2021 S.T. Yau High School Science Award (Asia)

Research Report

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Title of Research Report

Engineering Flexible, Conductive Ecoflex™ Infiltrated $Ti_3C_2T_x$ MXene/Graphene Oxide Aerogel as Strain Sensor

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Abstract

Recent years, there have been continuing advances in $Ti_3C_2T_x$ MXene material to achieve a strong synergistic effect among the high electrical conductivity, hydrophilicity, and rich surface chemistry of MXene materials. However, challenges remain in many applications such as wearable electronics because MXene materials inherently possess poor structural robustness due to the repulsion of its negatively charged nanosheets in the process of fabrication. Herein, we utilise the excellent hydrophilicity of biomimetic hierarchical MXene[2,3] to fabricate MXene/Graphene Oxide (GO) aerogel. Following, we coated the prepared aerogel with Ecoflex™ elastomer to transform weak aerogels into sustainable strain sensors, utilising MXene's high conductivity. The resulting strain sensor can be fine-tuned by changing the concentration ratio of MXene and GO to achieve desirable functionality.

Keywords: MXene, Graphene Oxide (GO), Aerogel, Ecoflex™ elastomer, Moloch horridus

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We would like to thank NUS and NUS High school of Mathematics and Science for supporting this research project. We would also like to thank Dr Ding Meng, a research fellow from the department of chemical and biomolecular engineering in NUS, for the guidance to handle the equipments used in this project. Last but not least, we would like to thank Prof Chen Po-yen from NUS for granting us this project.

Commitments on Academic Honesty and Integrity

We hereby declare that we

1. are fully committed to the principle of honesty, integrity and fair play throughout the competition.
2. actually perform the research work ourselves and thus truly understand the content of the work.
3. observe the common standard of academic integrity adopted by most journals and degree theses.
4. have declared all the assistance and contribution we have received from any personnel, agency, institution, etc. for the research work.
5. undertake to avoid getting in touch with assessment panel members in a way that may lead to direct or indirect conflict of interest.
6. undertake to avoid any interaction with assessment panel members that would undermine the neutrality of the panel member and fairness of the assessment process.
7. observe the safety regulations of the laboratory(ies) where we conduct the experiment(s), if applicable.
8. observe all rules and regulations of the competition.
9. agree that the decision of YHSA(Asia) is final in all matters related to the competition.

We understand and agree that failure to honour the above commitments may lead to disqualification from the competition and/or removal of reward, if applicable; that any unethical deeds, if found, will be disclosed to the school principal of team member(s) and relevant parties if deemed necessary; and that the decision of YHSA(Asia) is final and no appeal will be accepted.

(Signatures of full team below)

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Introduction

MXenes belong to a booming class of 2D early-transition metal carbides/carbonitrides that have hydrophilic surfaces and high electrical conductivity. The general chemical formula of MXenes is $M_{n+1}X_nT_x$, where M represents an early transition metal, X, a carbon and/or nitrogen, and T, a surface termination such as O, OH, or F. (n = 1, 2, or 3). Similar to graphene oxide (GO), these 2D nanomaterials exhibit large specific surface area and rich surface chemistry, thus enabling countless emerging appliances such as wearable electronics[2], solar evaporation device[3], electromagnetic interference (EMI) shielding[4] and more.

Among these, flexible strain sensors present promising applications in wearable electronics. Recently, nanosheets, especially $Ti_3C_2T_x$ MXene, are reported to be the ideal constituent blocks[8] for constructing highly efficient conduction networks in polymer matrices such as MXene fibre, films, or 3D aerogels, owing to their intriguing layered structure and high conductivity. The interconnected 3D architecture further enhances its electrical conductivity by having a higher areal loading of 2D Material. However, the weak gelation between MXene nanosheets often result in poor porous architecture in MXene Aerogel and some fabrication processes may have a high energy-consumption (e.g., chemical vapor deposition), thereby resulting in high material and manufacturing cost.

