.14E-4

Table 2. Parameters of elements for samples with different Ni concentrations.

	20 vol% Ni	25 vol% Ni	30 vol% Ni	35 vol% Ni
R ₁ (Ohm)	1233	910.8	777.2	791.1
CPE ₁ (S s ⁿ)	1.08E-10	1.7741E-10	2.0625E-10	4.0697E-10
n ₁	0.91137	0.89459	0.90614	0.8765
R ₂ (Ohm)	97742	75862	48633	41950
W-R	1.2431E7	2.2722E6	2.5736E6	4.5242E6
W-T	61.02	20.39	25.24	59.57
W-P	0.98187	0.92403	0.89463	0.9859
CPE ₂ (S s ⁿ)	4.2263E-7	3.6784E-7	6.5116E-7	6.3544E-7
n ₂	0.44413	0.50867	0.45999	0.51816
R ₃ (Ohm)	4.7431E5	4.183E5	3.67E5	6.6058E5
χ^2	2.5343E-4	4.16E-4	1.3286E-4	1.3436E-4

Table 3. Parameters of elements for samples with different Ni concentrations without pores.

	No Ni	40% Zonyl	50% Zonyl	70% Zonyl
R ₁ (Ohm)	263.9	199.2	554.8	769.6
CPE ₁ (S s ⁿ)	2.6434E-10	1.8065E-11	3.3271E-11	3.2627E-11
n ₁	0.87024	0.9111	0.90074	0.90907

R ₂ (Ohm)	61178	3.657E6	6.0732E5	2.91E5
W-R	8.3359E5	2.6046E7	2.5514E6	84152
W-T	10.78	23.846	4.505	0.081854
W-P	0.82734	0.23815	0.25977	0.46964
CPE ₂ (S s ⁿ)	4.6677E-6	1.518E-8	3.5834E-8	6.8153E-8
n ₂	0.88823	0.69512	0.69872	0.56845
R ₃ (Ohm)	1.7432E5	1.4315E7	2.0725E6	1.0655E6
χ^2	3.83E-4	4.91E-4	3.84E-4	7.19E-4

Table 4. Parameters of elements for samples with different Zonyl concentrations.

The capacitive behaviour of the materials according to example embodiments likely originated from the incorporation of fluorosurfactant. The Nyquist plot of the materials without fluorosurfactant (**Fig. 24a-b**) showed the disappearance of a capacitive loop at a high frequency range. In other words, it was found that the surfactant was significant for the electrical properties of the composite according to example embodiments. A higher concentration of the surfactant can cause a more significant impedance decrease and a large shift of phase angles (**Fig. 24c-d**). The highly asymmetric characteristics of the surfactant molecules according to example embodiments, containing both C-F groups and ethoxyl groups, causes the adsorption/desorption interactions of the molecules with the various interfaces in the composite. Hence, it is hypothesized that the interactions between the surfactant and the neighbouring materials (in an example embodiment PVDF / HFP, μ Ni particles and electrodes), are the primary causes of the capacitive loops. Pores inside the composites according to example embodiments may also contribute to the capacitive loops (**Fig. 25**).

More specifically, Fig. 24a shows Nyquist plot and **Fig. 24b** Bode plot of Foam 25 μ Ni with no addition of fluorosurfactant. The plots show different electrical behaviour as compared to Foam 25 μ Ni with fluorosurfactant addition. Only one obvious semicircle can be seen within the range of the frequency tested in the Nyquist plot. **Fig. 24c** shows Nyquist plot and **Fig. 24d** Bode plots for samples with different fluorosurfactant concentrations. **Fig. 24** shows Nyquist plot and **Fig. 24f** Bode plot for the sample without μ Ni. Samples with various fluorosurfactant concentrations significantly affect the impedance of the composite materials. The radii of the first semicircles that appear in the leftmost of the Nyquist plot decreased dramatically from around 4.5 MOhm to less than 500 kOhm when the surfactant concentration increased from 40 to 70 wt%, respectively, whereas the radii of the second observable semicircles also decreased accordingly. On the other hand, **Fig. 22d** shows obvious right-shift of the peaks, from around 10^1 to 10^2 Hz, with an increasing amount of fluorosurfactant added. This indicates that the electrical performance of the composites may correlate closely to the surfactant. The sample without μ Ni particle incorporation shows two peaks at low and high frequencies range, respectively, indicating that there are two separate capacitive mechanisms.

Fig. 25 shows Nyquist and Bode phase plots of foam and non-porous materials of different μNi loadings. **Fig. 25a**, Nyquist plots and **Fig. 25b**, Bode plots for foam samples with different μNi . **Fig. 25c**, Nyquist plot, and **Fig. 25d**, Bode plots for nonfoam samples different μNi . To test the impedance of the materials, samples with different Ni concentrations were cut into $1 \times 1 \text{ cm}^2$ size and sandwiched by two gold sheets, which were then connected to the MFIA LCR meter for impedance scanning from 10^{-1} to 10^6 Hz .

The samples without pores exhibited much smaller radii on the semicircles at the high-frequency range, which decreased from 120 kOhm to 50 kOhm when μNi loading increased from 20 to 35%, respectively. This is consistent with the fact that the materials become denser without the pores, which is favorable for the electrical conduction within the materials. The Bode phase plots of composites without pores show that the two peaks with positions similar to those samples without pores remain in the curves. The shape of the curves and the positions of the peaks show high similarity when comparing with the samples with pores. The difference in the sample with 35% μNi loading may arise from the percolation of μNi particles. This indicates that although there might be some minor variations, such as a slight shift in the phase angles and positions of the peaks, the dominating mechanism may remain invariant when pores are removed from the sample.

The dielectric permittivity of the foam composite materials according to example embodiments (with 3-D electrodes) was also measured in the frequency range of 0 - 10^5 Hz (**Fig. 4b**). The samples have large permittivity values because of the dispersed fluorosurfactant and μNi fillers in the material matrix, as shown in the Energy Dispersive Spectroscopy (EDS) mapping (**Fig. 26**). Fluorosurfactant molecules improve the permittivity in the material via the realignment of dipole centres. A comparative sample with no surfactant showed ~ 8.5 times lower permittivity compared to materials with surfactant (**Fig. 4b**).

More specifically, **Fig. 26** shows EDS mapping of **Fig. 26a**, base elastomer, **Fig. 26b**, base elastomer without fluorosurfactant, and **Fig. 26c**, Foam 25 μNi . Oxygen concentration was negligible when no fluorosurfactant was added, revealing the distribution of fluorosurfactant in Foam material. μNi particles are dispersed throughout the foam material.

Remarkably, Foam 30 μNi according to an example embodiment has a high permittivity of $\sim 94,000$ at a frequency of 1 Hz. This is because the μNi particles form conducting paths across the matrix of the material. Maxwell-Wagner effect induces high dielectric constant of the near-percolation composites at low frequencies. As frequency increases, frequency-dependent relaxation causes a decrease in the dielectric permittivity of the composites. At 1 kHz, the permittivity of Foam 30 μNi according to an example embodiment remains high at 370, and can be used in a large array of piezocapacitive sensors where high baseline capacitances are desired because capacitance scales linearly with electrode area. It was found that non-porous samples have slightly higher permittivity than the foam samples (**Fig. 27**) from the higher volume concentration of μNi . More specifically, **Fig. 27a** shows permittivity and **Fig. 27b** loss tangent of the materials with different μNi concentration.

The balance between the conductivity and dielectric permittivity provides the opportunity for using piezo-impedances (resistance and capacitance) operation in tactile sensing. When pressure (P) < 10 kPa, the sensitivity of foam sensors according to example embodiments in piezoresistive mode increases from 11.4 MPa^{-1} to 98.2 MPa^{-1} as μNi loadings increasing from 20 vol% to 30 vol% (**Figure 4c**). For foam sensor with 30 vol% μNi , the sensitivity was 1.25 MPa^{-1} when $10 \text{ kPa} < P < 100 \text{ kPa}$. In piezocapacitive mode, the sensitivity shows a similar trend as the piezoresistive behaviour with higher sensitivities (**Figure 4d**). When $P < 10 \text{ kPa}$, the sensitivity reached 378 MPa^{-1} for foam sensor according to an example embodiment with 30 vol% μNi and remained at 218 MPa^{-1} when $10 \text{ kPa} < P < 100 \text{ kPa}$ (**Fig. 28**). In an example embodiment, the sensor response time was as fast as 19 ms (**Fig. 29**), which is comparable to other existing sensors. The sensor according to an example embodiment can also restore its initial state after its exposure to different temperatures and humidity levels (**Figs. 30 and 31**).

More specifically, **Fig. 28a** shows resistance change vs normal pressure, **Fig. 28b** capacitance change vs normal pressure. The sensitivity of resistance change and capacitance change was calculated as shown below:

$$S_R = \frac{\delta \left(\frac{(R_0 - R)}{R_0} \right)}{\delta P}$$

$$S_C = \frac{\delta \left(\frac{(C - C_0)}{C_0} \right)}{\delta P}$$

Both the S_R and S_C increased with the increasing μNi loadings. When $P < 10 \text{ kPa}$, the S_R reached 98.2 MPa^{-1} for foam 30 μNi , which is ~ 9 times of the sensitivities (11.4 MPa^{-1}) of the foam 20 μNi . Meanwhile, the S_C of foam 30 μNi (378 MPa^{-1}) increased even higher, at ~ 19 times compared to the foam 20 μNi (19.7 MPa^{-1}). The change of S_R with different μNi loadings became gentle when $10 \text{ kPa} < P < 100 \text{ kPa}$, increasing from 0.944 MPa^{-1} (foam 20 μNi) to 1.25 MPa^{-1} (foam 30 μNi). Nevertheless, the change in S_C was still high at the same pressure range, increasing from 1.97 MPa^{-1} (foam 20 μNi) to 218 MPa^{-1} (foam 30 μNi). The S_C is always higher than S_R , which can be attributed to the incorporation of fluorosurfactant and μNi . The resistive behaviour was built on the percolation of μNi in the base elastomer. When $P < 10 \text{ kPa}$, the porous structure in our foam was compressed first and caused a big change in resistance. When the materials were compressed further, the resistance change slowed down and led to a small S_R change. Meanwhile, The capacitive behaviour was contributed by the interactions and interfaces of the electrode/surfactant, μNi /surfactant, and μNi /PVDF-HFP. More μNi loadings can bring more μNi /surfactant and μNi /PVDF-HFP interfaces, leading to a high S_C even when $P > 10 \text{ kPa}$.

Fig. 29a shows pressure sensing response time. The right figure shows the magnified curve of the left one. The response time was as fast as 33 ms upon loading of 5.4 kPa, while the response time upon releasing of the load was 19 ms. The sensor response time is comparable to existing sensors. **Fig. 29b** shows the response time for foam as proximity sensor according to an example embodiment can be limited by the hand moving rate. When human hand approached

the sensor with slow rate, the response time was 124 ms, and Fig. 29c, For fast moving hand, the response time can reach 24 ms.

Fig. 30 shows foam 30 μ Ni sensor responses to temperature, according to an example embodiment. Both impedance (**Figs. 30a-c**, absolute impedance, resistance and capacitance) and impedance change (**Figs. 30d-f**, change in absolute impedance, resistance and capacitance) shows response to temperature (constant relative humidity at 60 %). As the temperature increased, resistance decreased whereas capacitance increased. The absolute impedance (combination of resistance and capacitance) decreased. However, the impedance change shows the opposite behavior. The resistance increased moderately while capacitance decreased. The absolute impedance change increased from ambient environment to 25 °C then barely changed. Both impedance and impedance change can recover to its initial state after being brought back to the ambient environment.

Fig. 31 shows foam 30 μ Ni sensor responses to humidity, according to an example embodiment. Both impedance (**Fig. 31a-c**, absolute impedance, resistance and capacitance) and impedance change (**Fig. 31d-f**, change of absolute impedance, resistance and capacitance) shows response to humidity (temperature maintained at 70 °C at all the tested humidity levels). Resistance and resistance change upon loading decreased whereas capacitance and capacitance change shows the opposite behaviour. The absolute impedance shows the similar trend as the resistance. Both impedance and impedance change can recover to its initial state at ambient environment.

Mechanical force distribution according to an example embodiment

An foam sensor according to an example embodiment was developed that could identify force distribution and direction by embedding four 3D electrodes and one ground electrode within the foam matrix (see also Methods according to an example embodiment, below). An as-prepared foam sensor 500 according to an example embodiment is self-encapsulated and flexible (**Fig. 5a, b**). In this manner, four sensing zones were obtained: E1, E2, E3, and E4 (**Fig. 5c**). When both normal and shear forces were applied simultaneously, the differential signals from the sensors allows determining the general direction of the applied force (**Figure 5c**). For example, when a diagonal force 502 was applied from G to E1 direction, E1 showed the largest resistance change while the other three zones have smaller resistance changes.

In another example, the resistance change when the force was applied between E2 and E3 was measured (**Fig. 32**). To estimate the applied force vector, calibration is first conducted on the foam according to an example embodiment (see also "Methods according to example embodiments", below). The calibration of the foam sensor according to example embodiments is based on the assumption that the calibration of a pair of electrodes (e.g., E1 and G) can also be used for the rest of the pairs of electrodes, since all electrode pairs are identical and independent of each other according to an example embodiment. The estimated shear (F_x and F_y) and normal forces (F_z) showed a good accuracy compared with the measured forces (**Fig. 5d**). The accuracy between the peak force value of the predicted and measured forces are (95

± 3 %), (98 ± 1) %, and (88 ± 6) % for F_x , F_y , and F_z , respectively. Although only diagonal directions were applied in the demonstration, it can be extended to all directions, as will be appreciated by a person skilled in the art.

More specifically, **Fig. 32a** shows a photograph of foam sensor according to an example embodiment with 4 zones for force distribution and direction identification test. **Fig. 32b** schematically illustrates foam sensor (25 vol% μNi) according to an example embodiment in detecting the direction and force distribution. **Left**, illustration of the deformation of a pixelated foam sensor according to an example embodiment under external force loading; **right**, resistance change response to the external force loadings.

Proximity and tactile pressure sensing according to an example embodiment

Intriguingly, foam according to an example embodiment can also be used for proximity sensing. The fluorosurfactant and near-percolation μNi particles in an example embodiment provide high dielectric permittivity values, enabling foam according to an example embodiment to function well as a capacitive proximity sensor where the electrical field changes from the electrodes can be detected. In contrast, a control sample of 25 vol% Ag nanoflakes (Ag Nfs) (see also "Methods according to example embodiments", below, and **Fig. 33**) with high conductivity is not preferred for a proximity sensor (**Fig. 34**). The effect on the sensor capacitance versus the distance of the human finger to the foam according to an example embodiment was measured (**Figure 6b** and **Fig. 35**). The capacitance decreases as a human finger moves towards the sensor because the electric fields couple with the finger and reduce the effective capacitance between the 3D electrodes. When the finger contacts the foam according to an example embodiment and pressure was applied, the LED 602 on the right increased in intensity as resistance decreased with applied pressure (**Fig. 6c**). A simple circuit was demonstrated whereby both capacitance and resistance signal can be used for proximity sensing and pressure sensing, respectively, according to example embodiments (**Fig. 36**).

More specifically, **Fig. 33a** shows resistance change response of material with 25 vol% Ag nanoflakes (Ag Nfs) and 25 vol% μNi , according to an example embodiment, under 100 kPa. Samples with Ag Nfs were not able to generate consistent foams like the samples with μNi . **Fig. 33b** shows capacitance change response of material with 25 vol% Ag nanoflakes and 25 vol% μNi under 100 kPa. **Fig. 33c** shows resistance response of material with 25 vol% Ag Nfs under 100 kPa. **Fig. 33d** shows capacitance response of material with 25 vol% Ag Nfs under 100 kPa. The material with 25 vol% Ag Nfs shows much smaller resistance and capacitance change than Foam 25 μNi , according to an example embodiment, mainly due to the low resistance of the 25 Ag Nfs. It is noted that Ag Nfs can nevertheless be used as possible particles in example embodiment with reasonable concentrations. The above results merely demonstrate that Ag Nfs used with the same concentration as the μNi is not a preferred example embodiment. However, reducing the Ag Nfs concentration can provide good example embodiments., which is believed to be due to the higher conductivity of the Ag Nfs.

Fig. 34 shows proximity test of the foam sensor according to an example embodiment. **Inset:** cross-section of foam sensor (3D electrodes was buried inside the Foam 25 μ Ni); Graph shows the capacitance change response on proximity test. During the test, a human finger will approach the sensor with a distance of 3 cm, 6 cm, 9 cm, respectively. The control sample (with very low resistivity) shows no proximity performance.

Fig. 35a shows capacitance response of foam sensor as a proximity sensor according to an example embodiment. **Fig. 35b** shows resistance response of the foam sensor as a proximity sensor according to an example embodiment. Capacitance decreased while resistance increased when the foam sensor worked as a proximity sensor. An increase in μ Ni loading led to an increase in initial capacitance and a decrease in initial resistance.

Fig. 36 shows the electrical circuit for proximity and pressure LED demonstration, according to an example embodiment.

As described above, inspired by the innervated human mechanosensory system, an example embodiment of the present invention can provide a self-healing artificially innervated foam (foam) piezo-impedance tactile sensor using an elastomeric polymer with metal particle composites. It was shown that innervating the foam material with embedded 3D electrodes, one can operate a tactile sensor according to an example embodiment in piezo-resistive or piezo-capacitive modes. The foam sensor according to an example embodiment can differentiate between various force directions. Furthermore, the foam sensor according to an example embodiment can function as a proximity sensor in capacitive mode, enabling smarter human-machine interactions in emerging augmented reality and robotic skin applications.

Methods according to example embodiments

Fabrication of foam material for use in an example embodiment: With reference to **Fig. 14a**, fluorosurfactant (Zonyl FS-300) was dried in an oven at 70 °C and other chemicals were used as purchased. 2 g of PVDF-HFP (3M) was dissolved in acetone and stirred for at least 4 hrs. 1.7 ml of fluorosurfactant was added to the solution and stirred for 24 hrs. 46 μ l of DAP was added dropwise to the stirring solution. After 30 min, the solution turned light yellow. μ Ni microparticles were added to the solution and the mixture was mixed using a SpeedMixer (FlackTek) at 2500 rpm for 2.5 min. The mixture was cast into a 2.5 x 5 x 0.2 cm³ glass mold (width x length x height). The volume fraction of μ Ni particles in the polymer was calculated based on PVDF-HFP (**Table 5**). The material was then heated on a hotplate at 70 °C for 30 min to self-foaming by evaporating acetone. To crosslink the polymer, the material was heated to 120 °C for 30 min.

Vol% relative to P(VDF-HFP)	Wt% relative to foam composite	Vol% relative to foam composite	Density of foam composite
--------------------------------	-----------------------------------	------------------------------------	------------------------------

20	38.20	7.580	1.766
25	45.18	10.31	2.030
30	51.44	12.73	2.202
35	57.10	14.53	2.264

Table 5. μNi concentrations.

Other materials for use in different embodiments include, but are not limited to:

Polymer: PVDF-based fluoropolymer. For example, PVDF-TrFE, PVDF-CTFE

5 Fluorosurfactant: 3M fluorosurfactant FC-4434, 3M fluorosurfactant FC-4432

Crosslinker: Binucleophiles such as diamines. For example, di-n-butylamine and hexamethylene diamine.

Particles with nanoscale surface features: Ag nanoflakes, carbon nanotube (CNT), graphene, metal nanowire, etc.

10 **Fabrication of control material:** Control sample with Ag Nanoflakes (Ag Nfs) was prepared by following the same procedures as above but changing μNi to Ag Nfs. The control samples of μNi -base elastomer composite with no pores were prepared by cooling the μNi , PVDF-HFP, fluorosurfactant, and DAP mixture for slow solvent evaporation before crosslinking.

15 **Fabrication of 3D electrode patterns:** The electrode patterns on the flexible PCB for use in an example embodiment were designed and etched ($\text{HCl}:\text{H}_2\text{O}_2 = 1:3$ (v/v)). The 3D electrodes were prepared by soldering copper wire with a radius of $75\ \mu\text{m}$ on the designed planar point electrodes. The height of the 3D electrodes was $\sim 1.2\ \text{mm}$. The rest of the planar electrode pattern was insulated by Kapton tape (3M). Copper wires were soldered to the flexible PCB to electrically connect it with the external power source.

20 Preparing the flexible PCB by etching according to example embodiments is a well-developed method. Any copper etchant can be used for flexible PCB preparation, such as, but not limited to, FeCl_3/HCl etchant, CuCl_2/HCl etchant, $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ etchant.

25 **Electrical characterization:** Samples with different μNi concentrations were prepared and cut into $1 \times 1\ \text{cm}^2$ size and sandwiched by 2 gold-sputtered foils. Then the samples were connected to an LCR meter (MFIA) for impedance analysis (R and C connected in series). The bulk resistance of the materials was fitted from the Nyquist plot using the Z-view software from the intercept on the real-axis at a high frequency. To characterize the I-V curves, $1 \times 1\ \text{cm}^2$ samples were placed on gold interdigital electrodes and connected to Keithley 2450. I-V characteristics were also characterised using a motorized z-axis stage (Newmark Systems). Force gauge
30 (Newmark Systems) was used to apply loads to the sensors.

