Macromolecular bridging-enhanced holey graphene oxide-based film and its humidity deformation response

Highlights
The macromolecular cross-linking can effectively inhibit the swelling of GO film

Modified holey graphene oxide homogeneous film exhibit a sensitive response to humidity

This feature depends on the effective control of the GO film interlayer spacing
Macromolecular bridging-enhanced holey graphene oxide-based film and its humidity deformation response

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SUMMARY
The interaction of water molecules with graphene oxide (GO) at the interface or surface will lead to the reversible deformation response of GO-based materials. However, the fabrication of structurally stable and highly sensitive GO-based humidity-responsive films remains a challenge. Since the stability and sensitivity of GO-based humidity-responsive devices are significantly limited by the deformation differences between different components. Herein, we demonstrate that polyamidoamine (PAMAM) bridge-enhanced carboxylated holey GO (hGC/PAMAM) films are sensitive to moisture and exhibit excellent stability in water. Experiments and molecular dynamics (MD) simulation show that the formation of N-C=O between PAMAM and GO sheets significantly increased the interlayer bonding force. Dynamic monitoring of the surface strain of the hGC/PAMAM films showed that the strains spread a gradient from the high-humidity to the low-humidity side, causing asymmetric expansion along the horizontal and vertical directions. This work will provide a better understanding of the mechanism of water molecule transport between layers.

INTRODUCTION
In the long history of development and elimination, the creatures have derived a variety of exquisite intelligence and unique properties, such as pinecones. Pinecones close when wet (or open when dried), because the variation of environmental humidity makes the aligned layers of nano- and mesoscale change conformation and undergo bending deformation.1,2 Inspired by nature, actuators driven by water/moisture/humidity or their gradients have attracted increasing growing interest, are holding great potential in a variety of applications.3–8

In recent years, graphene oxide (GO) has been explored as an excellent component for smart actuation systems driven by a water-related trigger, owing to its intriguing physical and chemical features.9–12 Based on the sensitive properties of GO to moisture, many unique GO-containing stimuli-responsive actuators have been developed, showing potential applications in energy conversion and controllable deformation.14–25 For example, Cheng et al. prepared the asymmetric structure of graphene and GO fibers via the positioned laser reduction of GO fibers,26 which displayed a predetermined motion in a well-defined manner upon moisture exposure. Ruoff et al. fabricated a macroscopic actuator based on a GO and carbon nanotube (GO/CNT) bilayer film,27 which demonstrated remarkable actuation depending on the variation of humidity. In these cases, the GO layer plays a major role in the humidity deformation response of the bilayer structures. It is worth noting that the bilayer actuators are subject to poor interlayer attachment and even the delamination of the two layers during the locomotion process. Hence, Ge et al.28 prepared an efficient moisture actuator with homogeneous GO film. It is well known that GO is popular in 2D materials because of the large number of oxygenated functional groups on its surfaces and edges which is easy to be modified and self-assembled for extensive application.29–31 However, the abundant hydrophilic functional groups on the surface make the layer-by-layer GO-based material very hydrophilic and thus endows it with a high tendency to absorb water and swell in humid or aqueous environments, greatly diminishing its target properties. Furthermore, it is difficult to maintain a uniform and orderly structure for a long time for GO after some modifications, such as porous for better permeability,32,33 and interlayer crosslinking for better mechanical properties and water stability.34,35 The worse homogeneous structure of modified GO

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is a great challenge for moisture actuators. Therefore, at this stage, it is still a challenge to prepare structurally stable and highly humidity-sensitive GO-based humidity-sensitive films.