Recently, Kerui et al[2,3] reported a method involving biomimetic hierarchical MXene structures following the rough textures of the West African Gaboon vipers' black scales. In nature, such hierarchical textures are present in a diversity of animals, serving not only as light harvesters[3], but also as moisture harvesters[6] in tropical habitat. This ability to hold/store water makes hierarchical MXene (or crumpled MXene) valuable in the fabrication of 3D MXene aerogel via a cation-induced gelation process[10]. To date, several other methods, such as 3D template method, and freeze-casting, have all been proposed to construct 3D MXene structures. However, the one-step deposition on a crumpled MXene film followed by freeze-drying is a fast and reusable method (Figure 1) which promotes green chemistry while showing no significant deviation from the MXene Aerogel prepared from literature (Figure 4a).

Nevertheless, it has remained a challenge to develop MXene-based strain sensors with remarkable mechanical properties[5]. In recent years, advances such as the incorporation of graphene oxide (GO) have been developed. Herein, conductive, and compressible aerogels are engineered via the addition of GO nanosheets (MG Aerogels), together with the infiltration of Ecoflex™ elastomer to fill the interior of the aerogel. Furthermore, the performance of Ecoflex™ infiltrated MG Aerogel as a strain sensor is accessed.

Methodology

Synthesis of Graphene Oxide Nanosheets.

The Graphene Oxide (GO) nanosheets (6 mg/ml) were purchased and further condensed via centrifugation.

Synthesis of $Ti_3C_2T_x$ MXene Nanosheets.

$Ti_3C_2T_x$ MXene nanosheets were prepared according to literature[2].

Fabrication of crumpled 2D Materials film.

The preparation of crumpled 2D Materials film were prepared according to literature[2].

Fabrication of MXene/GO Aerogel by ion-diffusion-induced gelation on crumbled 2D Material Film.

The MXene nanosheets was diluted to 10 mg mL^{-1}. Meanwhile, the crumpled 2D-material film was wet in the $MgCl_2$ solution for a desired time/by drop casting $MgCl_2$ solution. Afterwards, the 10 mg mL^{-1} MXene solution were drop casted onto the surface of crumpled 2D films with Mg^{2+} ions. After the gelation process, the MXene Aerogel was obtained directly by freeze-drying the hydrogel. Different MXene:GO Aerogels concentration ratio of 7:3, 5:5, 3:7 and pure GO were also produced. The total concentration was kept constant at 10 mg mL^{-1}. The MXene/GO Aerogels were respectively coded as 10/0, 7/3, 5/5, 3/7, 0/10 MG Aerogel.

Infiltration of Ecoflex™ and fabrication of a strain sensor.

Ecoflex™ 00-50 elastomers came as parts A and B. Parts A and B were weighted in a 1:1 ratio before mixing in a weighing boat. After mixing, the mixture was immediately poured gently onto the MG Aerogel sample. This is followed by vacuum degassing to eliminate any entrapped air for a period of 10 minutes. Afterwards, the Ecoflex™ infiltrated Aerogel was exposed under room temperature for 2 hours.

The casting was conducted with a small weighing boat as the container and primary base. Prior to infiltration, Ecoflex™ 00-50 elastomers were cast in the container as described above as a secondary base. Copper tape (0.2Ω) was pasted on the secondary base to serve as the connection. Then, the MG Aerogel was positioned above the secondary base and copper tape and glued with silver paste.

Afterwards, Ecoflex™ 00-50 were poured onto the Aerogel (as described above) to complete the strain sensor. The different MG Aerogels were respectively denoted as different MG strain sensors via their concentration ratio of MXene/GO.

Characterization.

XRD patterns, SEM images together with EDX mapping, XPS spectroscopy, electrical conductivities, and mechanical testing were taken.