Material characterization: The samples were imaged using an optical microscope (KEYENCE digital microscope) or an SEM (Zeiss sigma 300 with SmartEDS system). Mechanical testing was performed using an Instron Microtester 5500 instrument, testing at a rate of 1 mm s^{-1} . The samples for the tensile test were cut into dumbbell shape following ASTM D1708. Self-healing experiments were performed at room temperature or 70°C after bifurcating the samples and contact the cut regions for healing. Differential scanning calorimetry measurements from -70°C to 200°C with a heating speed of $20^\circ\text{C}/\text{min}$ were performed on TA Instruments DSC 25. Thermogravimetry Analysis is done from 40°C to 600°C , with a heating rate of 20°C on TA Instruments TGA Q500. The dielectric permittivity of the samples was measured using the Alpha-A high-performance frequency analyser (Novocontrol Technologies). FTIR-ATR measurements were performed on a VERTEX 70 spectrometer (Bruker) from 400 to $4,000 \text{ cm}^{-1}$.

Normal force detection: The pressure sensor according to an example embodiment was fabricated by directly casting polymer onto the 3D electrodes. The sizes of the sensors for normal force detection were $1 \times 1 \text{ cm}^2$. The sensor was characterised using a motorized z-axis stage (Newmark Systems). Force gauge (Newmark Systems) was used to apply loads to the sensors covered with a piece of $1.5 \times 1.5 \text{ cm}^2$ glass slide on a custom-built probe station, all interfaced through a computer. For the sensor performance at different temperatures and humidities, the foam sensor was tested in a temperature and humidity chamber (ESPECT SH-262). Weight was loaded ($\sim 5.4 \text{ kPa}$) on the foam sensor to test the sensor performance at all the tested conditions. All the impedance signals (including absolute impedance, resistance, capacitance and phase) were collected from the LCR meter simultaneously.

Shear force detection: The sensor for shear force detection according to an example embodiment was fabricated by direct casting as mentioned above. A piece of $1.5 \times 1.5 \text{ cm}^2$ glass slide was cast on top of freshly cast material and cured together for a firm attachment. The set-up of the shear force test could be found in **Fig. 37**. External forces were applied by pushing the glass slide sideways via a motorized x-y-axis stage (Newmark Systems). All the impedance signals (including absolute impedance, resistance, capacitance and phase) were collected from the LCR meter simultaneously.

More specifically, **Fig. 37** shows photographs of shear force test of foam sensor according to an example embodiment. **Fig. 37a**, before shear force applied, **Fig. 37b**, after the shear force applied. A glass slide 3700 with a bigger surface area than the top surface of the foam material adhered to the top of the foam sensor 3702. An x-y stage (with a pushing block 3704) was employed to push the glass slide 3700 horizontally and therefore applied a shear force to the foam sensor 3702.

Direction identification: The sensor for direction identification according to an example embodiment was fabricated by direct casting as mentioned above. The electrode patterns were designed with 4 pairs of electrodes as shown in **Figure 5a**. L-shaped acrylic pieces were adhered on top of the sensor by a cyanoacrylate adhesive (**Fig. 32a**). External forces were applied by pushing the L-shape acrylic via a motorized x-y-axis stage (Newmark Systems). Signals from the electrodes (E1, E2, E3, and E4) and the ground wire were collected via an

LCR meter. All the impedance signals (including absolute impedance, resistance, capacitance and phase) were collected from the LCR meter simultaneously.

Force vector estimation: First of all, a specific calibration setup (**Fig. 38**) has been prepared to acquire the applied force vector and the resistance change measured by a 3D electrode pair (i.e., E1 and G) according to an example embodiment. This is made possible by mounting the foam sensor 3800 on a six-axis load cell 3802 (Nano17, ATI Industrial Automation) and adhering a L-shaped acrylic structure 3804 on top of the foam sensor 3800. The calibration of the foam sensor 3800 is carried out by applying a shear force 3806 onto the L-shaped structure 3804 in the direction towards E1. In particular, the force is applied carefully with a motorized x-y-axis stage (Newmark Systems), and all resistance variations and force components were measured by the LCR meter (not shown) and load cell 3802, respectively. These data are recorded at a sampling rate of 40 Hz and a moving average filter is applied. With the dataset, calibration curves are formed according to an example embodiment, and the accuracy of the calibration was validated.

Proximity demonstration: The sensor for proximity demonstration according to an example embodiment was fabricated by using foam, connected to an LCR meter. Signals were collected when a human finger approached the sensor. For LED demonstration, the foam sensor was fabricated on a 4-electrode pattern. Two of the electrodes were connected to an proximity LED while the other two were connected to a pressure LED (**Fig. 36**). A DC power source was applied to activate the circuit.

Fig. 18 shows a flowchart 1800 illustrating a method of fabricating a crosslinked polymer network, according to an example embodiment. At step 1802, a polymer is mixed with a surfactant and a crosslinker in a solvent to form a mixture. At step 1804, particles with nanoscale surface features are dispersed in the mixture. At step 1806, the solvent is evaporated to generate pores in the mixture via void nucleation at the particles and void aggregation. At step 1808, crosslinking of the polymer is completed by curing to form the crosslinked polymer network comprising the particles with nanoscale surface features and the pores with the surfactant disposed in the polymer network via dipole-dipole interactions.

The particles and/or the surfactant may be chosen such that the elastomeric composite foam material exhibits a piezoimpedance property.

The polymer and/or the surfactant may be chosen such that the elastomeric composite foam material exhibits a self-healing property.

In one embodiment, a structure is provided comprising:

a crosslinked polymer network; and

a surfactant disposed in the polymer network via dipole-dipole interactions;

wherein the crosslinked polymer network further comprises particles with nanoscale surface features and pores.

The particles and/or the surfactant may be chosen such that the elastomeric composite foam material exhibits a piezoimpedance property.

- 5 The polymer and/or the surfactant may be chosen such that the elastomeric composite foam material exhibits a self-healing property.

The structure may comprise:

a carrier;

the crosslinked polymer network disposed on the carrier; and

- 10 an array of electrodes extending from the carrier at least partially through a thickness of the crosslinked polymer network;

wherein the electrodes are electrically contactable for detecting changes in electrical characteristics between pairs of electrodes.

- 15 The carrier may comprise a printed circuit board, PCB. The PCB may be flexible. The PCB may comprise conductive traces in electrical contact with respective ones of the electrodes.

The electrodes may comprise elongate structures. The elongate structures may comprise conductive wire.

The structure may exhibit resistive and/or capacitive tactile pressure sensing characteristics.

The structure may exhibit capacitive proximity sensing characteristics.

- 20 The structure may exhibit a non-linear I-V characteristic. A resistance of the structure may decrease with increasing tactile pressure.

The structure of may exhibit a permittivity of about 94,000 at a frequency of 1 Hz. The structure may exhibit a permittivity of about 370 at a frequency of 1 kHz.

The structure may exhibit a Young's moduli in a range from about 0.6 - 1.1 MPa.

- 25 The structure may exhibit most distributed pores within a range of about 100-700 μm .

The particles are be in range from about 20 weight% to 30 weight%.

- 30 **Fig. 39** shows a flowchart 3900 illustrating a method of fabricating a sensor device, according to an example embodiment. At step 3902, a carrier is provided. At step 3904, a crosslinked polymer network is disposed on the carrier, the crosslinked polymer network exhibiting a piezoimpedance property. At step 3906, an array of electrodes is provided extending from the carrier at least partially through a thickness of the crosslinked polymer network. At step 3908, interconnections are provided for electrically contacting the electrodes for detecting changes in electrical characteristics between pairs of electrodes.

The carrier may comprise a printed circuit board, PCB. The PCB may be flexible. The PCB may comprise conductive traces in electrical contact with respective ones of the electrodes.

The electrodes may comprise elongate structures. The elongate structures may comprise conductive wire.

- 5 The method may comprise the method of fabricating the crosslinked polymer network. The method may comprise the steps of:

mixing a polymer with a surfactant and a crosslinker in a solvent to form a mixture;

dispersing particles with nanoscale surface features in the mixture;

- 10 evaporating the solvent to generate pores in the mixture via void nucleation at the particles and void aggregation; and

completing crosslinking of the polymer by curing to form the crosslinked polymer network comprising the particles with nanoscale surface features and the pores with the surfactant disposed in the polymer network via dipole-dipole interactions.

- 15 Embodiments of the present invention can have one or more of the following features and associated benefits/advantages:

Feature	Benefit/Advantage
Foam structure based on solvent-evaporation methods	One-step foam fabrication No templates residues Self-encapsulation of sensor structure by direct casting
Pressure sensors with 3D electrodes for E-skin	Detect both normal force and shear force Recognize force direction
Illustrate both piezoresistive and piezocapacitive features for E-skin	High- κ , piezoresistive material Piezoresistive pressure sensing Piezocapacitive proximity sensing
Self-healing	Self-heal when heat at 70 °C

- 20 Aspects of the systems and methods described herein may be implemented as functionality programmed into any of a variety of circuitry, including programmable logic devices (PLDs), such as field programmable gate arrays (FPGAs), programmable array logic (PAL) devices,

electrically programmable logic and memory devices and standard cell-based devices, as well as application specific integrated circuits (ASICs). Some other possibilities for implementing aspects of the system include: microcontrollers with memory (such as electronically erasable programmable read only memory (EEPROM)), embedded microprocessors, firmware, software, etc. Furthermore, aspects of the system may be embodied in microprocessors having software-based circuit emulation, discrete logic (sequential and combinatorial), custom devices, fuzzy (neural) logic, quantum devices, and hybrids of any of the above device types. Of course the underlying device technologies may be provided in a variety of component types, e.g., metal-oxide semiconductor field-effect transistor (MOSFET) technologies like complementary metal-oxide semiconductor (CMOS), bipolar technologies like emitter-coupled logic (ECL), polymer technologies (e.g., silicon-conjugated polymer and metal-conjugated polymer-metal structures), mixed analog and digital, etc.

The various functions or processes disclosed herein may be described as data and/or instructions embodied in various computer-readable media, in terms of their behavioral, register transfer, logic component, transistor, layout geometries, and/or other characteristics. Computer-readable media in which such formatted data and/or instructions may be embodied include, but are not limited to, non-volatile storage media in various forms (e.g., optical, magnetic or semiconductor storage media) and carrier waves that may be used to transfer such formatted data and/or instructions through wireless, optical, or wired signaling media or any combination thereof. When received into any of a variety of circuitry (e.g. a computer), such data and/or instruction may be processed by a processing entity (e.g., one or more processors).

The above description of illustrated embodiments of the systems and methods is not intended to be exhaustive or to limit the systems and methods to the precise forms disclosed. While specific embodiments of, and examples for, the systems components and methods are described herein for illustrative purposes, various equivalent modifications are possible within the scope of the systems, components and methods, as those skilled in the relevant art will recognize. The teachings of the systems and methods provided herein can be applied to other processing systems and methods, not only for the systems and methods described above.

It will be appreciated by a person skilled in the art that numerous variations and/or modifications may be made to the present invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects to be illustrative and not restrictive. Also, the invention includes any combination of features described for different embodiments, including in the summary section, even if the feature or combination of features is not explicitly specified in the claims or the detailed description of the present embodiments.

In general, in the following claims, the terms used should not be construed to limit the systems and methods to the specific embodiments disclosed in the specification and the claims, but should be construed to include all processing systems that operate under the claims. Accordingly, the systems and methods are not limited by the disclosure, but instead the scope of the systems and methods is to be determined entirely by the claims.

Unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise," "comprising," and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in a sense of "including, but not limited to." Words using the singular or plural number also include the plural or singular number respectively. Additionally, the words "herein," "hereunder," "above," "below," and words of similar import refer to this application as a whole and not to any particular portions of this application. When the word "or" is used in reference to a list of two or more items, that word covers all of the following interpretations of the word: any of the items in the list, all of the items in the list and any combination of the items in the list.

CLAIMS

1. A structure comprising:
a crosslinked polymer network; and
a surfactant disposed in the polymer network via dipole-dipole interactions;
- 5 wherein the crosslinked polymer network further comprises particles with nanoscale surface features and pores.
2. The structure of claim 1, wherein particles and/or the surfactant are chosen such that the elastomeric composite foam material exhibits a piezoimpedance property.
3. The structure of claims 1 or 2, wherein the polymer and/or the surfactant are chosen
10 such that the elastomeric composite foam material exhibits a self-healing property.
4. The structure of any one of claims 1 to 3 comprising:
a carrier;
the crosslinked polymer network disposed on the carrier; and
an array of electrodes extending from the carrier at least partially through a thickness of the
15 crosslinked polymer network;
wherein the electrodes are electrically contactable for detecting changes in electrical characteristics between pairs of electrodes.
5. The structure of claim 4, wherein the carrier comprises a printed circuit board, PCB.
6. The structure of claim 5, wherein the PCB is flexible.
- 20 7. The structure of claims 5 or 6, wherein the PCB comprises conductive traces in electrical contact with respective ones of the electrodes.
8. The structure of any one of claims 4 to 7, wherein the electrodes comprise elongate structures.
9. The structure of claim 8, wherein the elongate structures comprise conductive wire.
- 25 10. The structure of any one of claims 4 to 9, exhibiting resistive and/or capacitive tactile pressure sensing characteristics.
11. The structure of any one of claims 4 to 10, exhibiting capacitive proximity sensing characteristics.
12. The structure of any one of claims 4 to 11, exhibiting a non-linear I-V characteristic.
- 30 13. The structure of claim 12, wherein a resistance of the structure decreases with increasing tactile pressure.

14. The structure of any one of claims 4 to 13, exhibiting a permittivity of about 94,000 at a frequency of 1 Hz.
15. The structure of claim 14, exhibiting a permittivity of about 370 at a frequency of 1 kHz.
- 5 16. The structure of any one of claims 1 to 15, exhibiting a Young's moduli in a range from about 0.6 - 1.1 MPa.
17. The structure of any one of claims 1 to 16, exhibiting most distributed pores within a range of about 100-700 μm .
18. The structure of any one of claims 1 to 17, wherein the particles are in range from about
10 20 weight% to 30 weight%.
19. A method of fabricating a sensor device comprising the steps of:
providing a carrier;
disposing a crosslinked polymer network on the carrier, the crosslinked polymer network exhibiting a piezoimpedance property;
- 15 providing an array of electrodes extending from the carrier at least partially through a thickness of the crosslinked polymer network; and
providing interconnections for electrically contacting the electrodes for detecting changes in electrical characteristics between pairs of electrodes.
20. The method of claim 19, wherein the carrier comprises a printed circuit board, PCB.
- 20 21. The method of claim 20, wherein the PCB is flexible.
22. The method of claims 20 or 21, wherein the PCB comprises conductive traces in electrical contact with respective ones of the electrodes.
23. The method of any one of claims 19 to 22, wherein the electrodes comprise elongate structures.
- 25 24. The method of claim 23, wherein the elongate structures comprise conductive wire.
25. The method of any one of claims 19 to 24, comprising the method of fabricating the crosslinked polymer network.
26. The method of claim 25, comprising the steps of:
mixing a polymer with a surfactant and a crosslinker in a solvent to form a mixture;
- 30 dispersing particles with nanoscale surface features in the mixture;
evaporating the solvent to generate pores in the mixture via void nucleation at the particles and void aggregation; and

completing crosslinking of the polymer by curing to form the crosslinked polymer network comprising the particles with nanoscale surface features and the pores with the surfactant disposed in the polymer network via dipole-dipole interactions.

5 27. A method of fabricating a crosslinked polymer network, the method comprising the steps of:

mixing a polymer with a surfactant and a crosslinker in a solvent to form a mixture;

dispersing particles with nanoscale surface features in the mixture;

evaporating the solvent to generate pores in the mixture via void nucleation at the particles and void aggregation; and

10 completing crosslinking of the polymer by curing to form the crosslinked polymer network comprising the particles with nanoscale surface features and the pores with the surfactant disposed in the polymer network via dipole-dipole interactions.

28. The method of claim 27, wherein particles and/or the surfactant are chosen such that the elastomeric composite foam material exhibits a piezoiimpedance property.

15 29. The method of claims 27 or 28, wherein the polymer and/or the surfactant are chosen such that the elastomeric composite foam material exhibits a self-healing property.