As stated above, we developed a macromolecular bridging-enhanced holey GO-based film with excellent water resistance and moisture deformation response. First, we prepared the holey graphene oxide (hGO) sheets with abundant in-plane nanopores through a convenient mild defect-etching reaction. Then, the carboxyl-functionalized holey graphene oxide (hGC) sheets were covalently cross-linked by polyamidoamine (PAMAM) to obtain a moisture responsive and water-resistant hGC/PAMAM homogeneous film. Tensile mechanical tests and molecular dynamics (MD) simulations showed that the combination of N-C=O covalent bonding between hGC sheets and PAMAM can effectively inhibit interlayer sliding, resulting in the hGC/PAMAM film possessing pristine GO film strength (~51.4 MPa). At the same time, the hGC/PAMAM film exhibited excellent water resistance, which did not re-disperse even after 1 h of sonication. The dynamic deformation monitoring of the films under humidity showed that the rapid infiltration of moisture along the channels resulted in a gradient expansion of strain in the transverse and longitudinal directions, which was the main reason for the bending deformation of the hGC/PAMAM films.

RESULTS AND DISCUSSION

Structure and self-assembling of holey graphene oxide/polyamidoamine

In order to achieve effective transmission paths of dendrimers and water molecules, we first construct a large number of in-plane nanopores on GO sheets via a convenient mild defect-etching reaction. The hGO sheets are then carboxylated to convert the hydroxyl groups (-OH) in the sheets to carboxyl (-COOH), followed by cross-linking via PAMAM to improve the bonding strength between the sheets. The fabrication of hGC/PAMAM film is illustrated in Figure 1A. Compared with GO, 0.5 mg/mL hGC/PAMAM dispersion is brownish black (Figure 1B), and a large number of nanopores can be seen through the transmission electron microscopy (TEM) test (Figure 1C). At the same time, as shown in the inset of Figure 1C, compared with GO (Figure S1), we observe clear electron diffraction spots of hGC/PAMAM have disappeared due to the presence of PAMAM.

The hGC/PAMAM sheets (Figure 1D) in the mixing solution are filtrated with the assistance of a vacuum to obtain the free-standing film by stacking PAMAM macromolecule in the layers of hGC sheets (Figure 1E). The mapping of the N element in the cross-section and surface of hGC/PAMAM film indicates the uniform distribution of PAMAM, as shown in Figures 1F, 1G, and S2. The resultant hGC/PAMAM films with different weight ratios of PAMAM are prepared by the same method and termed hGC/PAMAM-I, hGC/PAMAM-II, and hGC/PAMAM-III.

H$_2$O$_2$ can partially oxidize and etch the carbon atoms around the more active defective sites of GO, creating vacancies and gradually extending to result in a large number of in-plane pores of a few nanometers. Furthermore, under strong alkaline conditions, chloroacetic acid can activate GO sheets and convert the -OH in the plane to -COOH, which can be cross-linked with amide groups on PAMAM to significantly improve the mechanical strength of hGC films. X-ray Photoelectron Spectroscopy (XPS) analysis demonstrates the change of functional groups on the GO sheets and further confirmed the chemical cross-linking of GO with PAMAM dendrimers (Figure 2A). XPS results show that the hGC/PAMAM is mainly composed of C, O, and N elements (Figure S3). The C1s curve of hGC/PAMAM shows an additional binding energy peak at 287.6 eV, which is attributed to amide groups (-N-C=O). The peak at 285.8 eV represents the C-N bond contributions in the amine (CH$_2$-NH$_2$) (Figure 2B). This internal interaction mechanism can also be indicated by the Fourier transform infrared (FTIR) spectroscopy. For pure GO, the peaks at the wavenumber of 1734 cm$^{-1}$, 1222 cm$^{-1}$, and 1087 cm$^{-1}$ that represent the stretching vibrations of C=O, C-OH, and C-O, respectively. With the erosion of H$_2$O$_2$, the content of C=O decreases. The modification of carboxyl functionalization (i.e., hGC/PAMAM) results in the generation of a new N-H bending characteristic peak at a wavenumber of 3297 cm$^{-1}$. In addition, the peaks at 2935 cm$^{-1}$, 1539 cm$^{-1}$, and 691 cm$^{-1}$ correspond to the -CH$_2$-, N-H stretching, and N-H wagging, respectively, as shown in Figure 2C.