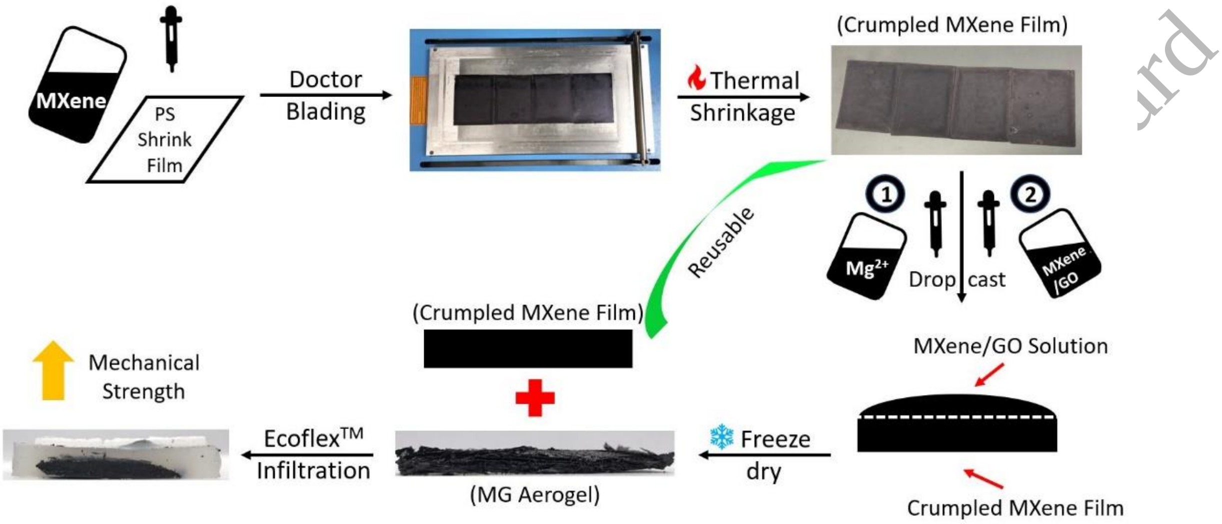

Fig. 1. Schematic illustrating the fabrication of crumpled MXene Film and Ecoflex™ infiltrated MG Aerogel.

Result and Discussion

Nature's moisture harvester.

The function of the crumpled 2D material film is inspired by the Moloch horridus, which is a nature's moisture harvester. Settling in the Australian desert, this lizard has specialised micro-structures on the integument[6] to spread out water at high velocity, especially towards the lizard's mouth. The micro-structures enable superhydrophilicity on the outer scale of the lizard, displaying high wettability. This phenomenon can be explained via capillary action, as the scale of the lizard are extremely rough, with many neighbouring micro-crests found in the vicinity of the scale. Therefore, the lizard is also known as the Australian thorny devil.

Biomimetic crumpled 2D Material film.

Taking inspiration from nature, the crumpled 2D Material film by synchronous thermal shrinkage of PS Shrink Film was constructed according to a reported work[2,3] by Kerui et al. After successful coating of 2D material on a shrink film, the biaxial contraction of the film under high heat results in a deformation of the original planar nanocoating into isotropic crumpled nanocoating. While the crumpled morphology can be utilised for its higher light to heat conversion efficiency[2,3], it also has excellent hydrophilicity and high water-storage capacities.