1/36

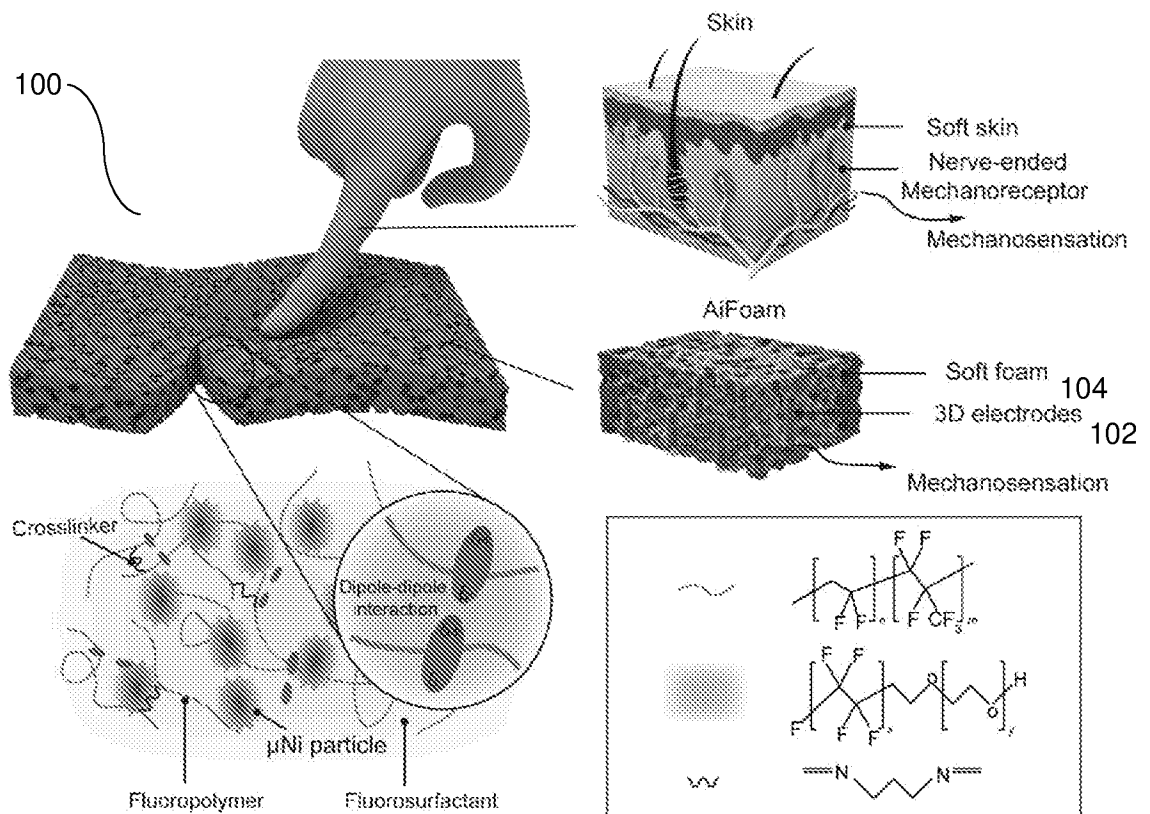


Fig. 1

2/36

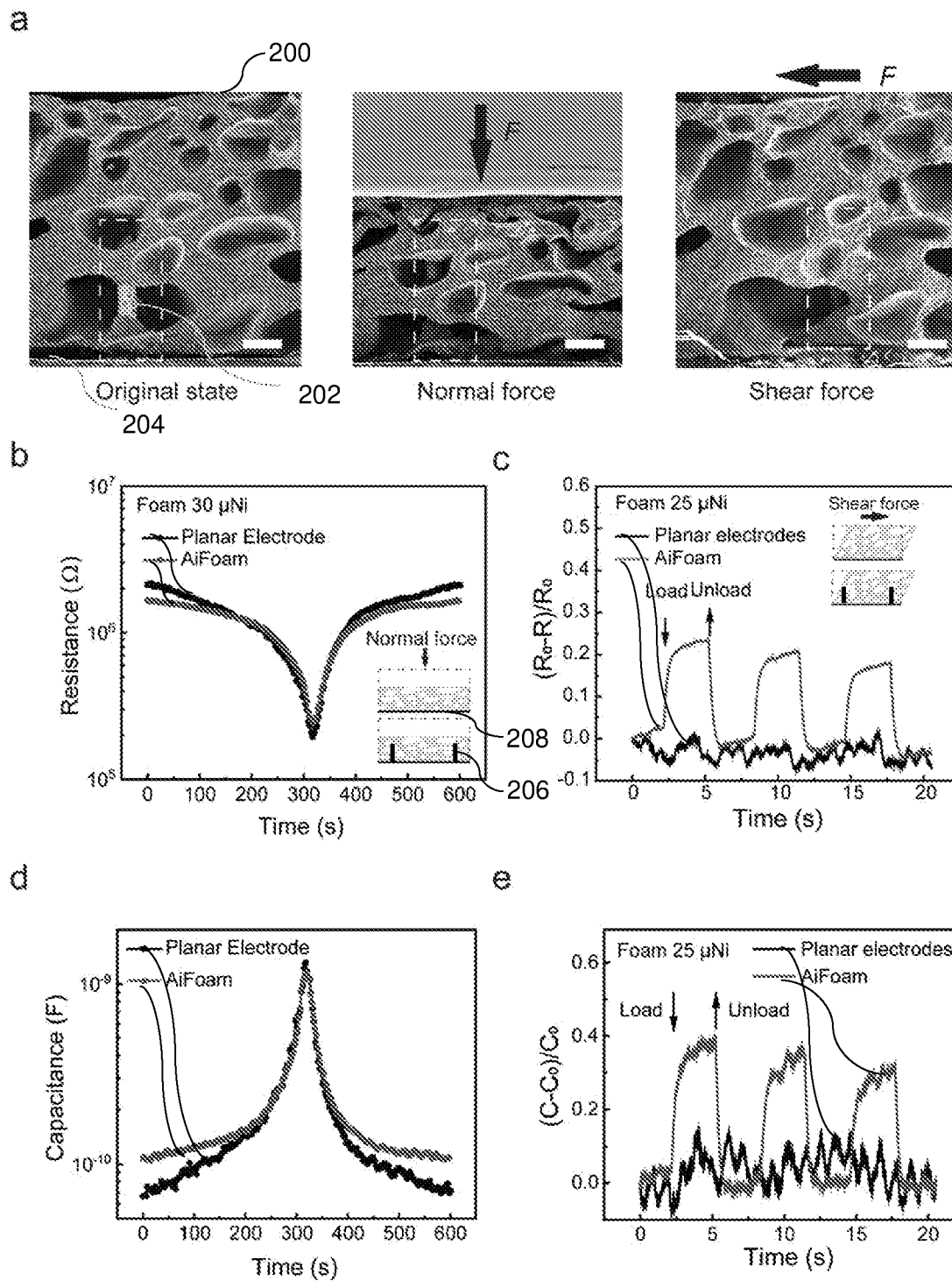


Fig. 2

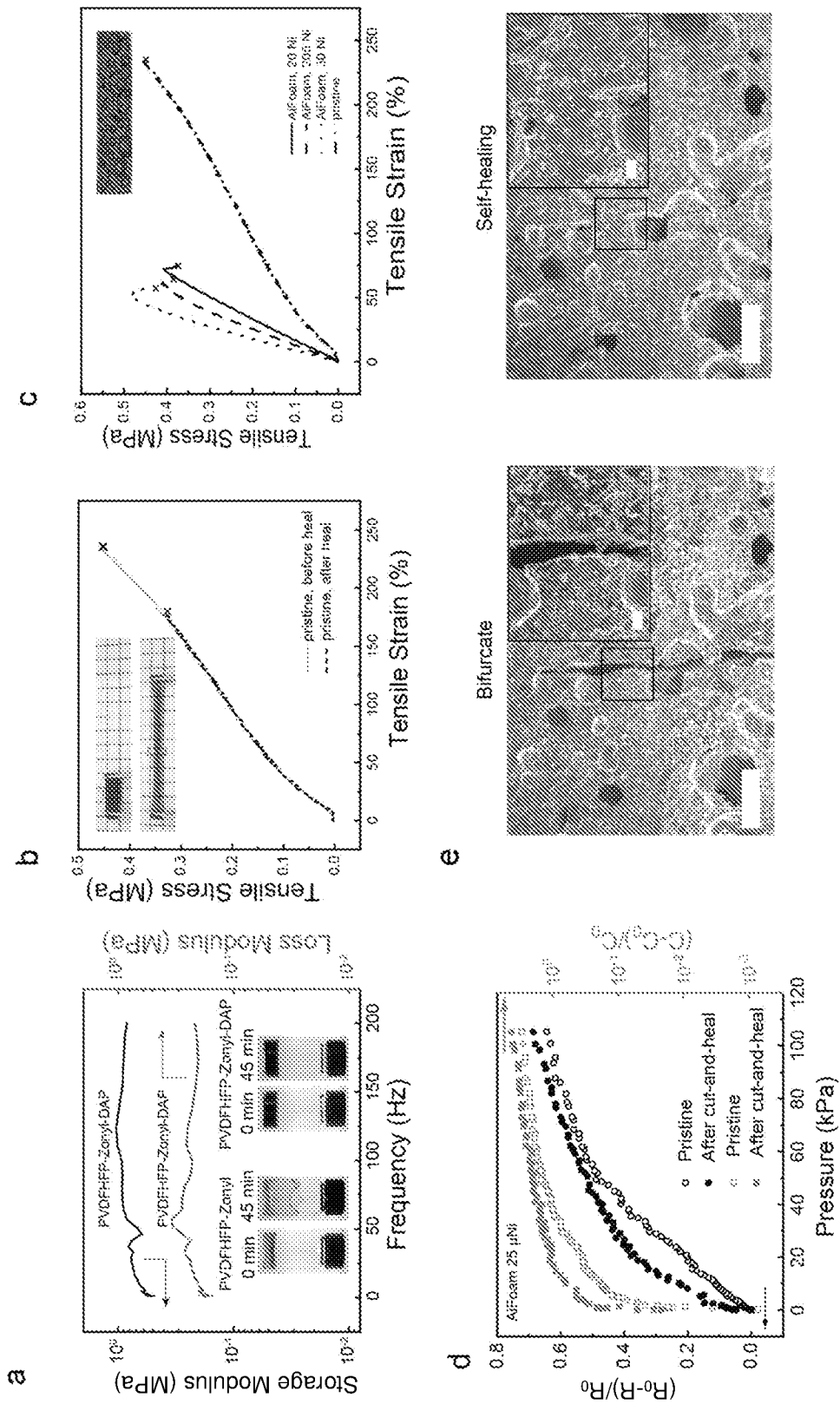


Fig. 3

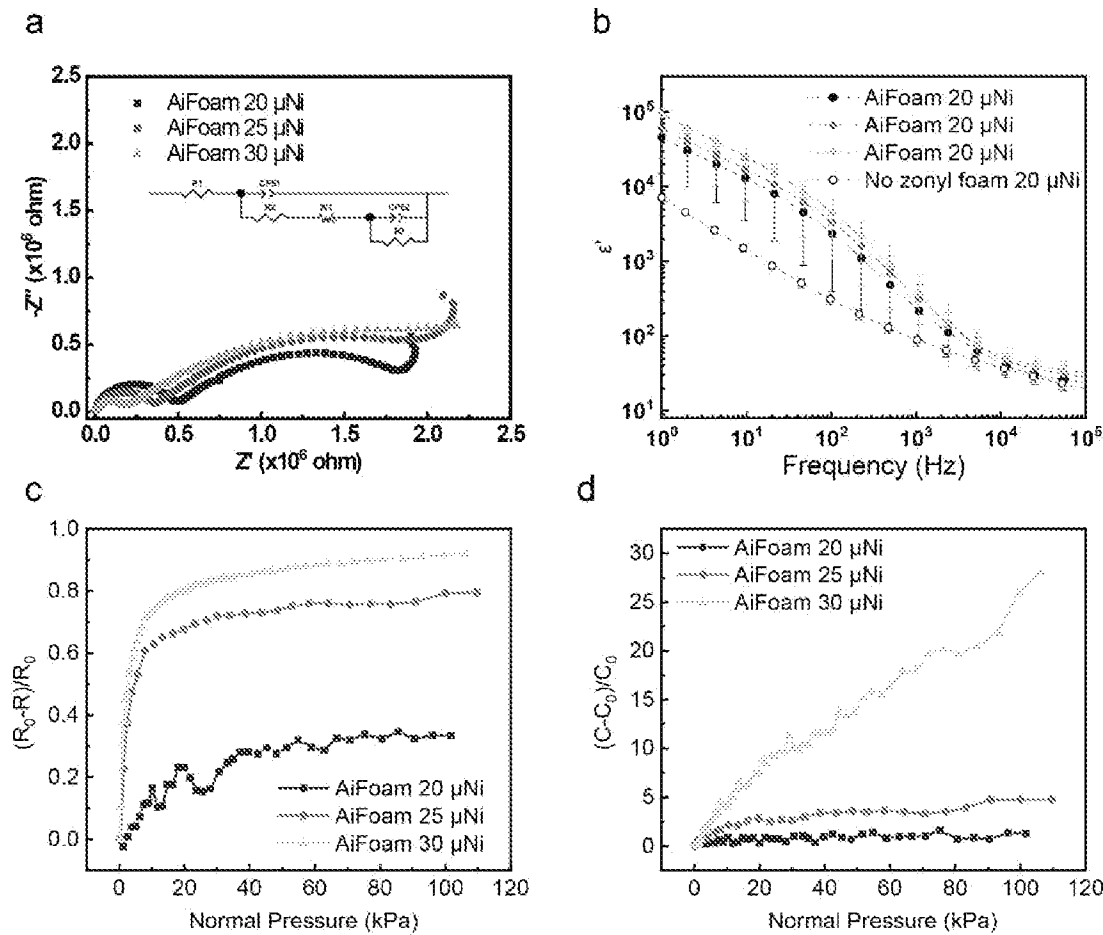


Fig. 4

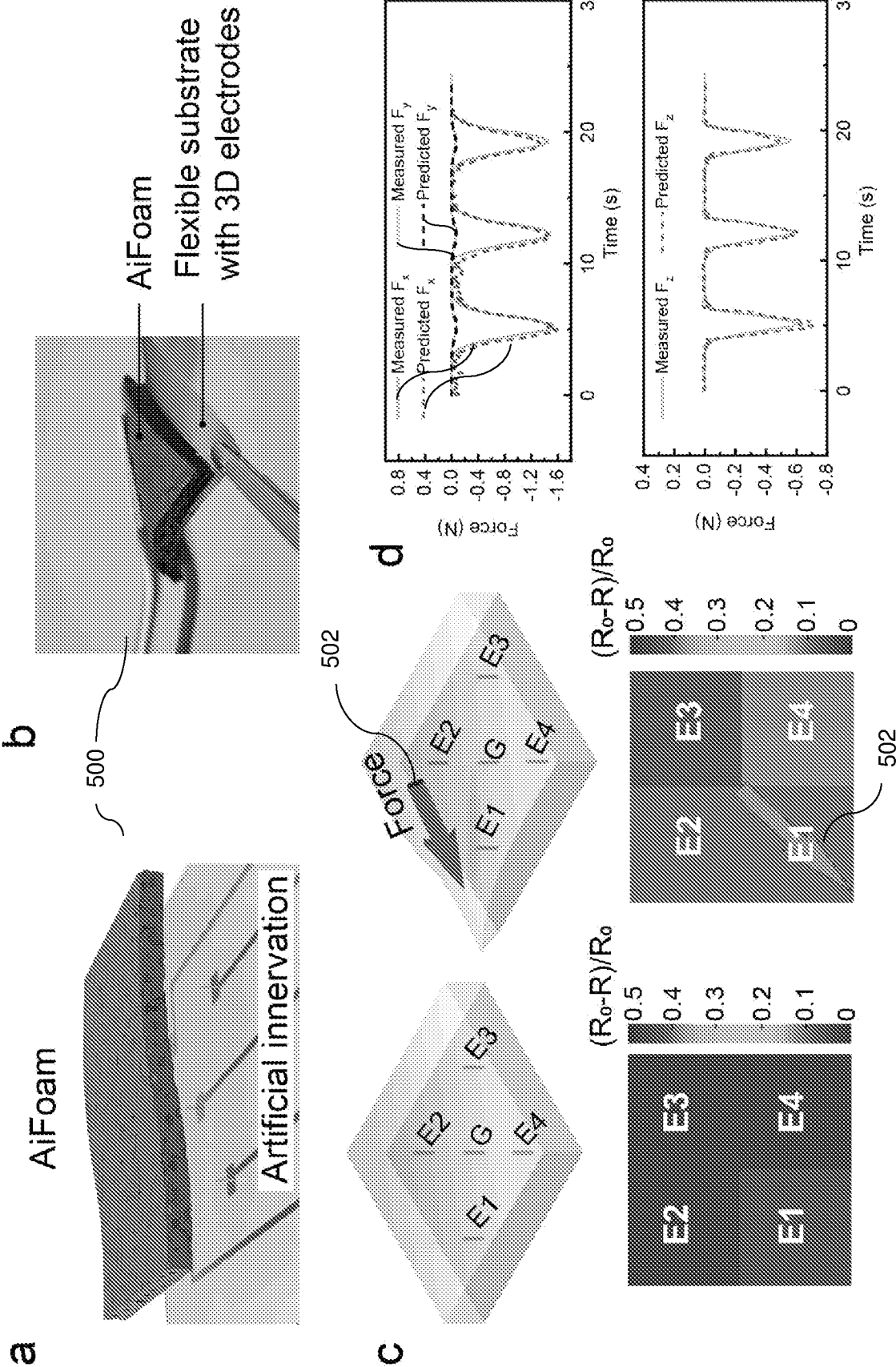


Fig. 5

6/36

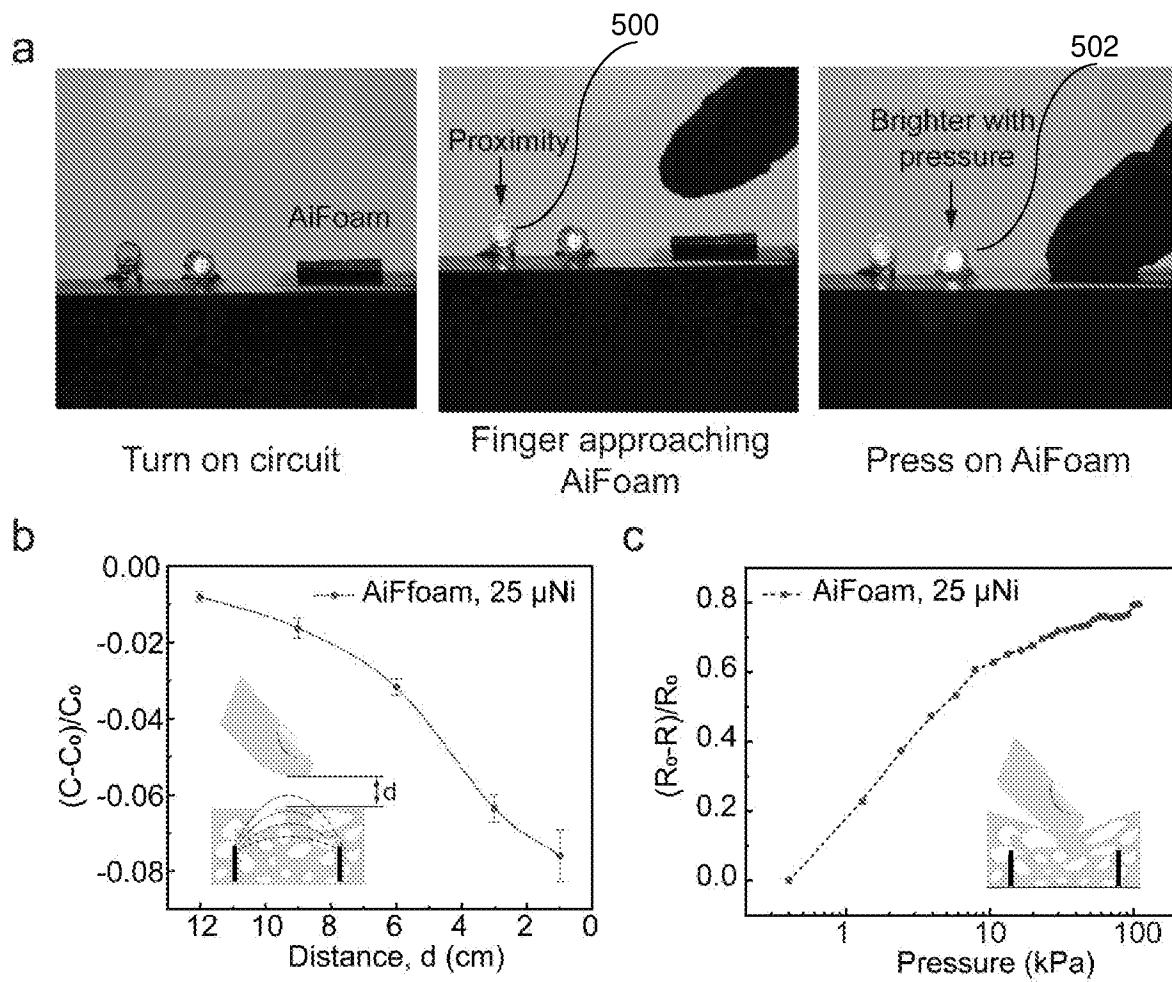


Fig. 6