Raman spectroscopy is used to further study the structural changes of the sheets. Figure 2D shows that GO has two distinct spectral peaks, the D and G bands that appeared at 1339 and 1594 cm$^{-1}$, respectively. The D and G bands of hGC/PAMAM appear at 1349 and 1599 cm$^{-1}$, respectively, without exhibiting significant changes in comparison with those of GO sheets. In addition, the I$_D$/I$_G$ ratio of hGC/PAMAM film increases slightly compared with pure GO, as shown in Figure 2D.
Mechanical properties of the holey graphene oxide/polyamidoamine film

The uniaxial tensile tests show that the covalent bonding between hGC and PAMAM can effectively inhibit interlaminar slip and crack arrest, and improve the bonding strength between hGC sheets, resulting in the hGC/PAMAM film with the same strength as pristine GO films. As shown in Figure 3A and 3B, when in-plane nanopores are introduced, hGO film shows a low tensile strength of 10.0 ± 1.7 MPa, and Young’s modulus of 0.71 ± 0.04 GPa due to the holey-induced sheets fracture and weak interlayer.
interactions. When PAMAM is introduced, the obtained hGC/PAMAM-I (the mass ratio of GO to PAMAM is 120:1) film shows a tensile strength of 14.7 ± 1.1 MPa and Young's modulus of 0.79 ± 0.16 GPa. When increasing the content of PAMAM, the obtained hGC/PAMAM-II (the mass ratio of GO to PAMAM is 80:1) film shows a tensile strength of 51.4 ± 1.9 MPa and Young's modulus of 4.1 ± 0.3 GPa, which are 5 times and 5.5 times higher than hGO film, respectively. This may be due to the N-C=O covalent bonding between PAMAM and hGC sheets, which inhibits the slippage between the hGC sheets and resist the crack propagation to some extent (Figure S4). The folds and curls of the lamellae in the fracture section of hGC/PAMAM films, as well as the jagged fracture section, further support the above conclusions, as shown in Figures 3C, 3D, and 3F. However, it is worth noting that when the content of PAMAM is increased, the tensile strength of hGC/PAMAM-III (the mass ratio of GO to PAMAM is 60:1) film decreases sharply (12.5 ± 5.9 MPa), and the Young’s modulus has no obvious change (4.06 ± 0.26 GPa). This may be due to the excessive introduction of PAMAM and re-stacking of hGC sheets, resulting in interlaminar cracking and failure to inhibit crack propagation, as shown in Figures 3E, and S4F. In the following, unless otherwise specified, hGC/PAMAM refers to the hGC/PAMAM-II. In fact, macromolecular cross-linking can also improve the mechanical properties of GO films (Figure S5).

To further investigate the mechanic mechanisms of hGC/PAMAM during the tensile process, detailed MD simulations are taken with bilayer hGC sheets. The schematic diagrams of the simulation model of hGC/PAMAM are shown in Figure 4A. There are two-layer hGC sheets with a length of 100 Å and width of 60 Å, and the overlapping region is 60 Å * 50 Å. The PAMAM molecules are set at the center of the overlapping region. It is indicated that PAMAM has connected the bilayer hGC sheets like a bridge as shown in Figure 4B. In the initial stage of stretching (Step I), for pure hGC sheets, the value of tensile force fluctuates due to the friction between sheets. Compared with pure hGC sheets, hGC/PAMAM has the same tendency at first during the tensile process. However, with the continuous stretching of the lamellar, the N-C=O bond connecting the hGC/PAMAM lamellar breaks (Step II), resulting in a
peak force of 10.1 nN. After that, the tensile force gradually decreases to a similar level to the pure hGC sheets (Step III), as shown in Figure 4C. The snapshots of hGC/PAMAM during the tensile process are displayed in Figure 4D. The N atoms which indicate the presence of PAMAM are moving with the stretching hGC sheets as a bridge between the hGC sheets until N-C=O bond comes to break down leading to the peak force. The tensile force of hGC/PAMAM increases to 10.1 nN compared to the 5.7 nN of pure hGC sheets, indicating the efficient confinement of sheets slip by interlayer covalent bonding.