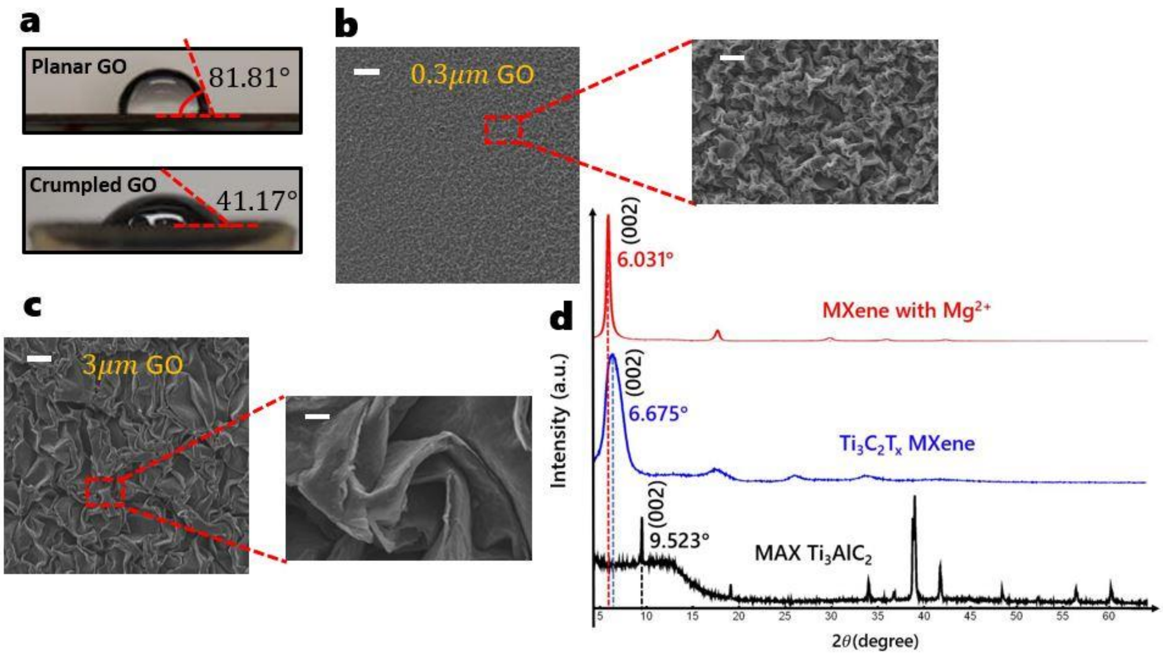

Fig. 2. (a) Water contact angle of nanocoated planar GO and crumpled GO film. SEM images of crumpled GO film (scale bar: 100 μm) with an enlarged image (scale bar: 10 μm) for (b) 0.3 μm and (c) 3 μm thick crumpled GO film. (d) XRD patterns of Ti_3AlC_2 MAX phase, MXene, and MXene Aerogel intercalated by Mg^{2+}.

For instance, the contact angle of water on planar coating of GO film decreases from 81.81° to 41.17° in crumpled GO film (Figure 2a). When characterised under a scanning electron microscope (SEM), many micro-crests formation in the crumpled GO films were observed (Figure 2b,c), mimicking the specialised micro-structures of the Australian thorny devil.

The high water-storage capacity of crumpled 2D films makes it an asset in the production of 2D material aerogel via the ion-diffusion-induced gelation process[10]. When highly concentrated salt solution is held onto the rough surface of the crumpled film, the cation can attract surrounding MXene/GO solution to form a MXene/GO gel layer along the film surface, via the electrostatic interaction and coordination bonding between negatively charged MXene/GO nanosheets (-O,-OH,-F) and the cation. This approach does not require any chemical functionality on the crumpled 2D film, with the area of the gel layer being directly proportional to the area of the crumpled 2D film, which can be flexibly adjusted. Furthermore, the isotropic crumpled structure enables homogenous distribution of the salt solution, and hence uniform thickness of the gel layer.

An increase in concentration, and thus areal mass of nanocoating prior to thermal shrinkage will result in an increase in the coating thickness (h) of the crumpled film[2]. As a result, the peak-to-peak distance (d) between micro-crests also increases. Observations from the SEM images (Figure 2b,c) confirms the increased distance (d) for a thicker GO crumpled film. This increment results in a higher water-storage capacity of the crumpled film.