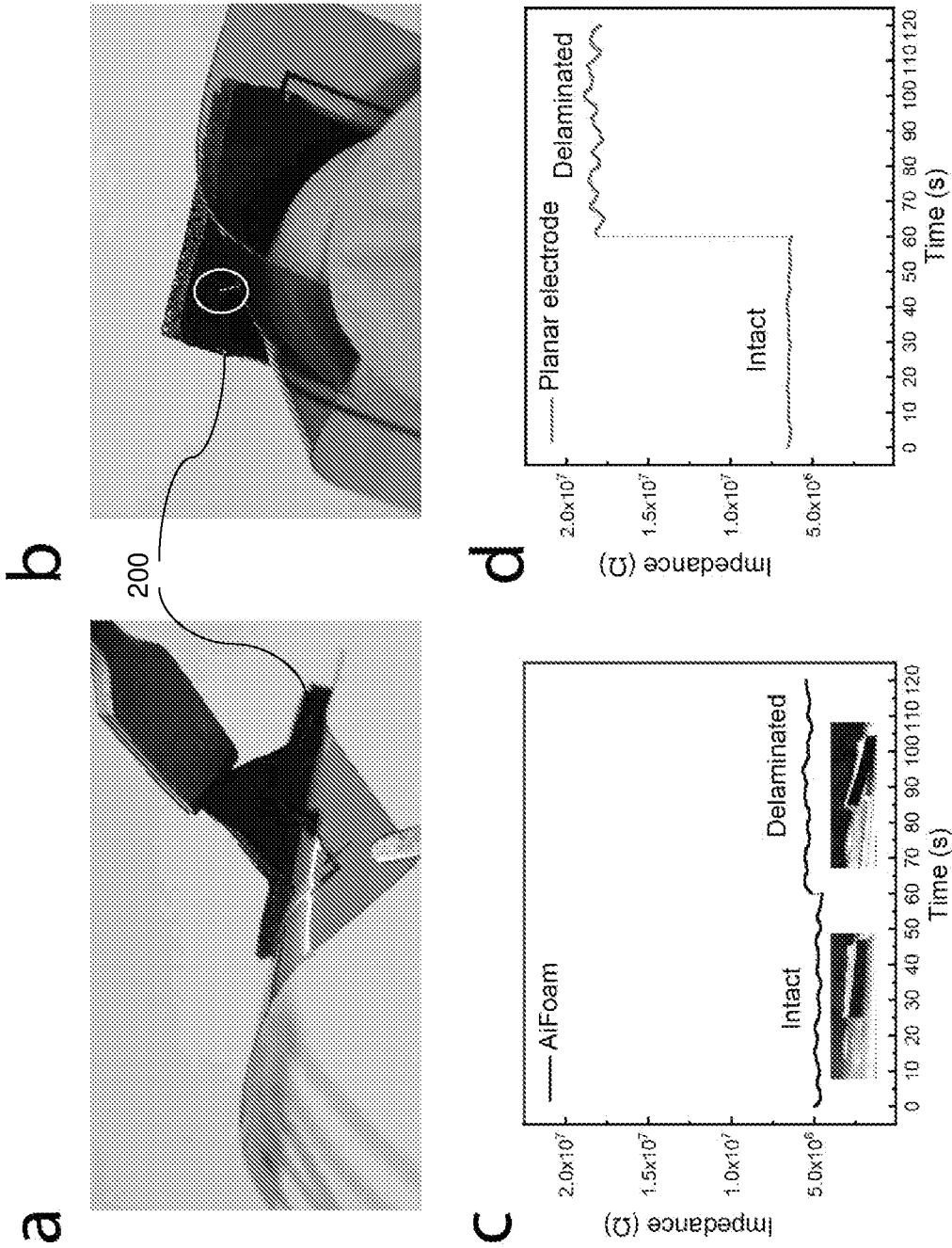


Fig. 7

8/36

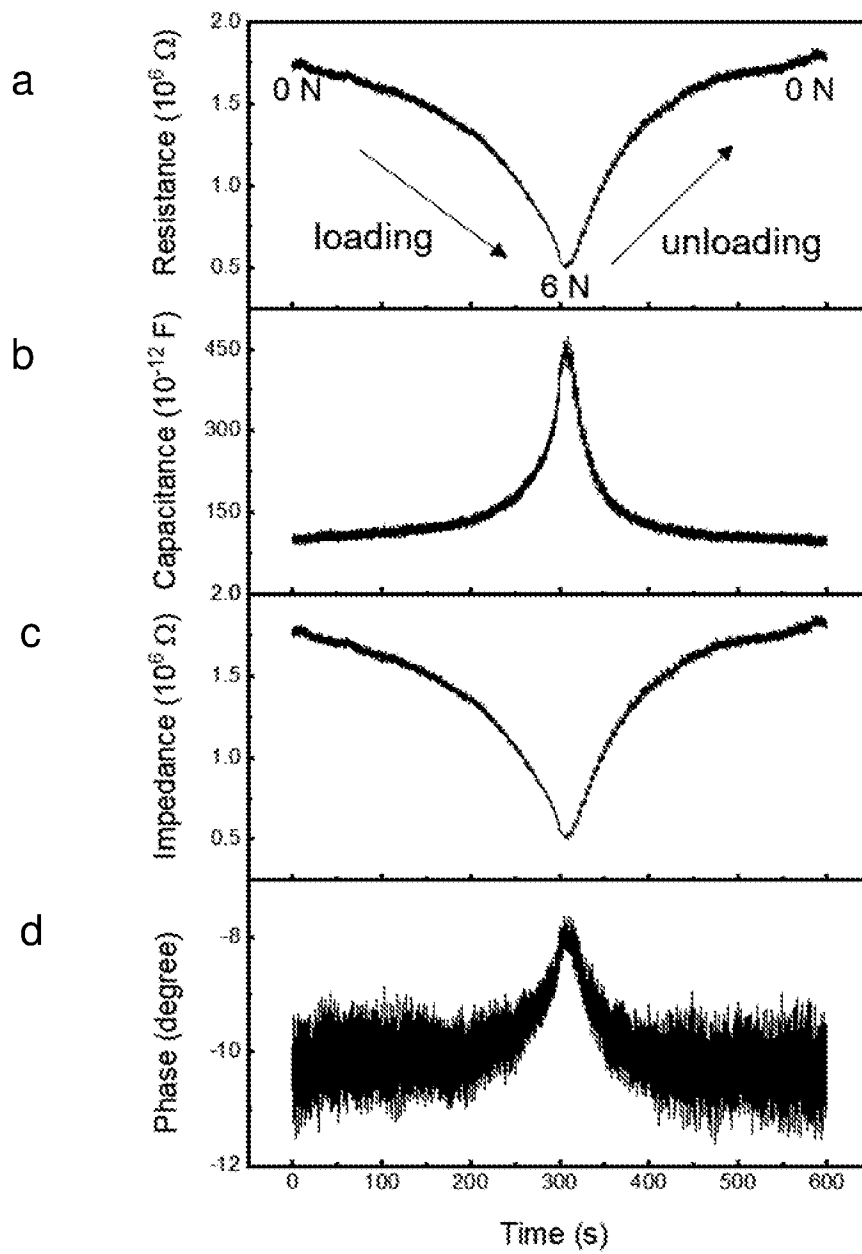


Fig. 8

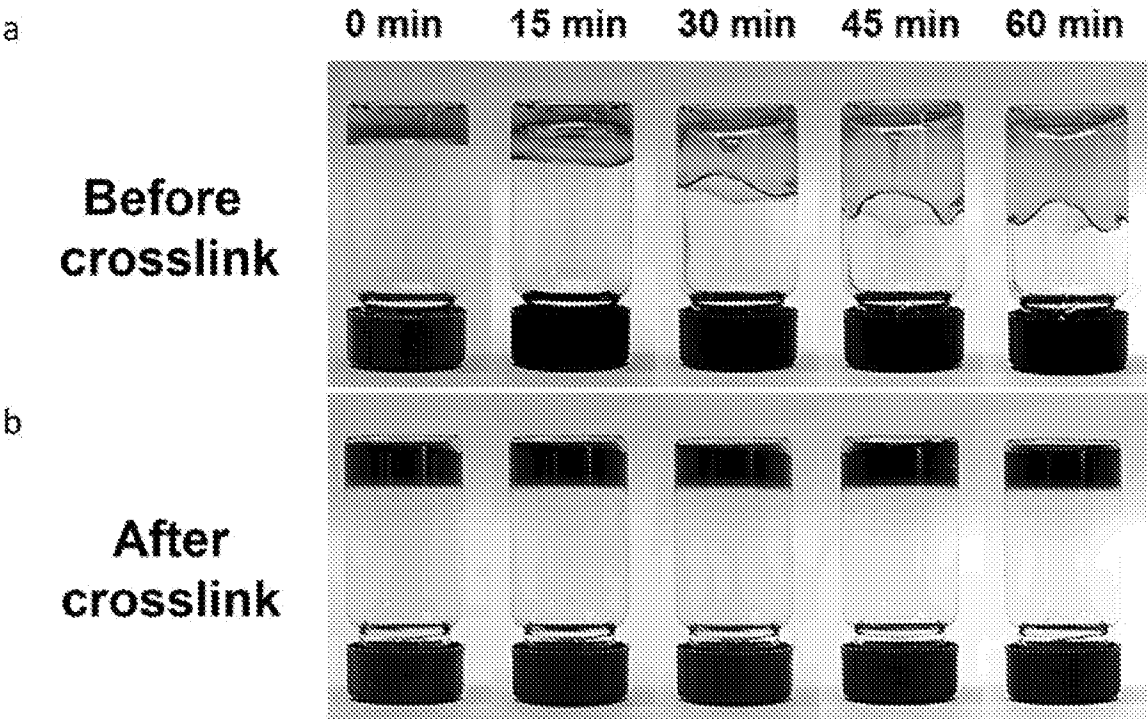


Fig. 9

10/36

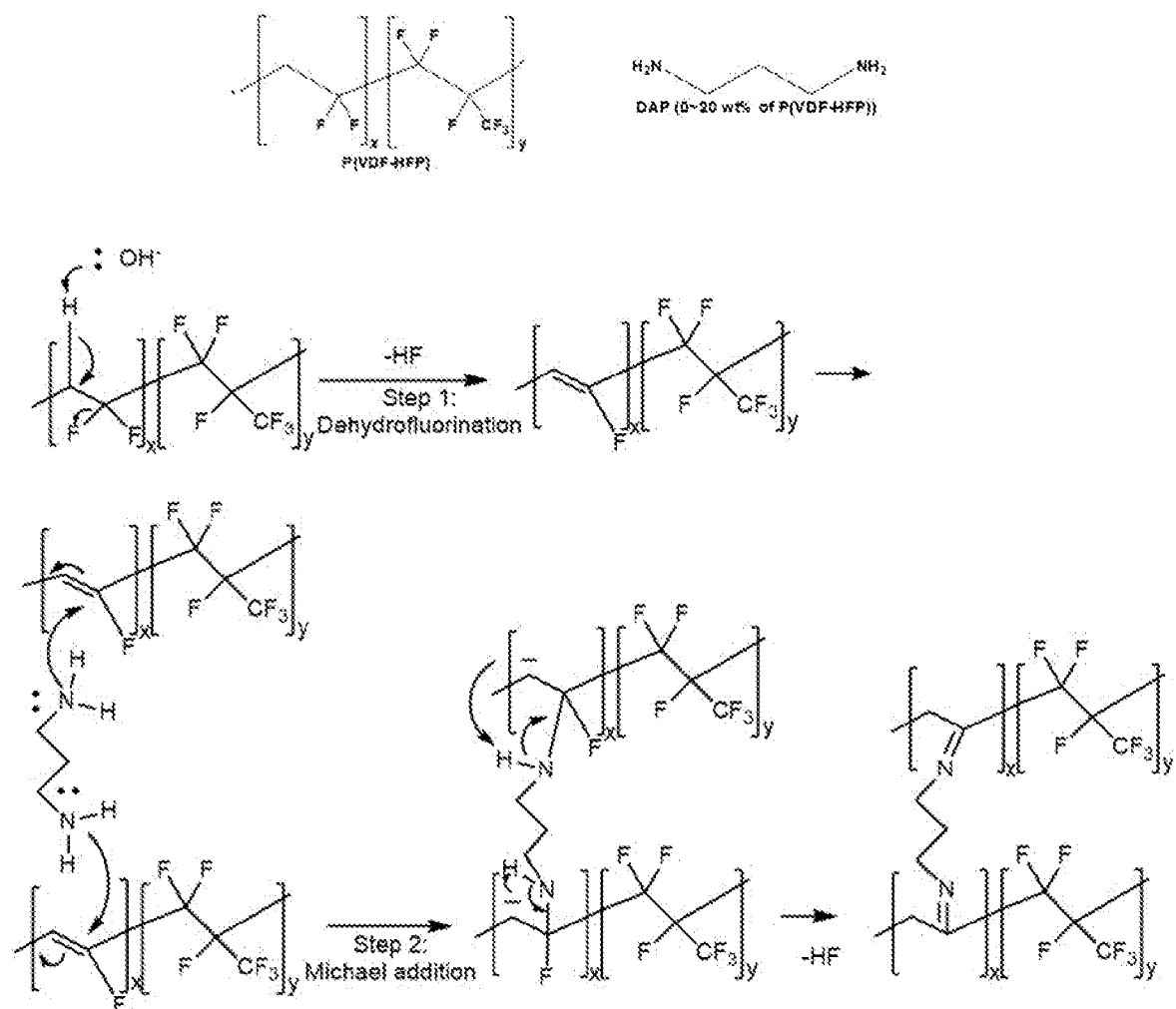


Fig. 10

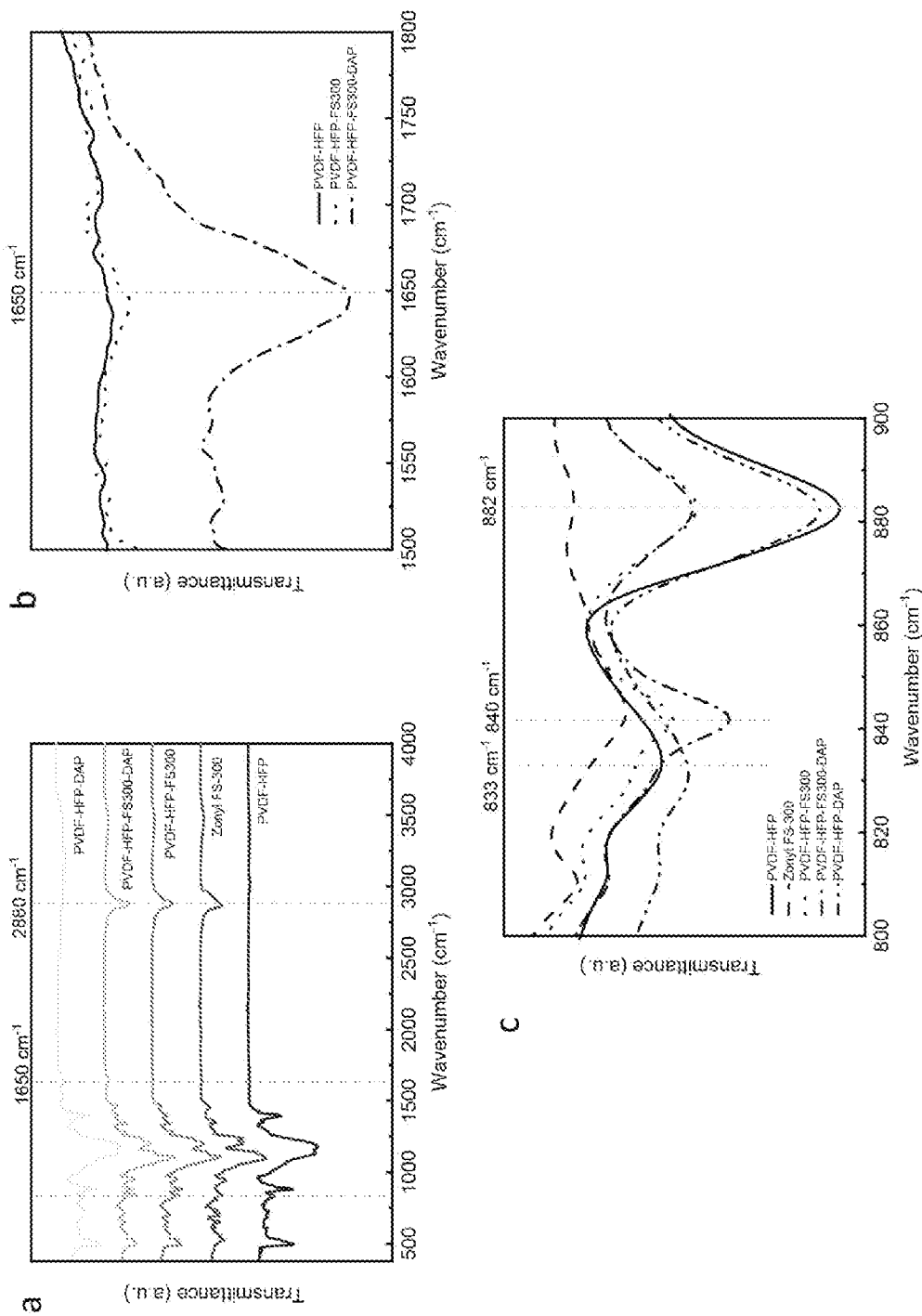


Fig. 11

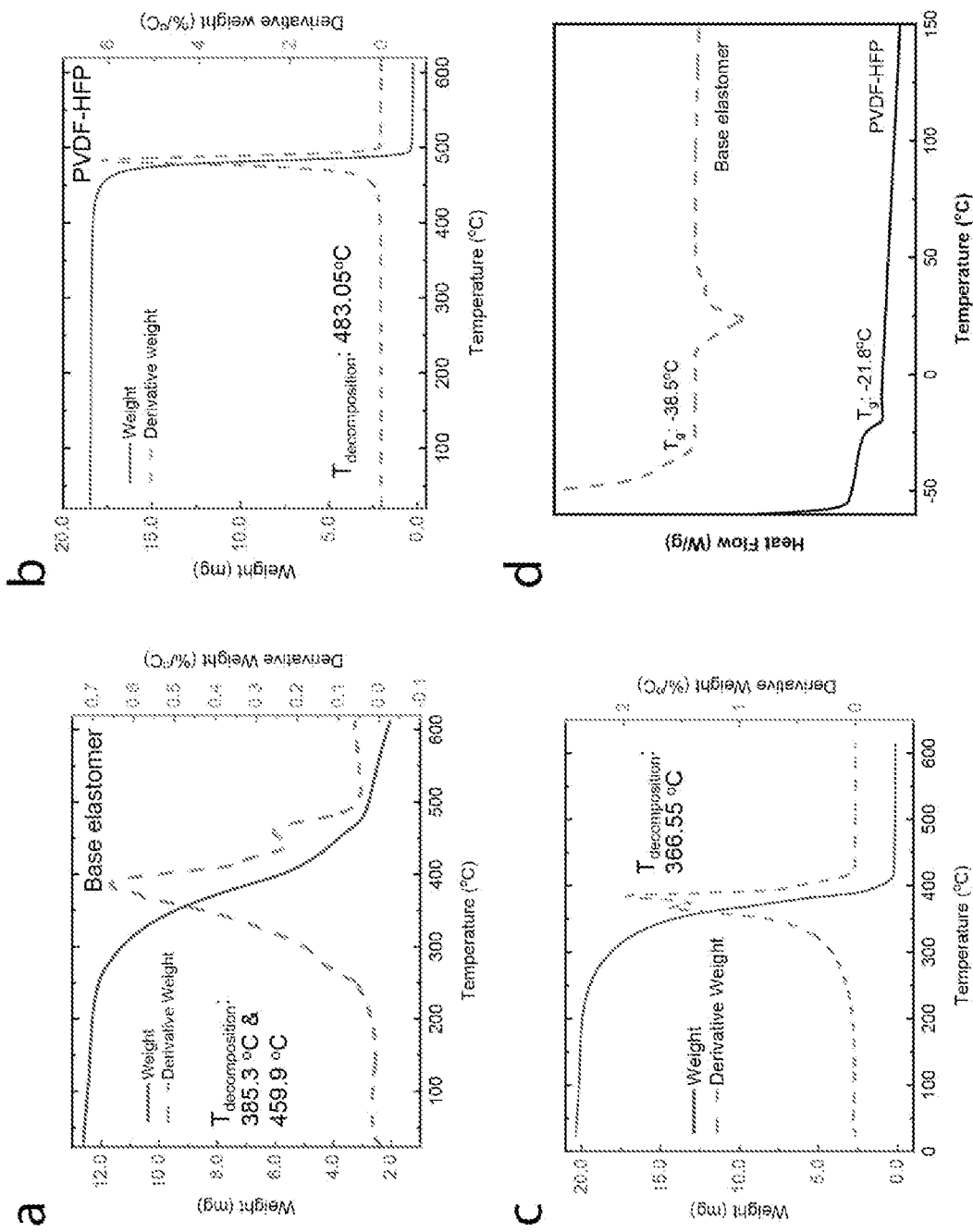


Fig. 12

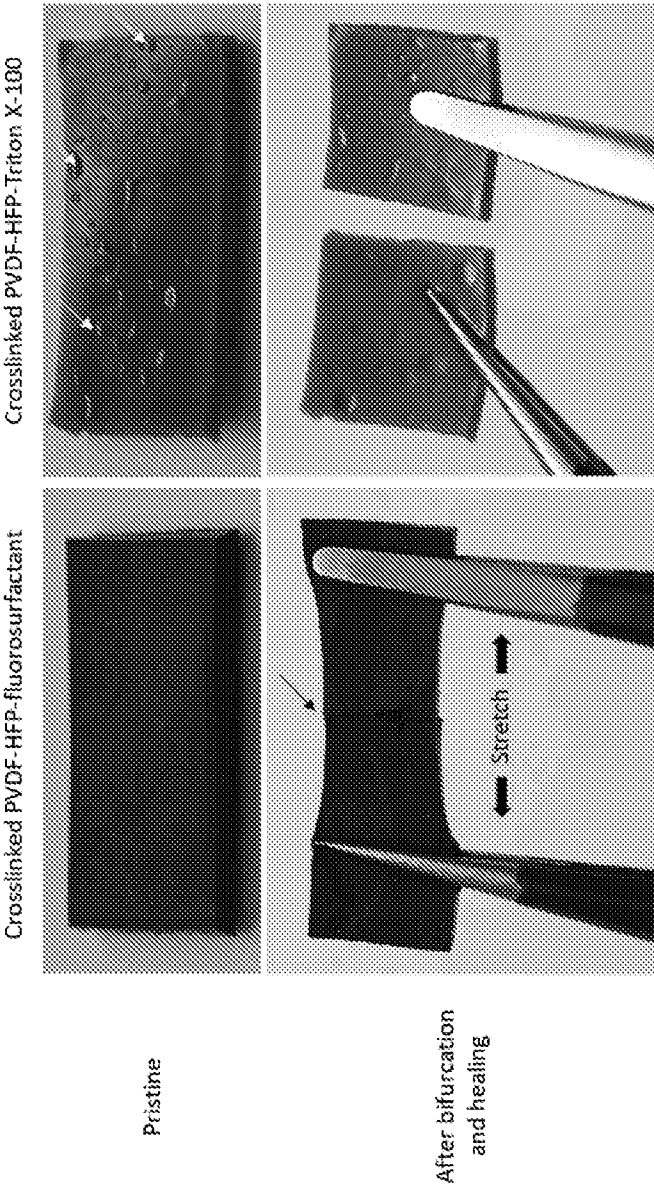


Fig. 13

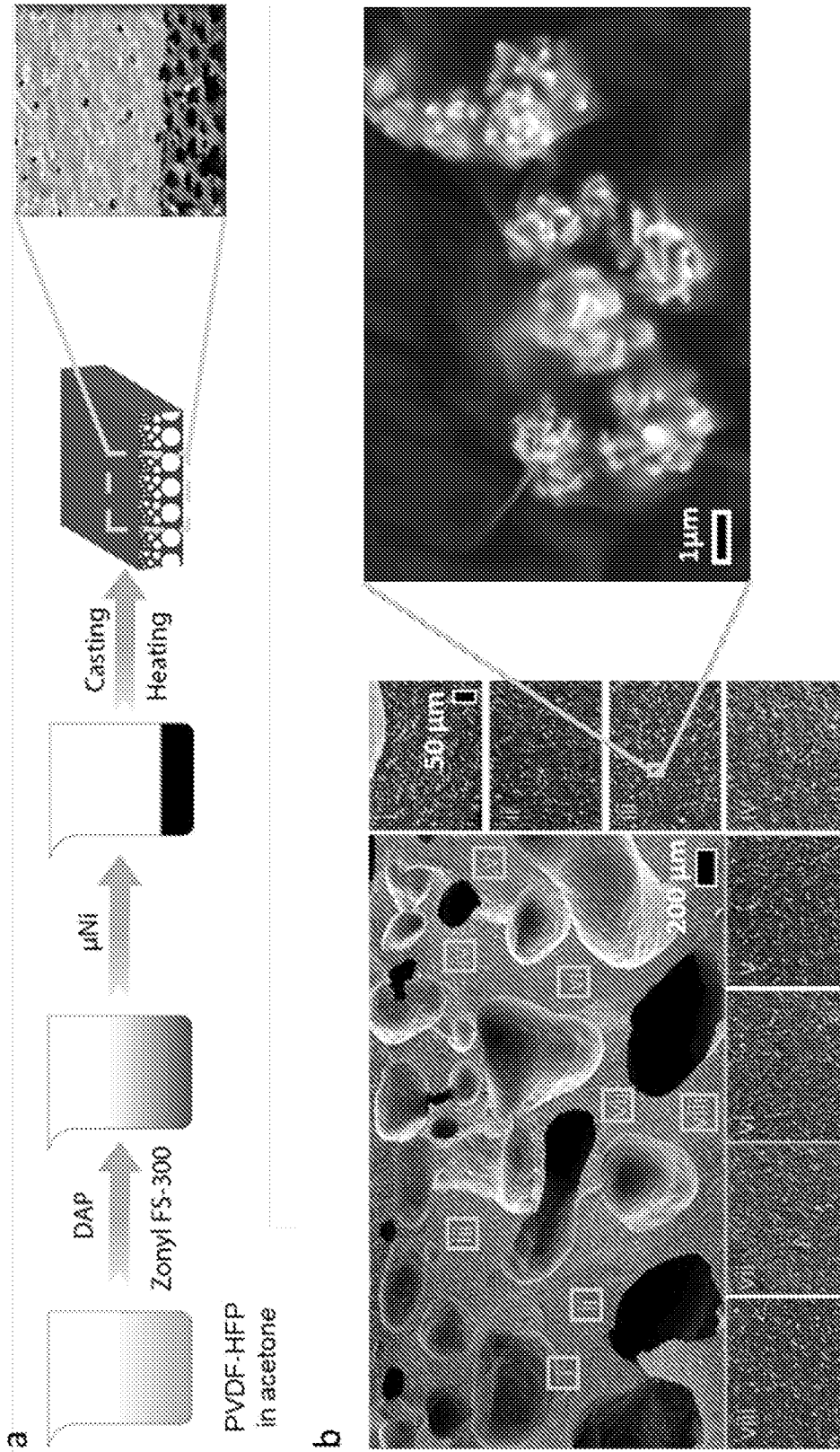


Fig 14

16/36

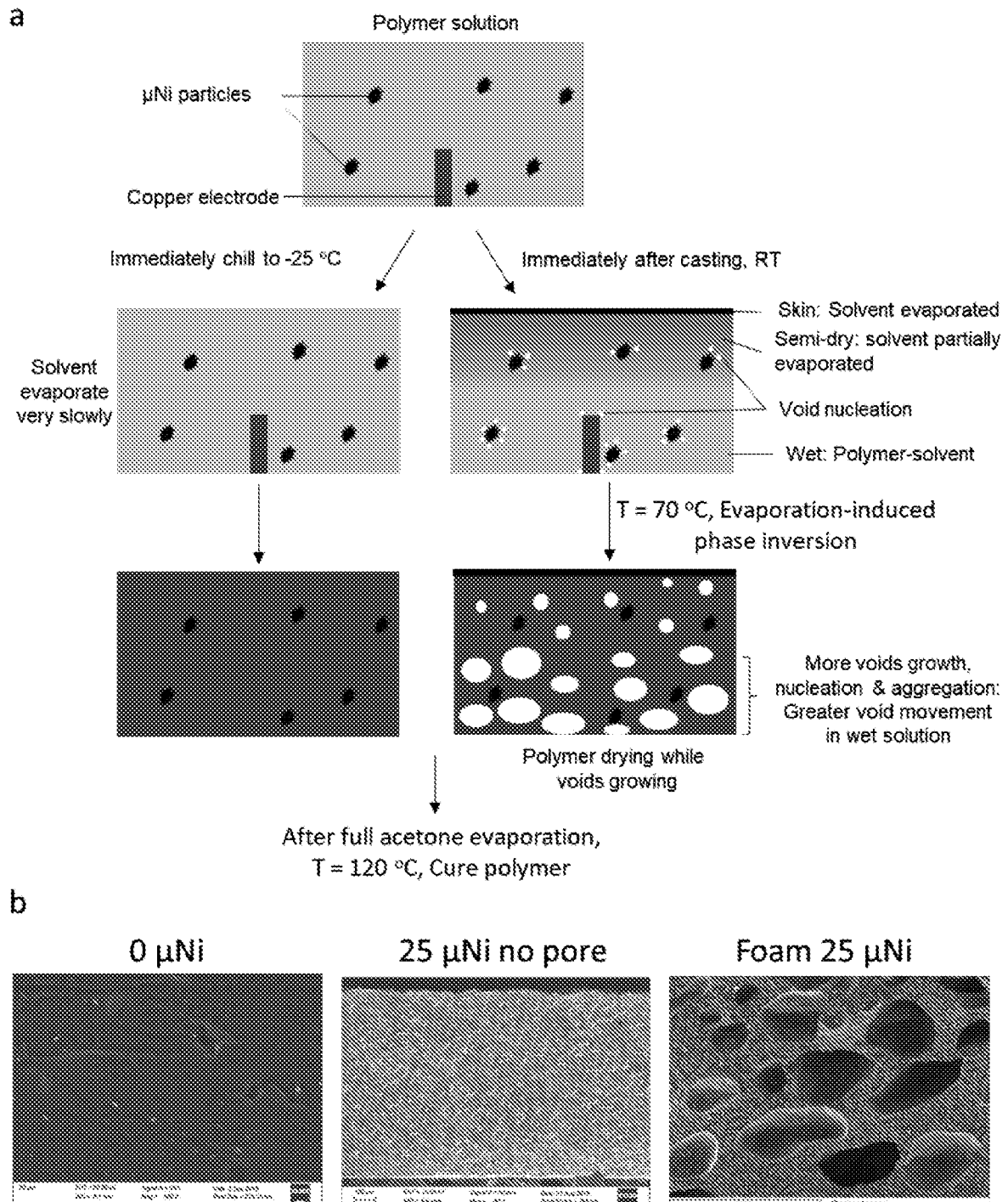


Fig. 16

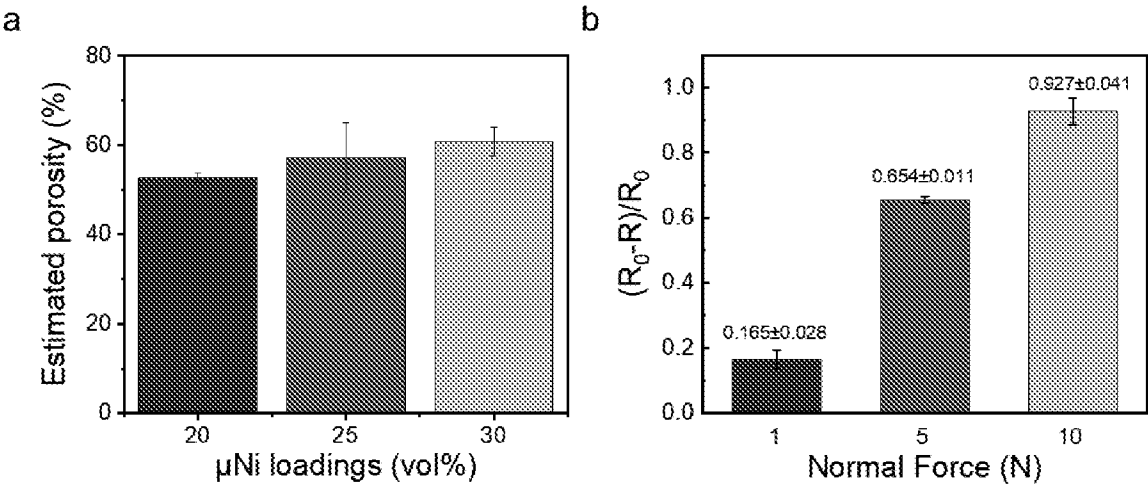


Fig. 17

18/36

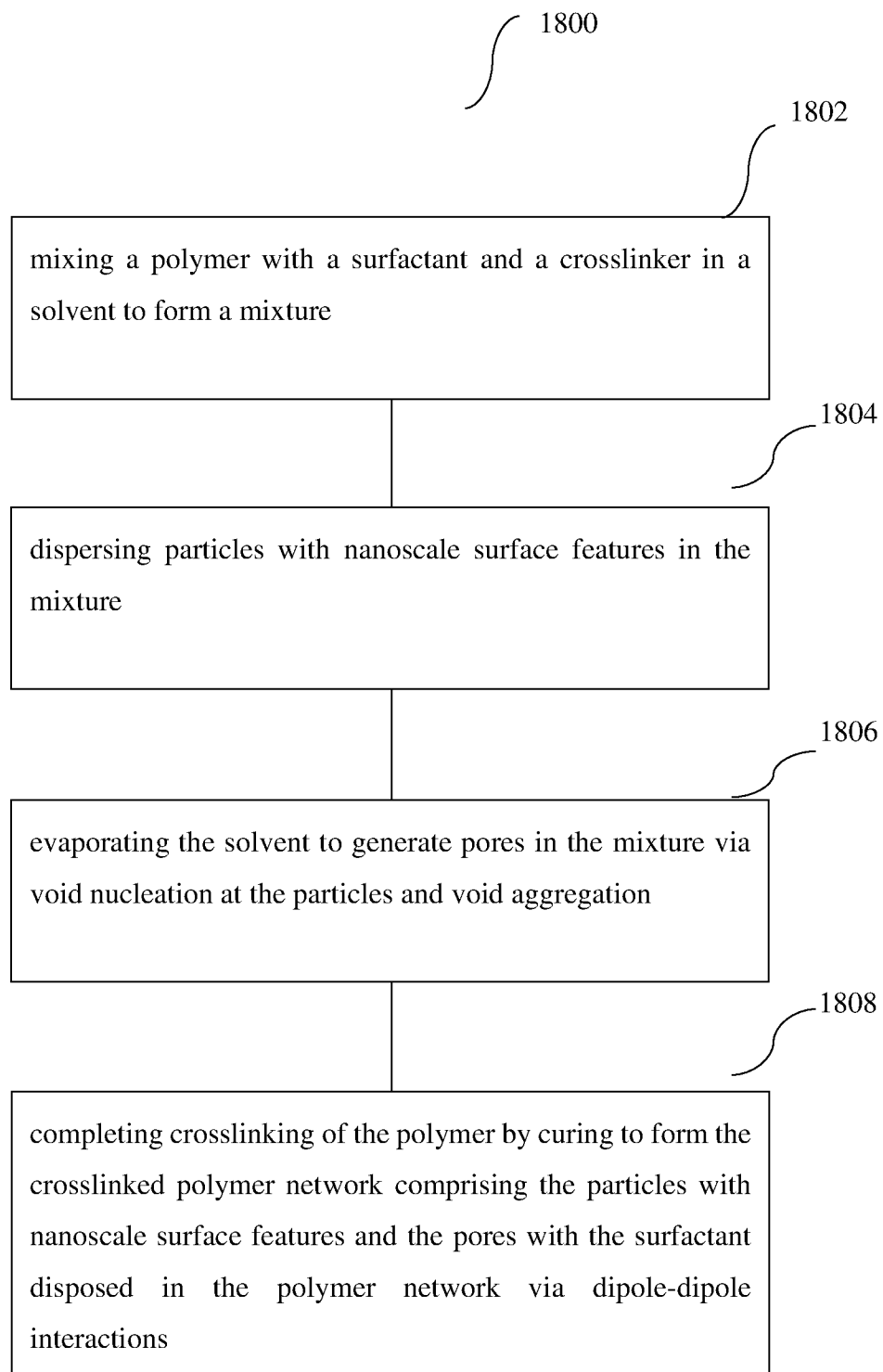


Fig. 18

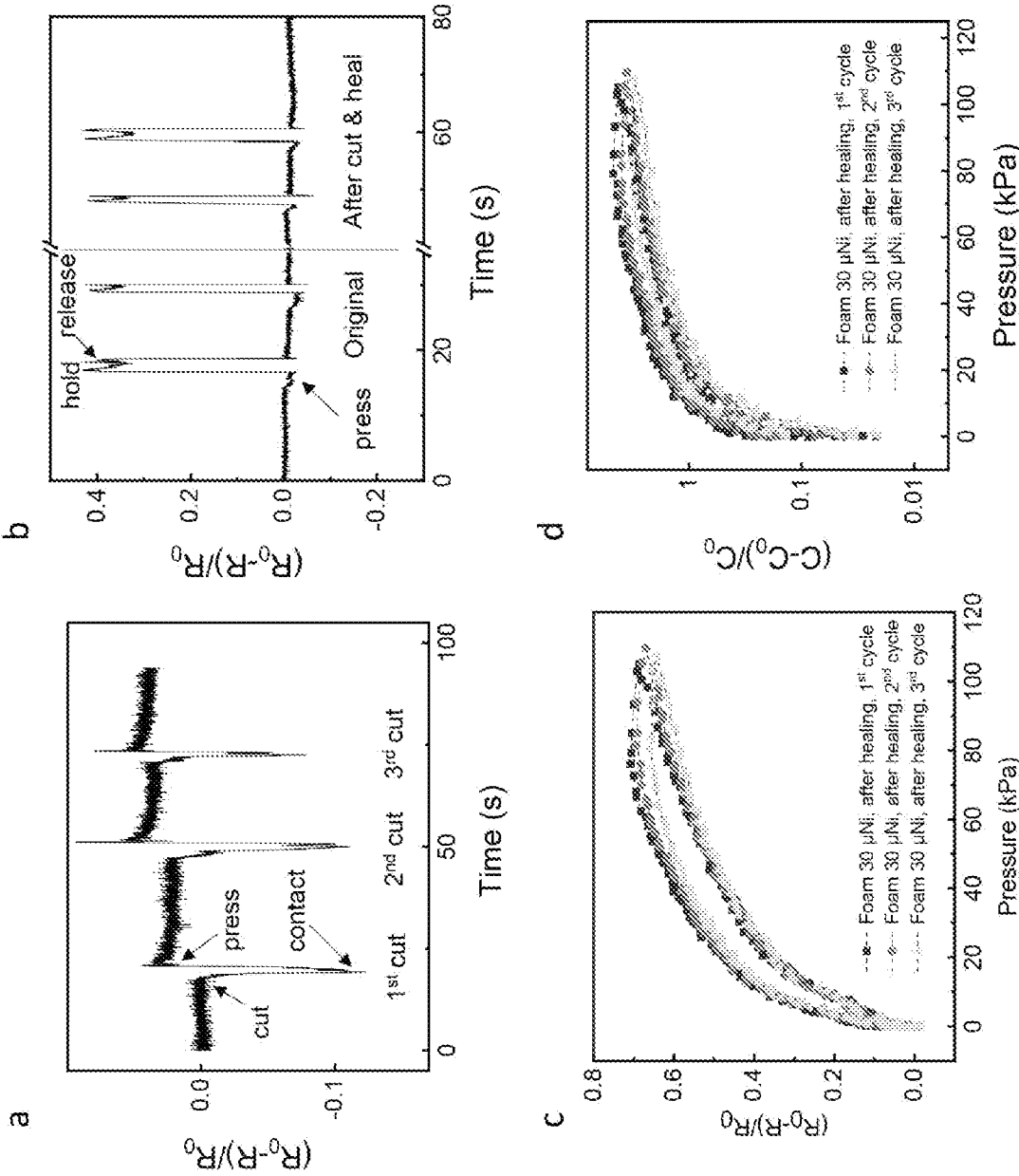


Fig. 19

20/36