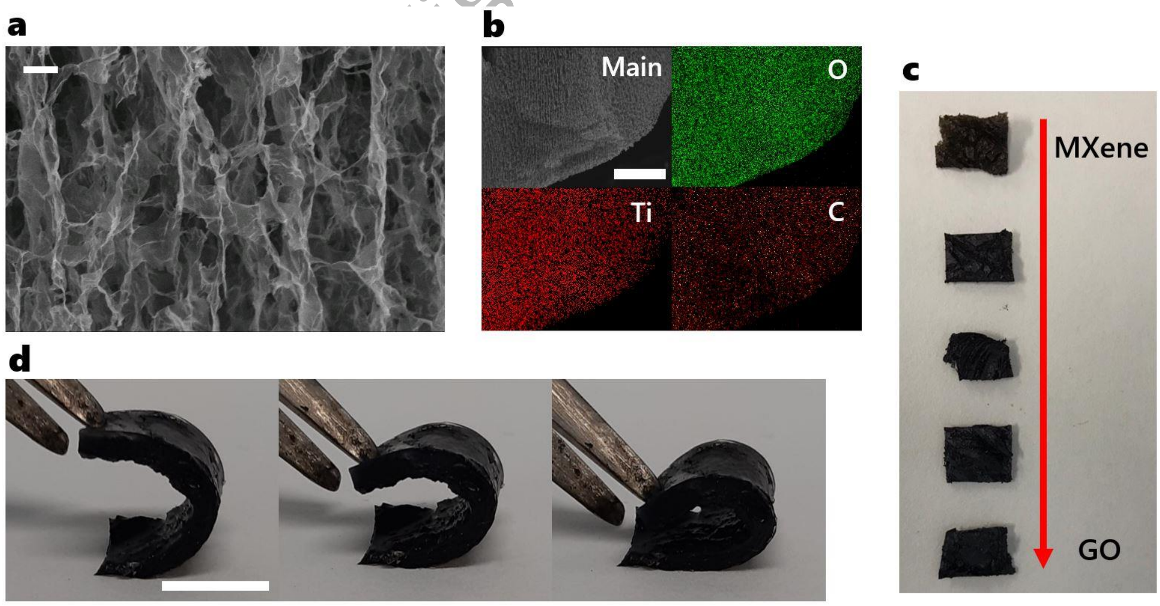

Fig. 3. (a) SEM image of MXene Aerogel (scale bar: 10 μm). (b) EDX spectroscopy elemental mapping of Oxygen, Titanium, and Carbon element (scale bar: 1 mm). (c) Images of MG Aerogel prior to Ecoflex™ infiltration arranged from pure MXene to pure GO. (d) Photographs of bending of Ecoflex™ infiltrated 5/5 MG Aerogel (scale bar: 1 cm)

Microstructure and Characterization of MXene Aerogel.

During the cation directed gelation, the sol-gel layer formed along the crumpled film is then freeze-dried, removing water content to produce a free-standing aerogel. The SEM image (Figure 3a) displays thin and spatial connection in the structure of MXene aerogel, resulting in the poor structural robustness and limited flexibility which is consistent with that reported in literature[1]. Nevertheless, energy dispersive X-ray spectroscopy (EDX) mapping of the MXene aerogels (Figure 3b) reveals a relatively even coating of the sol-gel layer (from the even distribution density of each element) prior to freeze-drying, thereby confirming our previous hypothesis of homogeneous distribution due to the isotropic crumpled film. Furthermore, the shift of the (002) peak from 6.675° (MXene) to 6.031° (MXene aerogel) in the X-Ray Diffraction (XRD) pattern (Figure 2d) demonstrates the successful Mg^{2+} intercalation between MXene sheets.

The X-ray photoelectron spectra (XPS) (Figure 4a) also reveals the elemental composition of MXene Aerogel, which closely resembles the XPS spectrum of a pristine MXene[5]. This demonstrates that the rich surface chemistry 2D MXene had not been altered, and that the aerogel will inherit a relatively high electrical conductivity like that of pristine MXene (conductivity: ca. 641 S m^{-1})

Enhanced Mechanical Stability in MG Aerogel and Ecoflex™ infiltrated Aerogel.