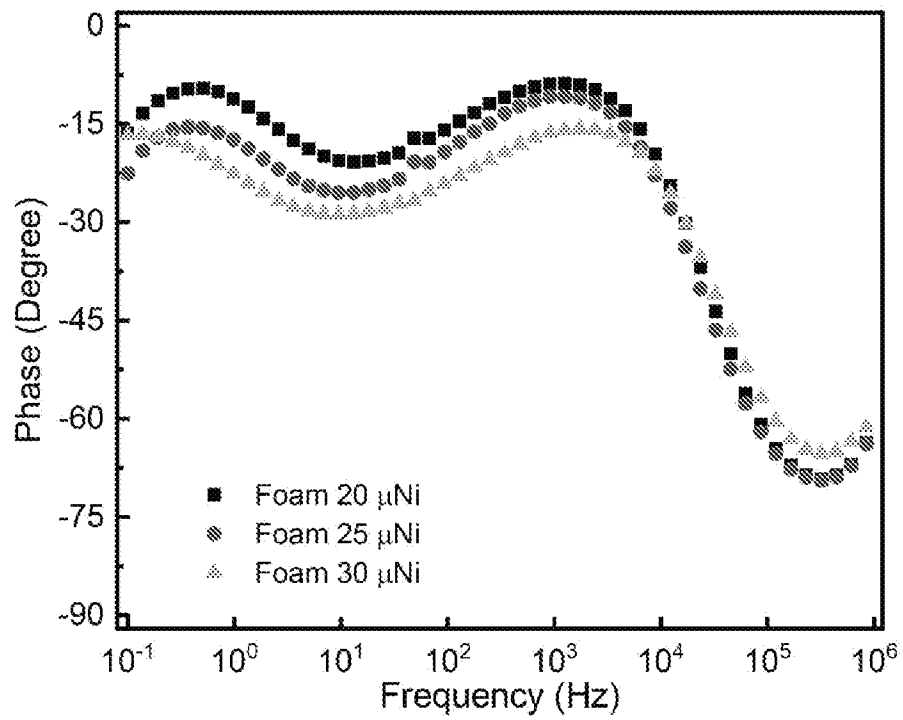


Fig. 20

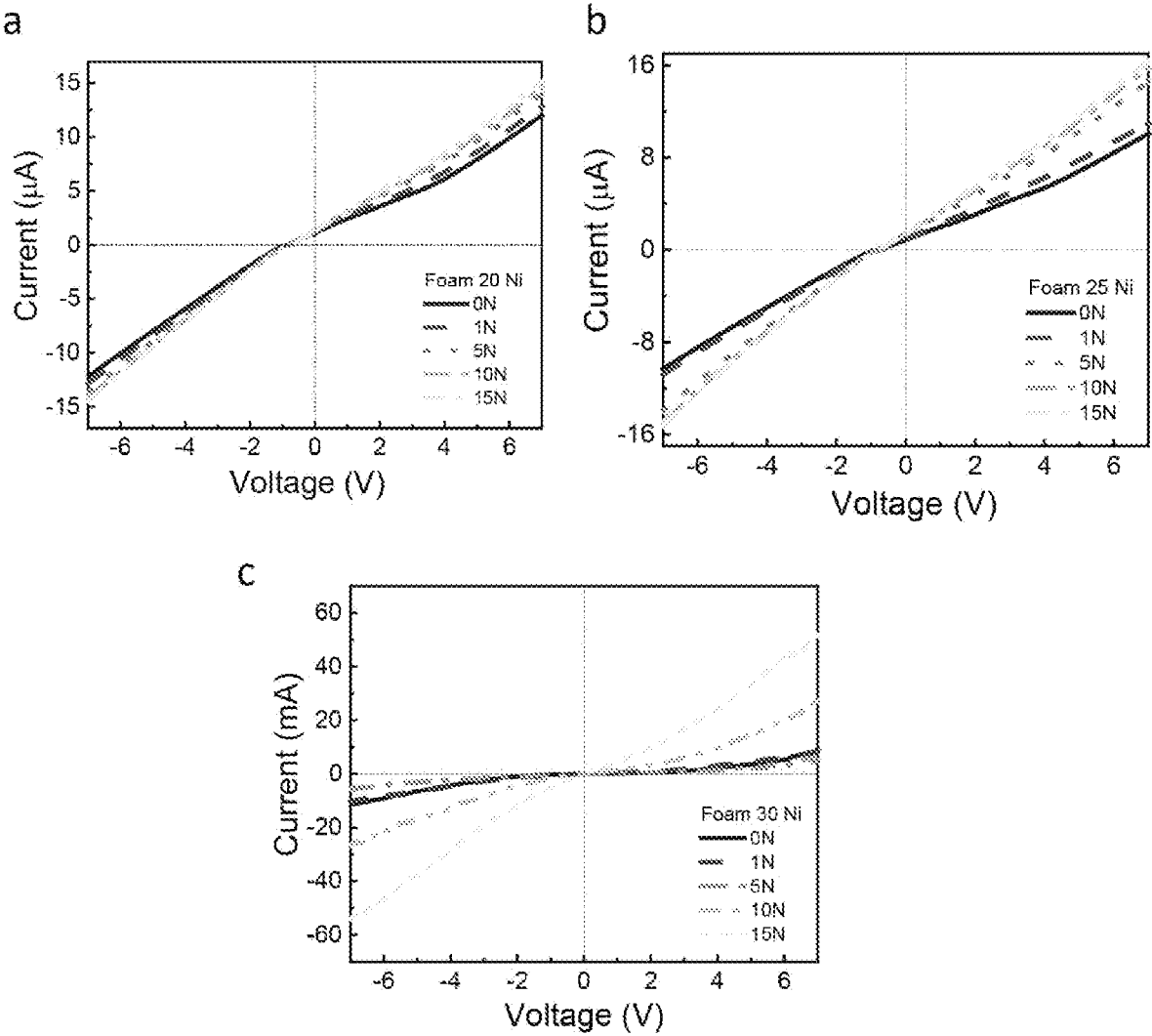


Fig. 21

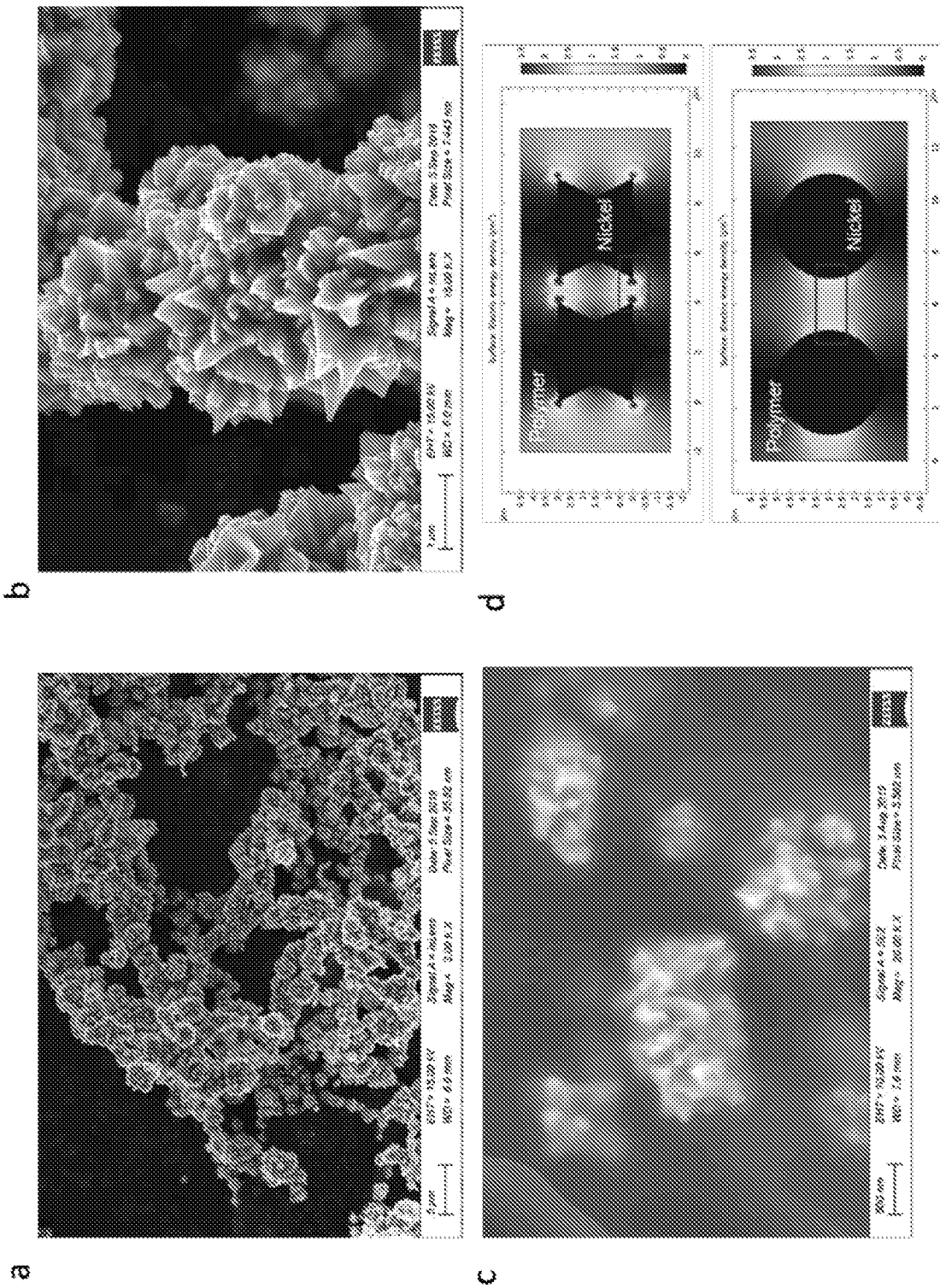


Fig. 22

23/36

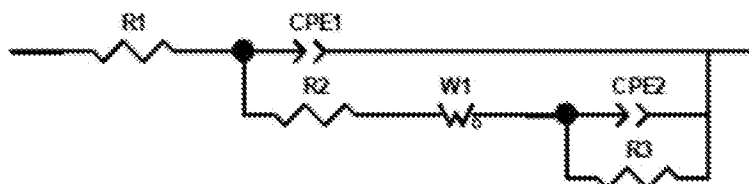


Fig. 23.

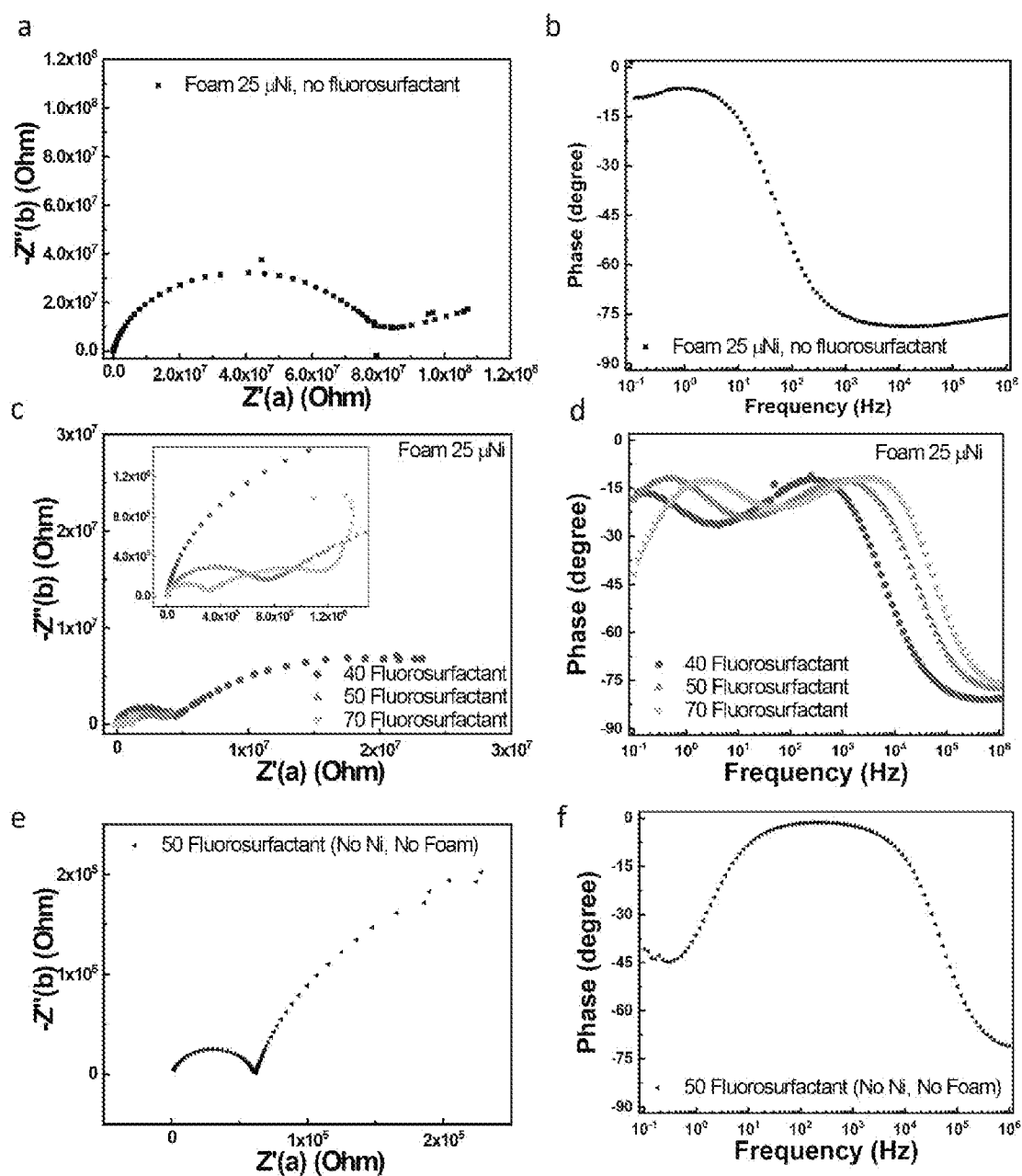


Fig. 24

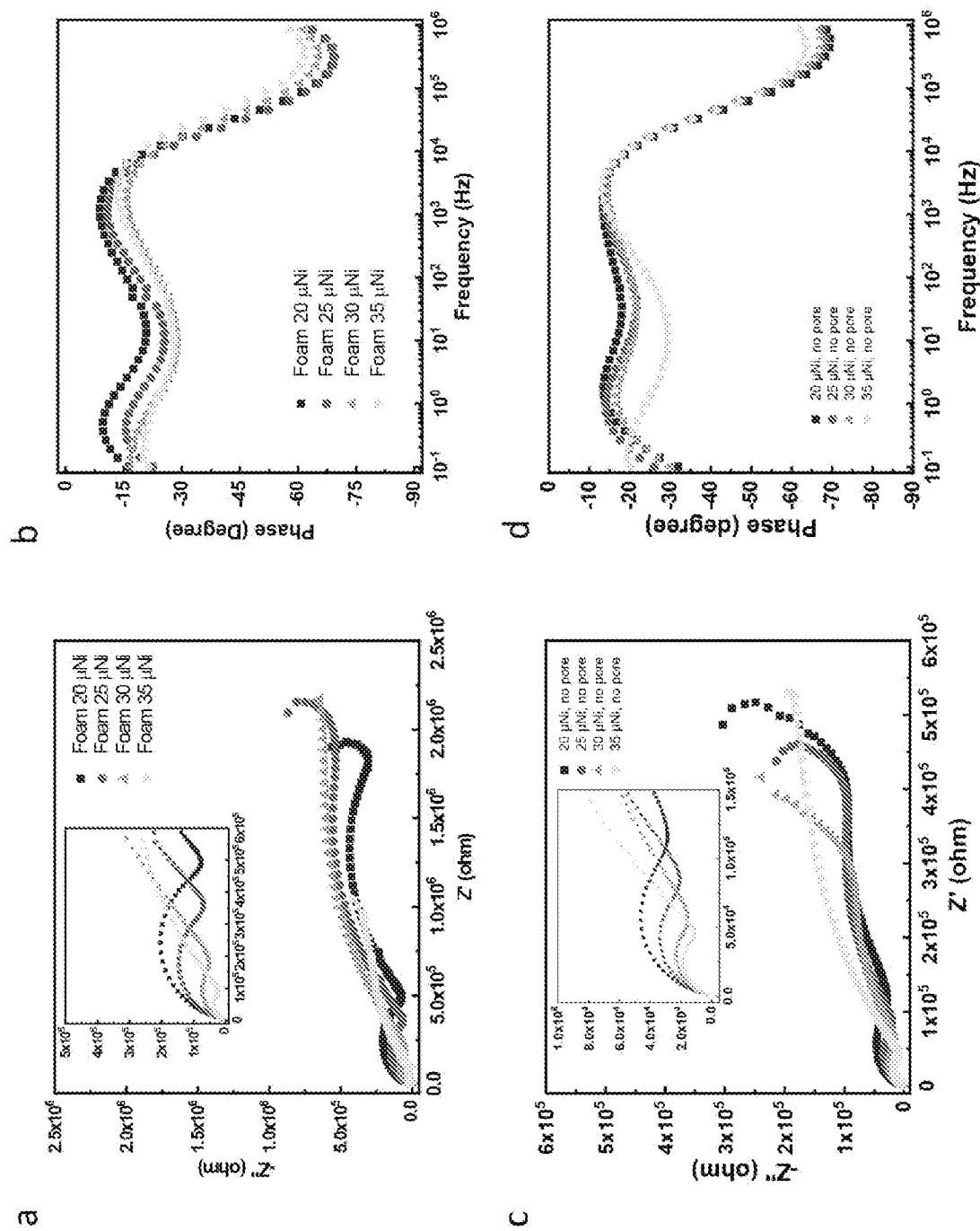
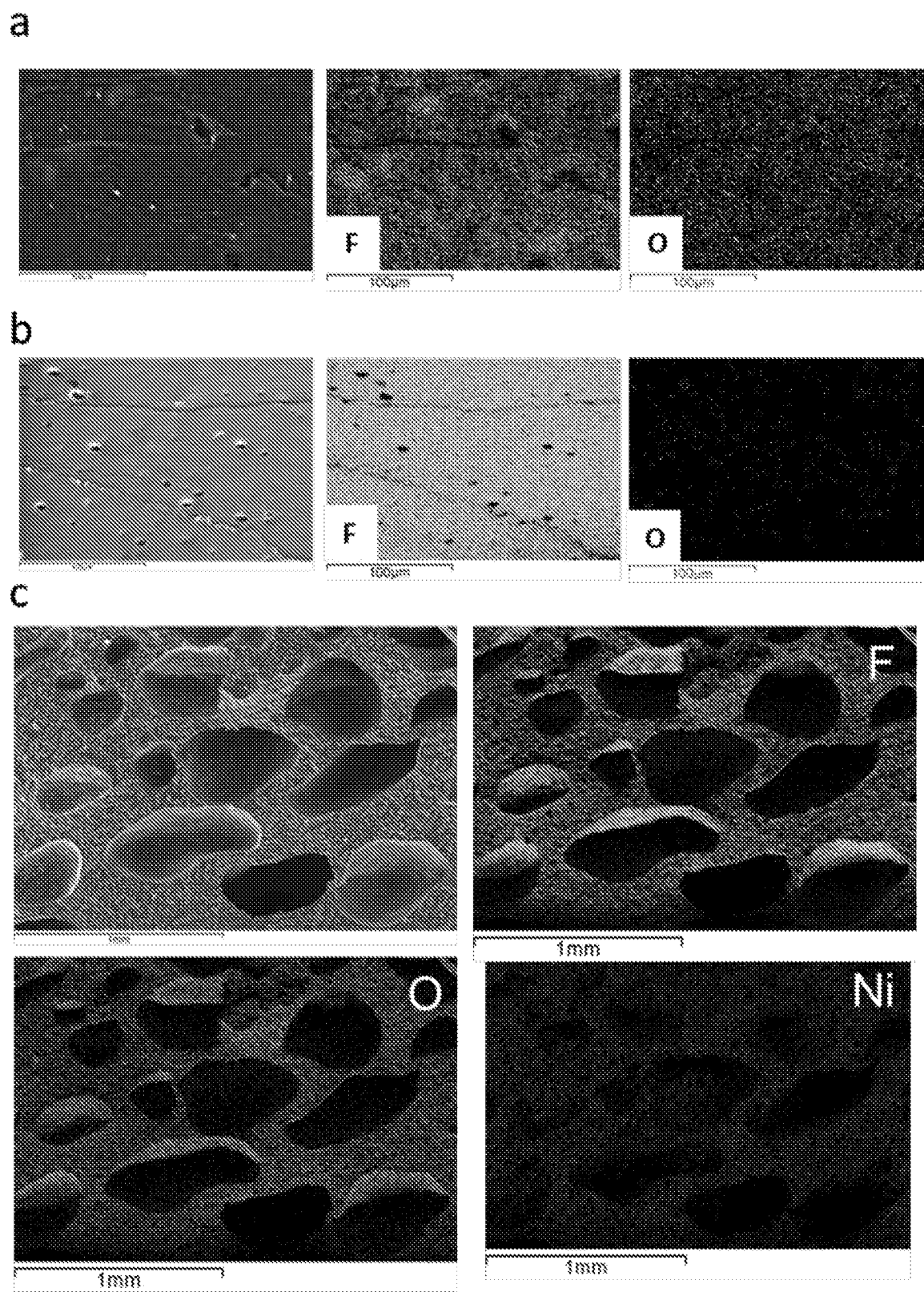


Fig. 25



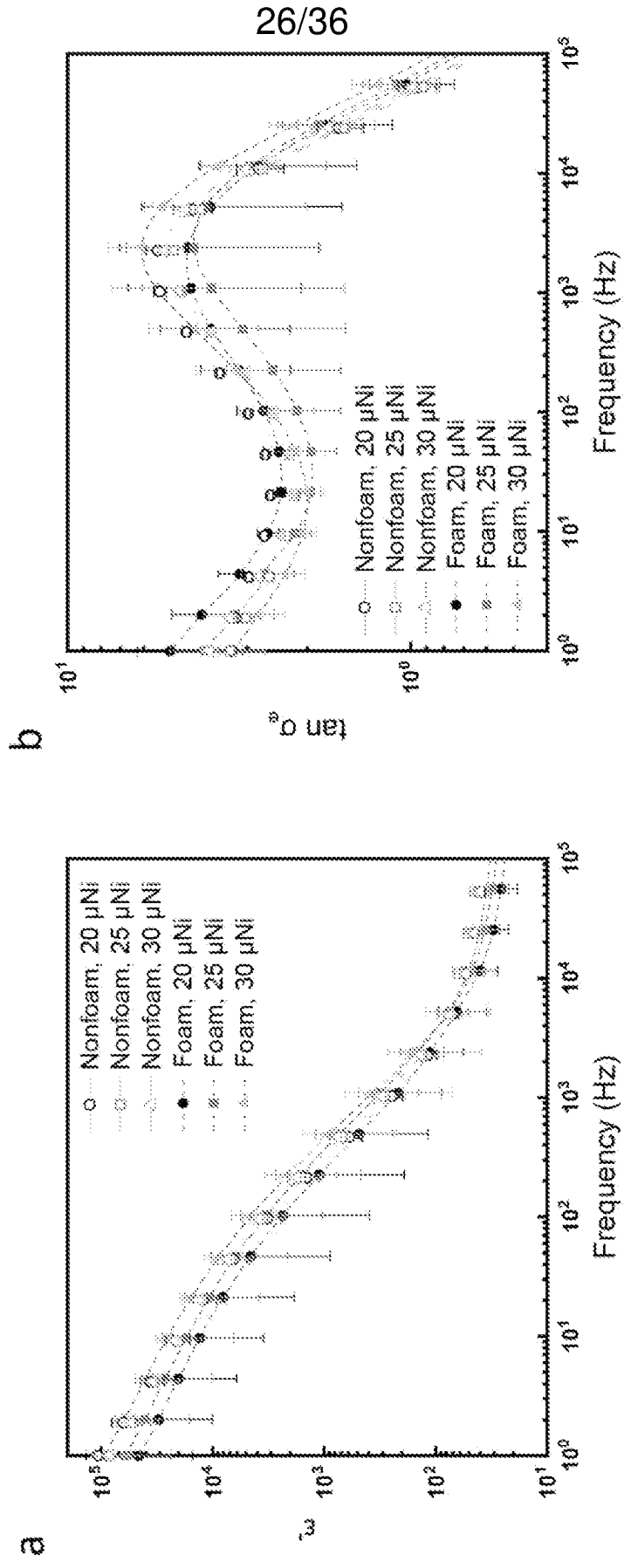


Fig. 27

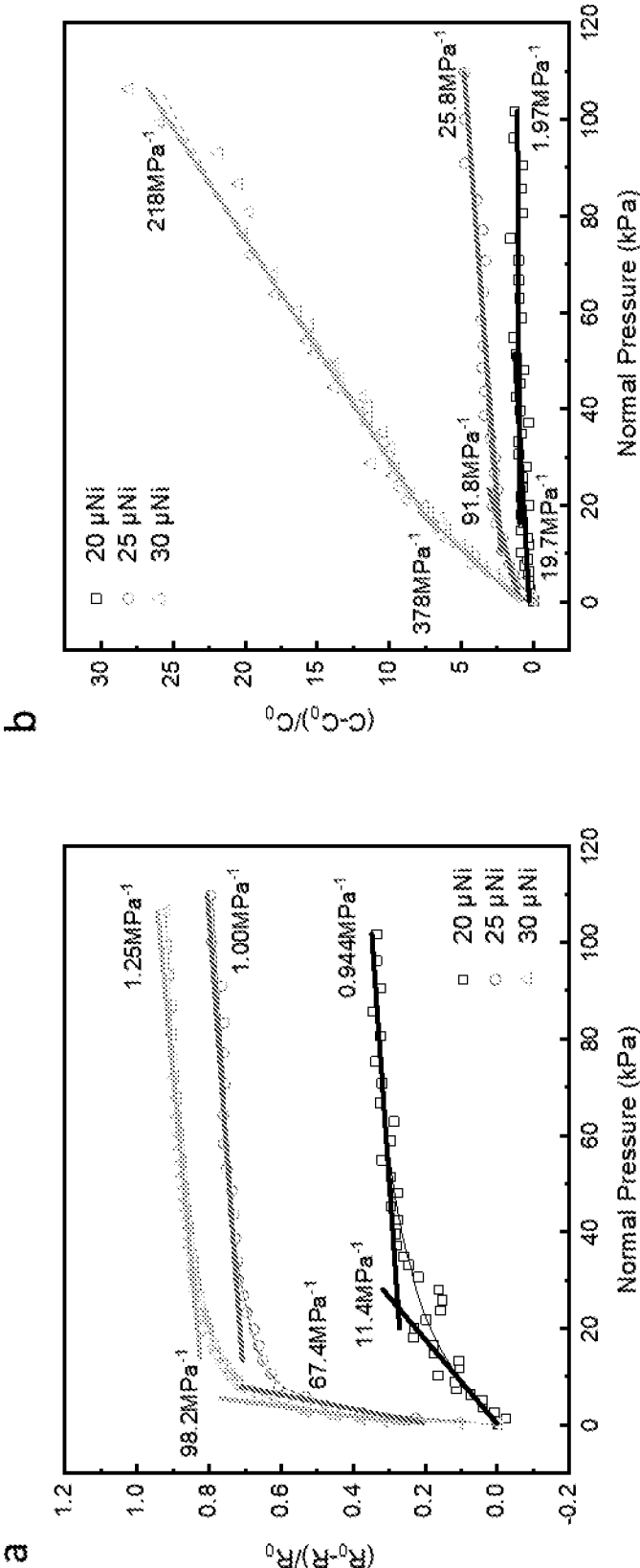


Fig. 28

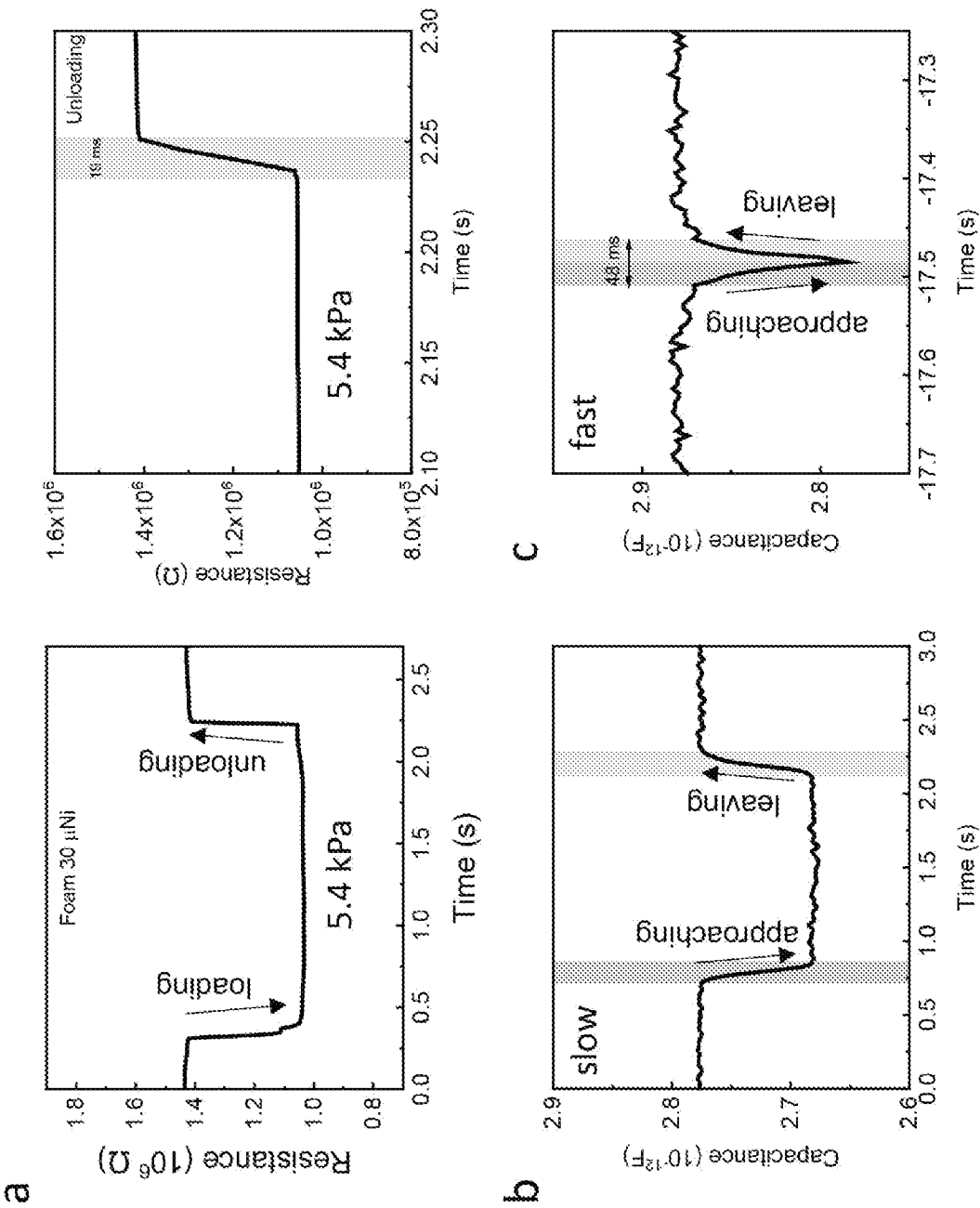


Fig. 29

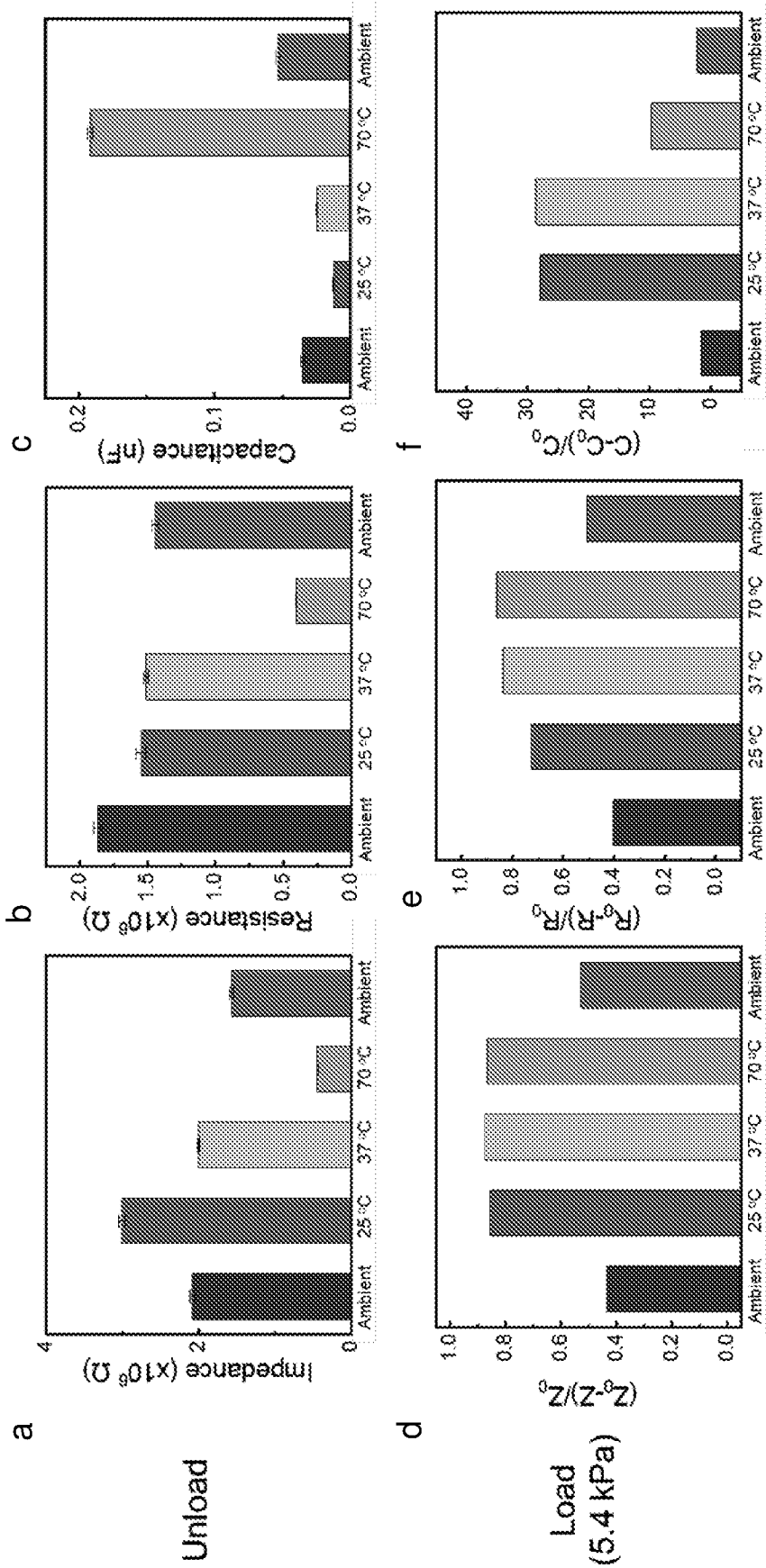


Fig. 30

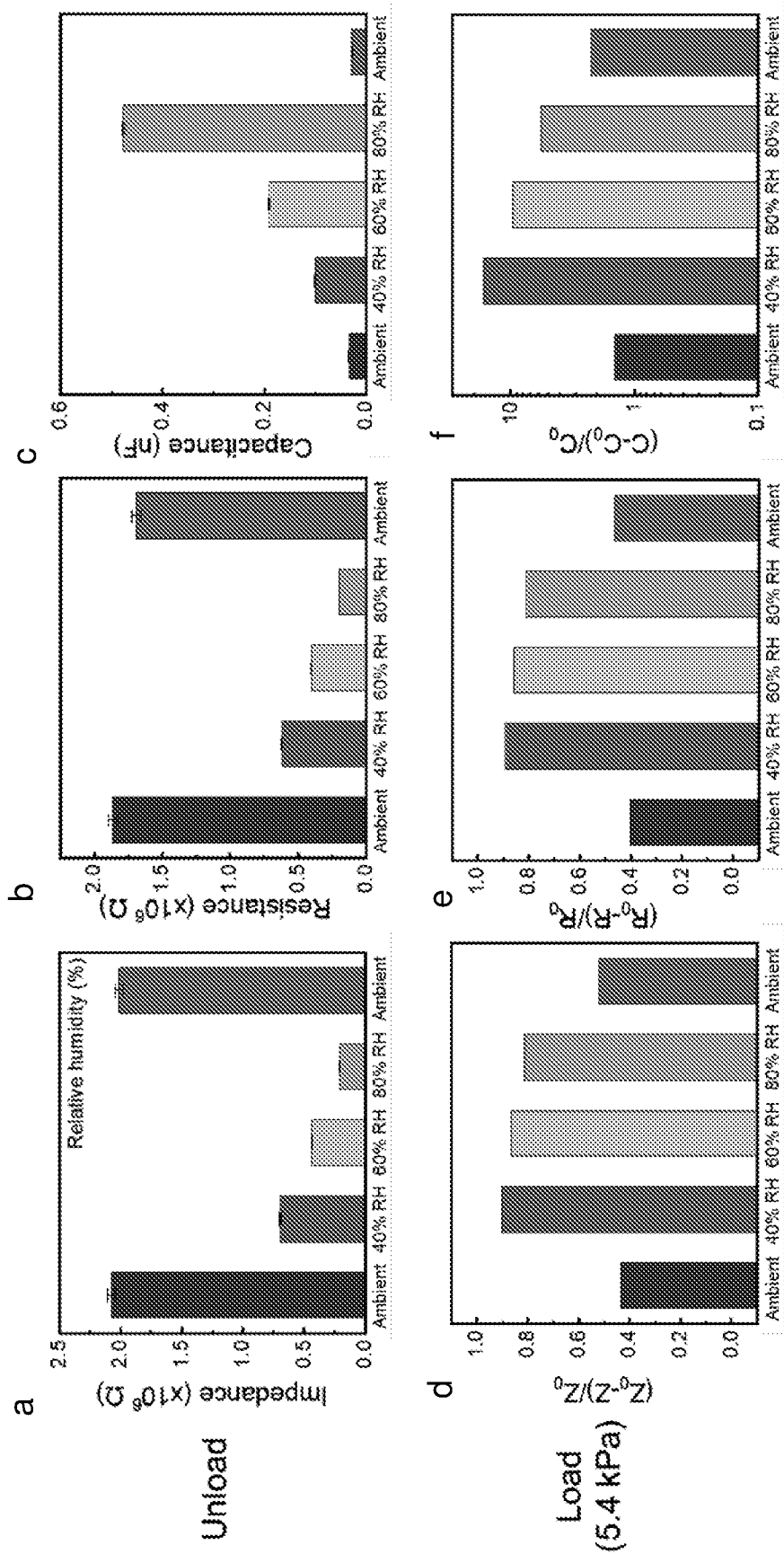


Fig. 31

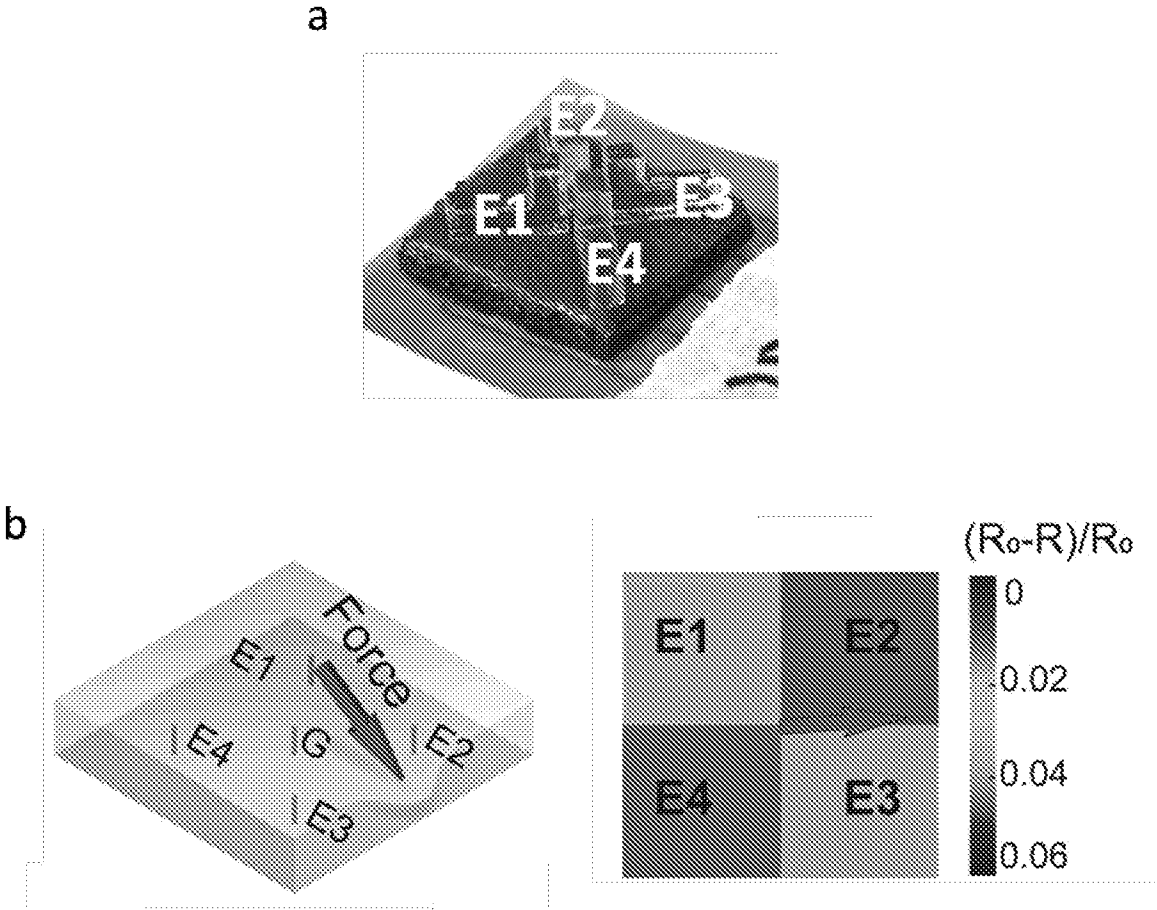


Fig. 32

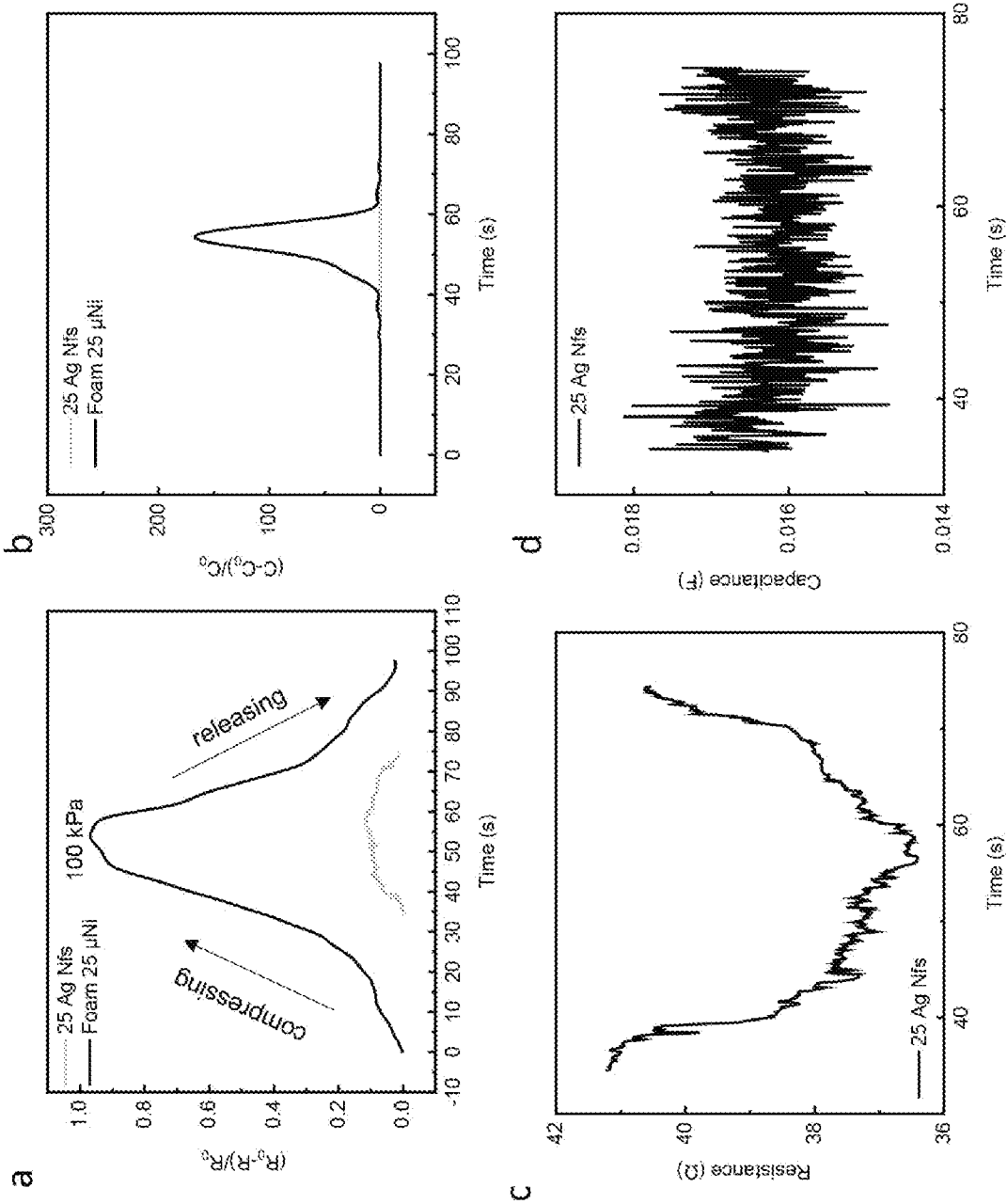


Fig. 33

33/36

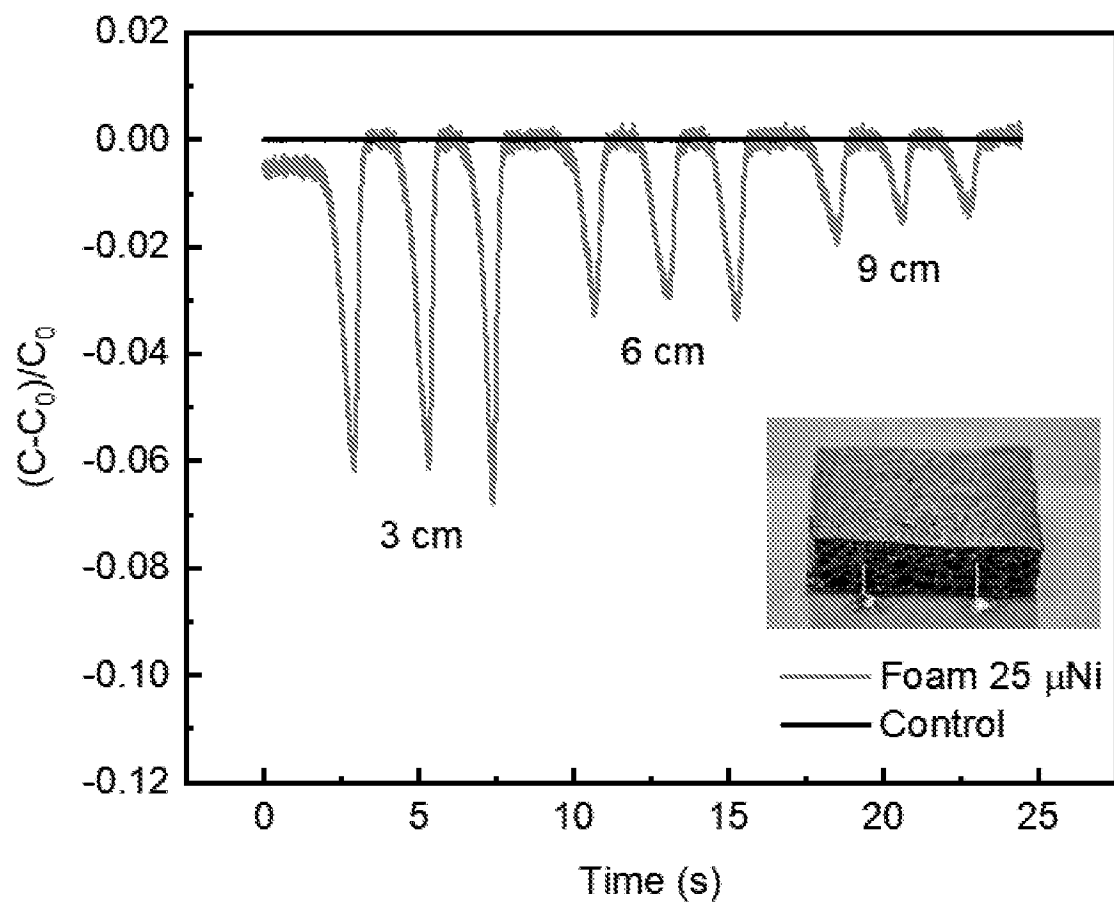


Fig. 34

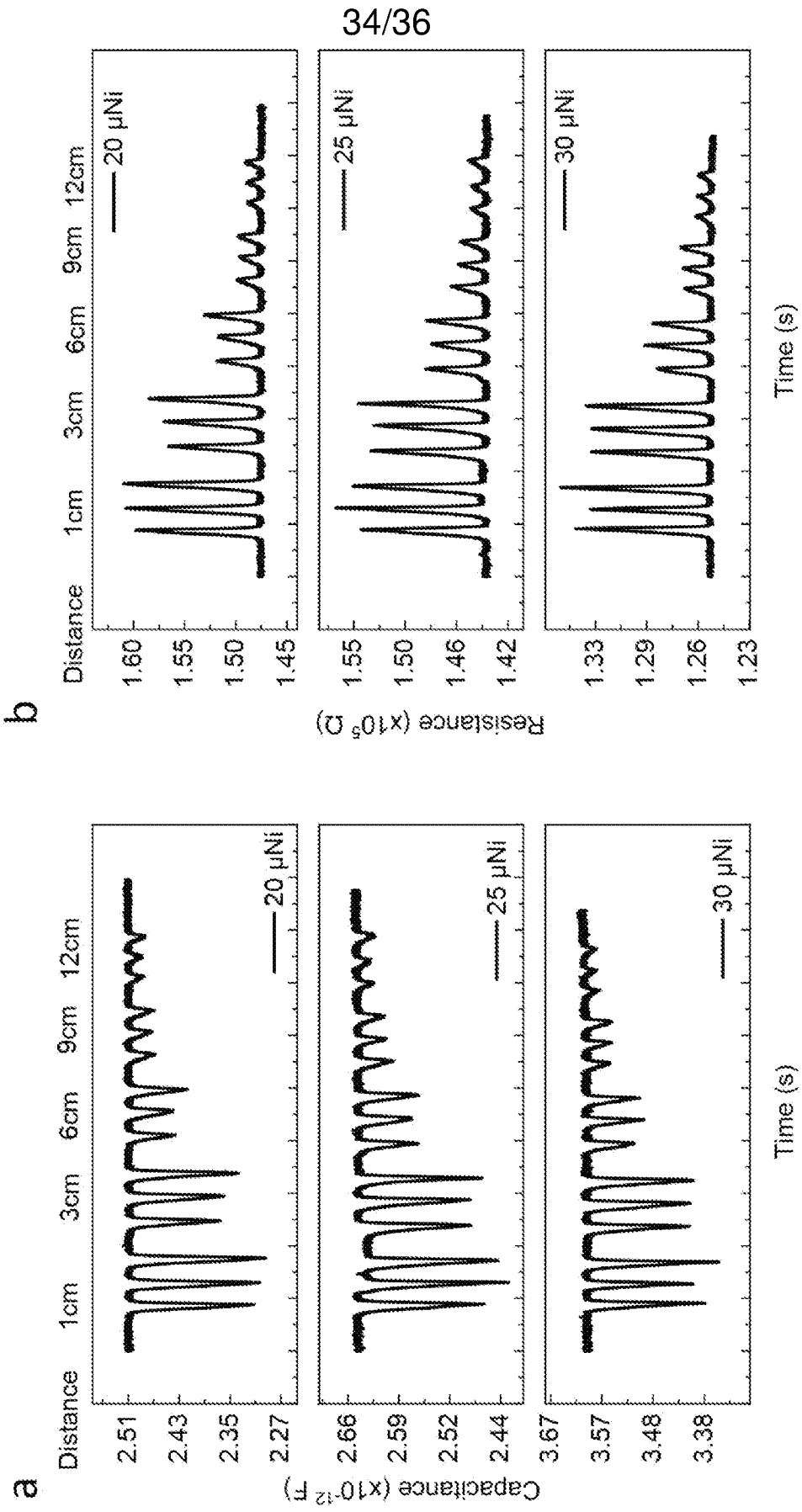


Fig. 35

35/36

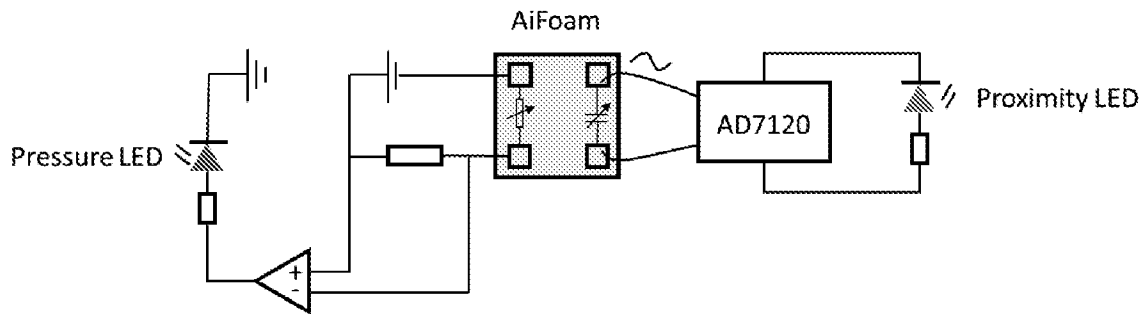


Fig. 36

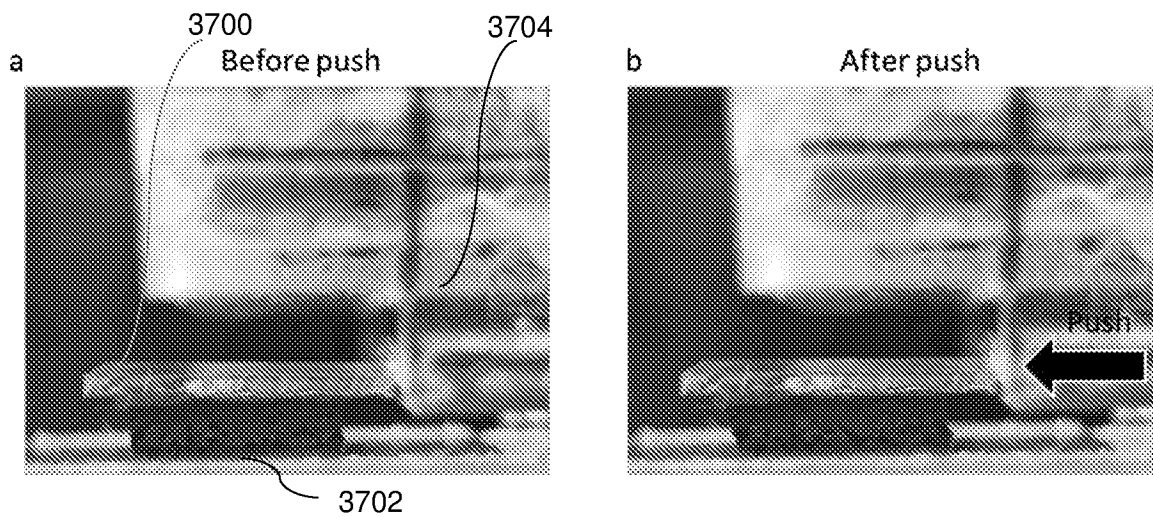


Fig. 37

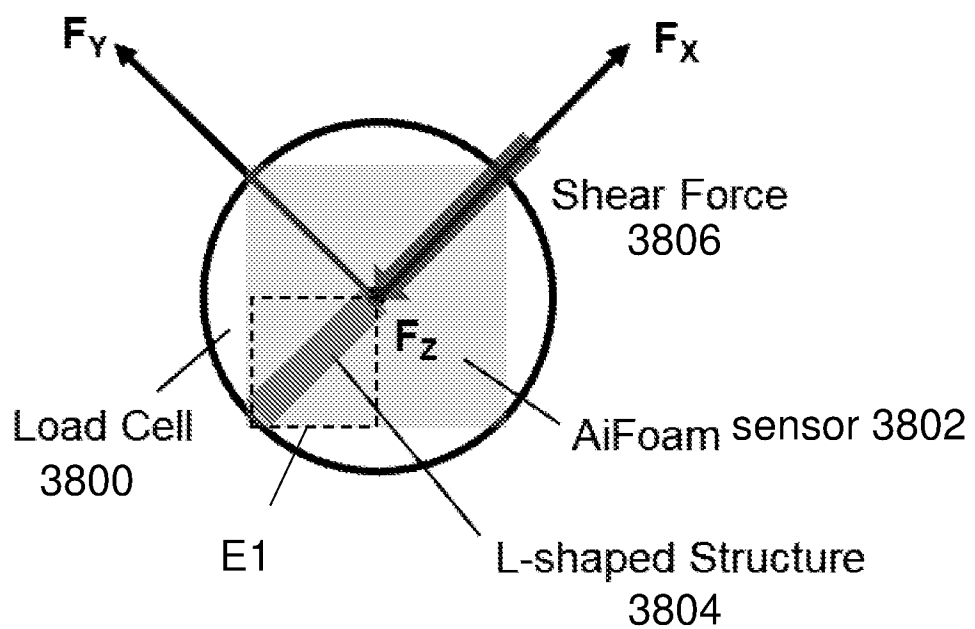


Fig. 38

36/36

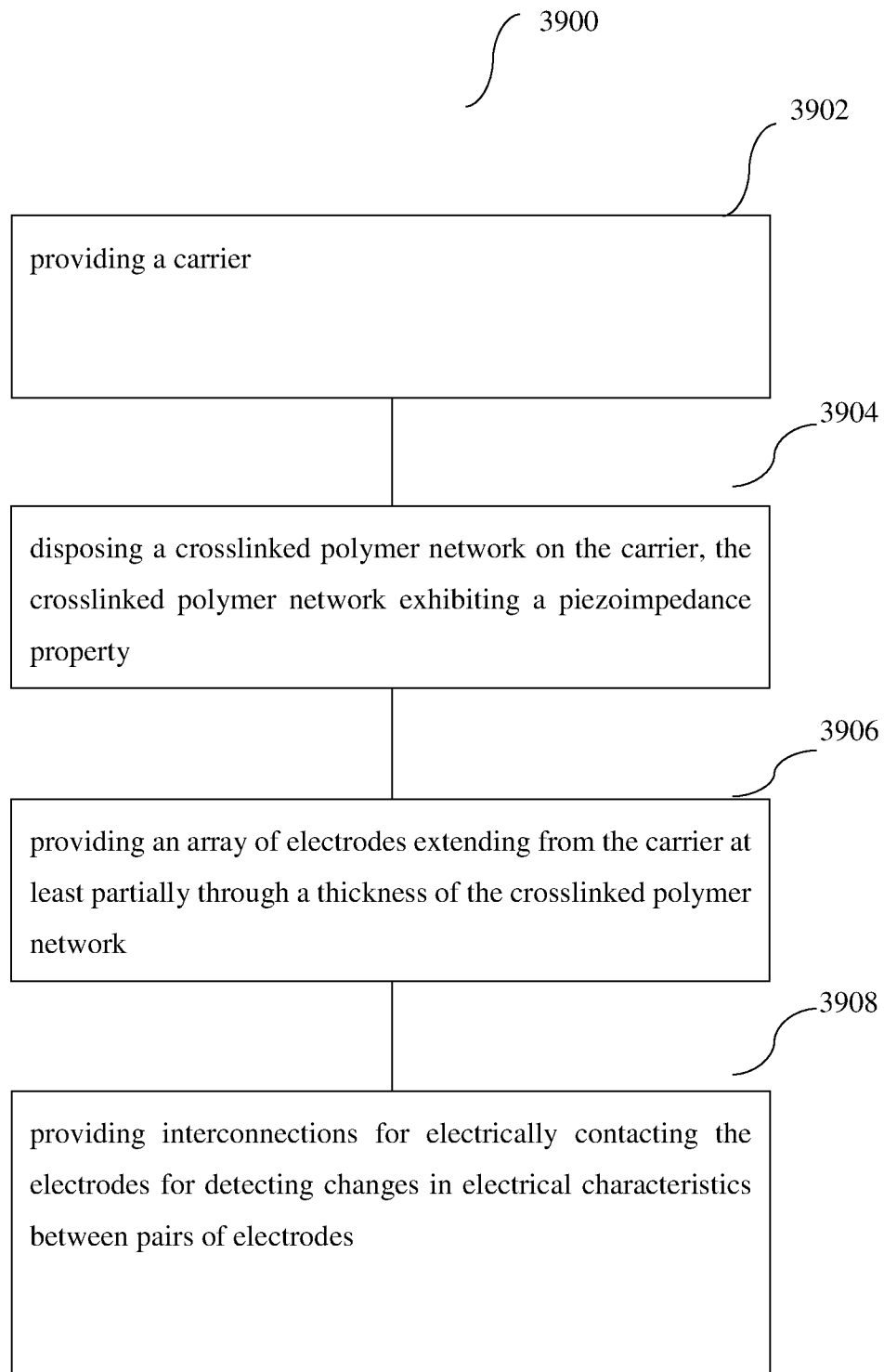


Fig. 39

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2021/050504

A. CLASSIFICATION OF SUBJECT MATTER

See Supplemental Box

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01B, B32B, C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Databases: C.Aplus, Compendex, Inspec, EPODOC and FAMPAT

Search terms: electronic skin, elastomer, foam, crosslink, fluoropolymer, fluorosurfactant, particles, piezoimpedance, self-healing, sensor, 3D electrode, 仿生皮肤, 传感, 泡沫, 交联 and other related terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 2017/0169914 A1 (SEKITANI, T. ET AL.) 15 June 2017 Figures 1-5; example 1; paras [0005]-[0008], [0069]-[0071], [0088], [0093], [0111] and [0125]	1-3, 16-18, 27-29 4-15
X	RAZAK, A. H. ET AL., Mechanically Compliant Electrodes and Dielectric Elastomers from PEG-PDMS Copolymers. <i>MRS Advances</i> , 24 May 2016, Vol. 1, No. 52, pages 3497-3508 [Retrieved on 2021-12-03] <DOI: 10.1557/ADV.2016.404> experimental procedures section-Preparation of CE-(PDMS-PEG) elastomers with surface-modified MWCNT; results and discussion section- Interpenetrating network of PDMS-PEG copolymer and ionic network; and conclusion	1-3, 16-18, 27-29
X	PRUVOST, M. ET AL., Polymeric foams for flexible and highly sensitive low-pressure capacitive sensors. <i>npj flexible electronics</i> , 4 April 2019, Vol. 3, pages 7(1-6) [Retrieved on 2021-12-03] <DOI: 10.1038/S41528-019-0052-6> Fig. 1-4; abstract; and Methods	1, 2

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

*Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

03/12/2021

(day/month/year)

Date of mailing of the international search report

06/12/2021

(day/month/year)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2021/050504

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YAO, S. ET AL., Wearable multifunctional sensors using printed stretchable conductors made of silver nanowires. <i>Nanoscale</i> , 5 December 2013, Vol. 6, No. 4, pages 2345-2352 [Retrieved on 2021-12-03] <DOI: 10.1039/C3NR05496A> Figure 1 and 2	19-26
X	SCHÄFFNER, P. ET AL., Microstructured single-layer electrodes embedded in P(VDF-TrFE) for flexible and self-powered direction-sensitive strain sensors. <i>Smart Materials and Structures</i> , 15 July 2020, Vol. 29, No. 8, pages 085040 (1-15) [Retrieved on 2021-12-03] <DOI: 10.1088/1361-665X/ab9f4c> Figures 1 and 2; and abstract	19-26