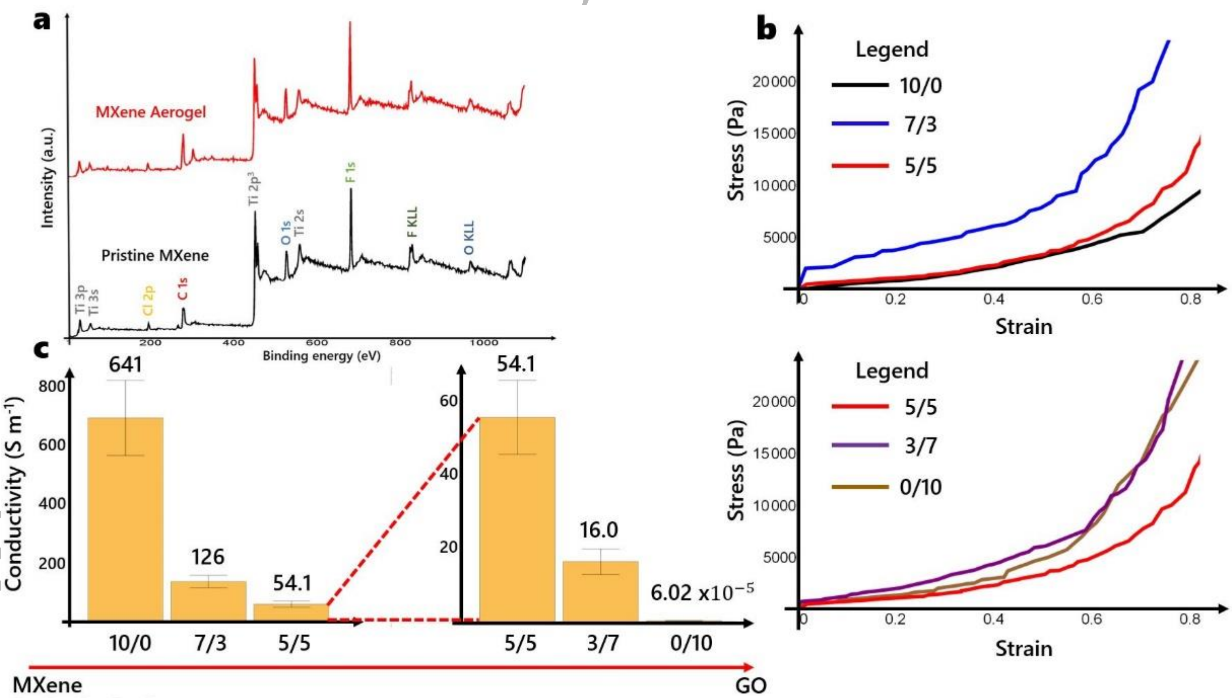

Fig. 4. (a) XPS survey spectra of MXene Aerogel and pristine MXene. (b) Compressive stress-strain curves of 10/0, 7/3, 5/5, 3/7, 0/10 MG Aerogels. (c) Conductivity of Ecoflex™ infiltrated MG Aerogel prior to internal fracture.

To address the weak structural integrity of MXene aerogel, various techniques had been developed and deployed. For example, introduction of other 2D Material such as polyvinyl alcohol (PVA) or cellulose nanofiber (CNF) to form interlayer hydrogen bond with MXene sheet can strengthen the integrity of the MXene film several times over. Recently, Ji Liu et al[5] successfully fabricated MXene/GO film with a high tensile strength of 209 MPa with electrical conductivity close to that of pristine MXene. Furthermore, the conductivity of GO can be readily tuned by tailoring the surface chemistry with a mild reduction process[7]. Herein, MXene/GO of different concentration ratio (10/0, 7/3, 5/5, 3/7, 0/10 MG Aerogel) were fabricated (Fig 3c). A compressive mechanical test was then conducted (Fig 4b) and all GO incorporated Aerogel have a better mechanical property than 10/0 (pure MXene) MG Aerogel. This trend may be accounted[4] by (1) the increased intercalation of the positively charged Mg^{2+} ions between adjacent nanosheets of both MXene and GO functional group, thus overcoming the electrostatic repulsive force present in pristine MXene nanosheets (which is negatively charged), and (2) interlayer hydrogen bonding between the terminated groups (−OH, −F, −COOH) of neighbouring nanosheets and, (3) 0/10 MG (pure GO) Aerogel is stronger than 10/0 MG (pure MXene) Aerogel due to an additional π−π interactions between the GO sheets.

To further enhance the mechanical robustness of the MXene aerogel for practical purposes such as a strain sensor, the interior porous compartment of the MG Aerogel is filled with flexible elastomer, via the procedure mentioned under "Infiltration of Ecoflex™ and fabrication of a strain sensor" (See above). The Ecoflex™ infiltrated Aerogel thus attain a high mechanical stability and flexibility and can be bent or pressed without any significant deformation (Figure 3d). The electrical conductivity of Ecoflex™ infiltrated MXene Aerogel remains high (ca. 641 S m^{-1}), but decreases notably as the GO content increases (Figure 4c). Herein, the GO solution is not reduced and the 0/10 MG Aerogel has a very low electrical conductivity. (ca. 6.02×10^{-5} S m^{-1})[7].

MG Aerogel performance as a strain sensor.