A	MATSUHIRA, N. ET AL., Printable elastic conductors by in situ formation of silver nanoparticles from silver flakes. <i>Nature Materials</i> , 15 May 2017, Vol. 6, pages 834-841 [Retrieved on 2021-12-03] <DOI: 10.1038/NMAT4904> abstract; section-Methods; and Fig. 1-3	-
A	WO 2019/231404 A1 (NATIONAL UNIVERSITY OF SINGAPORE) 5 December 2019 page 30	-
A	PARAMESWARAN, C. ET AL., Large area flexible pressure/strain sensors and arrays using nanomaterials and printing techniques. <i>Nano Convergence</i> , 9 September 2019, Vol. 6, No. 28, pages 1-23 [Retrieved on 2021-12-03] <DOI: 10.1186/S40580-019-0198-X> abstract	-
P,X	GUO, H. ET AL., Artificially innervated self-healing foams as synthetic piezo-impedance sensor skins. <i>Nature Communications</i> , 12 November 2020, Vol. 11, pages 5747 (1-10) [Retrieved on 2021-12-03] <DOI: 10.1038/S41467-020-19531-0 > Figures 1-6 and Methods	1-29

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2021/050504

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:

because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:

because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:

because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please refer to Supplemental Box (Continuation of Box No. III).

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2021/050504

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2017/0169914 A1	15/06/2017	CN 105940461 A EP 3104370 A1 KR 20160118243 A WO 2015/119217 A1	14/09/2016 14/12/2016 11/10/2016 13/08/2015
WO 2019/231404 A1	05/12/2019	CN 112292422 A	29/01/2021

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2021/050504

Supplemental Box

(Classification of Subject Matter)

Int. Cl.

H01B 1/22 (2006.01)

H01B 13/00 (2006.01)

B32B 27/06 (2006.01)

B32B 27/32 (2006.01)

B32B 5/20 (2006.01)

C08J 9/35 (2006.01)

G01L 1/18 (2006.01)

C08J 9/28 (2006.01)

C08J 3/24 (2006.01)

C08J 3/09 (2006.01)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2021/050504

Supplemental Box (Continuation of Box No. III)

This International Searching Authority found multiple inventions in this international application, as follows:

Group I – Claims 1-18, 26-29 are directed to a crosslinked polymer network comprising a surfactant, and nanofeatured and nanoporous particles; a method of fabricating the polymer network; and a method of fabricating a sensor device containing the polymer network.

Group II – Claims 19-25 are directed to a method of fabricating a sensor device comprising a carrier, a crosslinked polymer network, and an array of electrodes.

In the above groups of claims, the only feature common to two of the claimed inventions and which provides a technical relationship among them is a crosslinked polymer network.

However this feature does not make a contribution over the prior art because a crosslinked polymer network is commonly known, which cannot be a special technical feature. The other identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship.

Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a priori*.

Please refer to **Box No. IV** of Written Opinion of The International Searching Authority (Form PCT/ISA/237) for detailed explanation.