In this report, the electrical responses of Ecoflex™ infiltrated MG Aerogel to tensile and compressive deformation are studied. Initially, internal fracture occurs upon significant deformation and the overall resistance increases (Figure 5a). While the interior compartment of hollow MG Aerogel is filled with 0050-Ecoflex™, there exists thin connection within the Aerogel that are prone to breakage upon significant deformation. Therefore, breakage will induce small gap between the thin connection and increase the overall resistance of the Ecoflex™ infiltrated MG Aerogel. Nevertheless, the infiltrated Aerogel will reach a stable resistance and can be properly utilised as a strain sensor. Therefore, it is crucial that stronger aerogels are also examined to minimise the trade-off between degree of internal fracture and inherent conductivity.

Herein, three sensory tests are conducted on the MG Aerogel: bend-down test, bend-up test and point-press test (Figure 6). To ensure equal amplitude for the bending test cycle, the sensor was attached to a bendable backbone (ruler), and the ruler was pulled by a string to a constant displacement in each cycle. A pen was dropped from the same height onto the sensor and it was promptly retrieved during the point press test. Due to the construction of the strain sensor, there is an anisotropic response when we bend the aerogel up or down. Typically, bending corresponds to a tensile deformation, which will increase the resistance (Figure 5b). However, due to the outer layer of the sensor, bending up does not increase the horizontal distance and the process is akin to squeezing a lemon, which includes compression deformation leading to an initial decrease in resistance instead. (Figure 5c). Point press test on the other hand corresponds to a local deformation on the surface of the Aerogel. The resistance will increase due to the geometric effect[9] at the point of pressure. Herein, we conducted the point-press test repeatedly for around 4 minutes and the consistent fractional change indicates the stability of Ecoflex™ infiltrated MG Aerogel (Figure 7a).

As previously mentioned, the resistance of individual MG Aerogel will suffer a significant increase due to internal fracture. As such, the resistivity of the 'finalised' strain sensor needs to be measured again (Figure 7b). From the graph, it shows that 3/7 (and 0/10) MG Aerogel is not suitable owing to its high

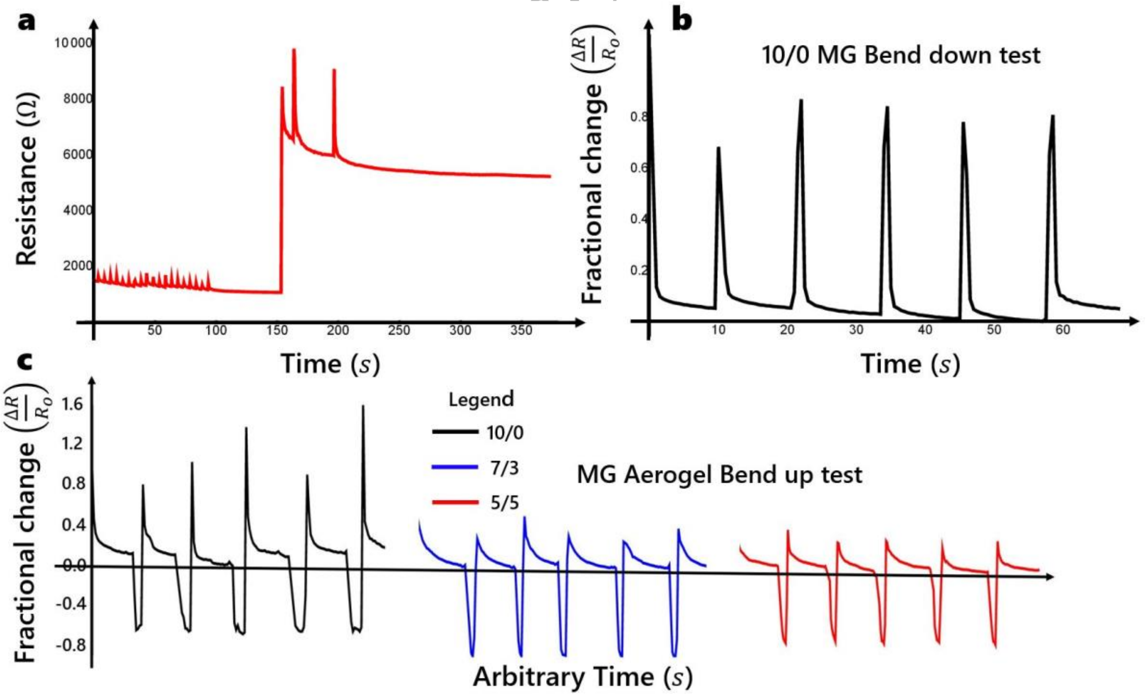

Fig. 5. (a) Increase resistance for 3/7 MG Aerogel due to internal fracture. G(b) Graph of fractional resistance change of 10/0 MG Aerogel against time during the bend-down test. (c) Graph of fractional resistance change of 10/0, 7/3, 5/5 MG Aerogel against time during the bend-up test.

resistivity. Furthermore, aerogel with the lowest resistivity (10/0 MG Aerogel) also shows the highest sensitivity (Figure 5c) in the bend-up test with the largest fractional change during the deformation. However, 5/5 MG Aerogel presents a more consistent fractional change during each deformation because of its high resistivity and better mechanical stability. As such, different concentration of MXene/GO combination can help provide the desired functionality of a strain sensor as per required by the user.

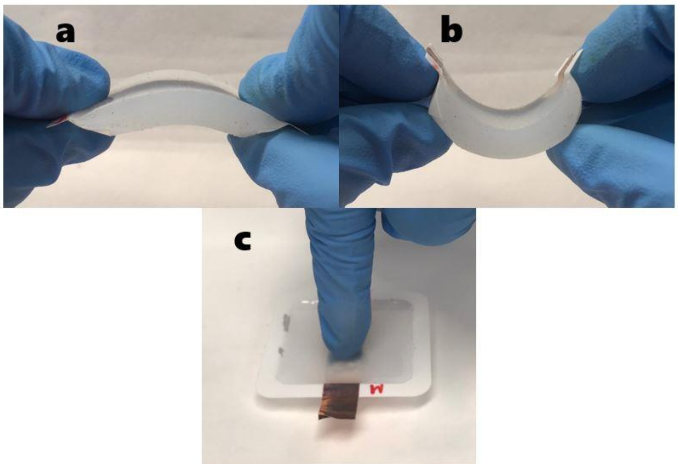

Fig. 6. Three sensory tests. (a) bend down test, (b) bend-up test, (c) point-press tests.

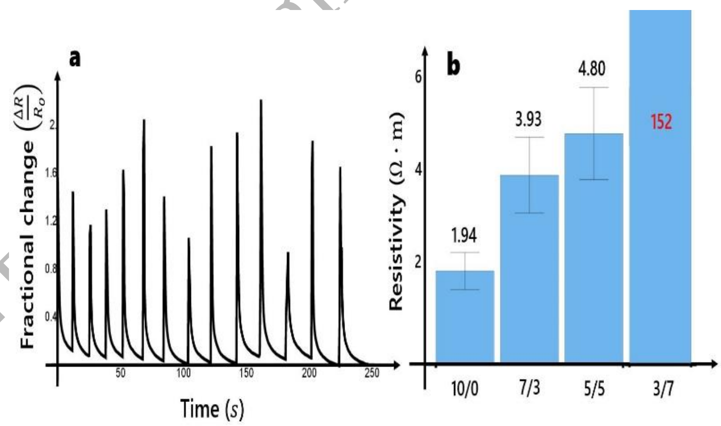

Fig. 7. (a) Repeated Point press test on 10/0 MG Aerogel for 250 s. (b) Resistivity of Ecoflex™ infiltrated MG Aerogel after internal fracture

Conclusion

In summary, we have developed a method of producing MXene/GO Aerogels using cheap, fast, and reusable crumpled MXene (or GO) films. The prepared aerogel is then further strengthened by filling its interior porous compartments with Ecoflex™ elastomer. The utilisation of the Ecoflex™ infiltrated MG Aerogel as a strain sensor is also investigated.

This method to prepare aerogel can be extended to a whole slew of composite 2D materials aerogel such as MXene/Montmorillonite (MMT) and MXene/reduced Graphene Oxide (RGO). With excellent conductivity and hydrophilicity, MXene presents promising aspect in both fabrication and functionality of sensors in wearable electronics, soft robotics, and prosthetics.

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