Figure 3. Mechanical characterization of the films
(A) Typical stress-strain strength curves.
(B) Tensile strength and Young’s modulus.
(C–E) SEM images for the fracture cross-section of hGC/PAMAM-I, hGC/PAMAM-II and hGC/PAMAM-III.
(F) Low- and high-magnification SEM images, and the EDS of elemental C, O, N of the fracture surfaces of the hGC/PAMAM films.
Water stability and moisture response of the holey graphene oxide/polyamidoamine film

The synergistic effect of the holey structure and interlayer crosslinking not only improves the tensile strength of hGC/PAMAM film but also endows the film with an excellent stability in water. Figure 5A shows that the hGC/PAMAM film kept its integrity even after sonication for 1 h, the hGC film was partially dispersed, while pure GO and hGO films were completely re-dispersed in water. It is worth noting that although the hGC/PAMAM film is water-tolerant, it is still hydrophilic (Figure S6). As mentioned above, XPS and FTIR results show that, like pure GO, the hGO, hGC, and hGC/PAMAM sheets mainly contain C=O, C–OH, and -COOH oxygen functional groups. The ionizable -COOH groups at the edges of the sheets make hGO hydrophilic, as evidenced by the good dispersion of the hGO sheets and the water contact angle (CA) (71.1°, Figure S6) of the hGO film. Although the edges of hGO are hydrophilic, its basal plane contains many unoxidized graphene nanodomains, which are hydrophobic. Therefore, like pure GO, the hGO, sheets should be amphiphilic, with an edge-to-center distribution of hydrophilic and hydrophobic domains (Figure S7). On this basis, the final hGCPAMAM film shows hydrophilicity (the CA of hGCPAMAM is 81.2°).

After immersing in water for 72 and 168 h and drying in the atmosphere, the hGC/PAMAM film exhibits a lower strength (43.8 MPa) but a higher breakage elongation (1.78%), as shown in Figure 5B. The hGC/PAMAM film after re-watering and drying shows nearly ideal elastic response before 0.45% strain and proceeded to a plastic region until breakage. X-ray diffraction (XRD) characterization of the d-spacing of the films in both dry and wet states shows that the interlayer expansion of hGCPAMAM is significantly suppressed in the wet state, compared to GO, hGO, and hGC (Figure 5C). The fracture surface and cross-section of the hGC/PAMAM film after soaking and drying are observed by SEM, the plastic

Figure 4. Molecular dynamics simulation of the stretching mechanism of hGC/PAMAM film
(A) Tensile test MD simulation model for hGC/PAMAM.
(B) The crosslink bond between bilayer in hGC/PAMAM.
(C) The force-displacement curves of pure hGC sheets and hGC/PAMAM under stretching.
(D) The snapshots of hGC/PAMAM during the tensile process. Step I, II and III correspond to the three stages of hGC/PAMAM stretching in (C). Detailed snapshots of peak points are shown in the figure below.

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deformation can be attributed to the flow between constituent hGC sheets, possibly accompanied by the stretching of wrinkles (Figures 5D and 5E). In addition, according to the mapping of the N element in Figure 5E, it can be seen that PAMAM is still uniformly distributed between the layers, indicating that the interlayer covalent bonding, which plays a major role in the mechanical properties of the film, has not changed, resulting in no obvious change in the strength of the hGC/PAMAM film. The above phenomenon may be due to the fact that when the dried hGC/PAMAM film is soaked in water, the water molecules enter the hGC sheets through nanochannels, resulting in an increase in the $d$-spacing and stretching of the partially wrinkled sheets.43 While, during water evaporation, water molecules seep out from the in-plane nanochannels, and the swollen sheets are re-stacked under the synergistic effect of covalent and hydrogen bonds (Figure 5F).

Moreover, the homogeneous hGC/PAMAM film exhibits a highly sensitive response to moisture. It can be seen from Figure 6A that the hGC/PAMAM film bends when placed on the palm at room temperature, and with a relative humidity (RH) difference of 20%, whereas it shows no locomotion when wearing a glove.
Interestingly, due to the RH difference of the palm, the hGC/PAMAM film can roll spontaneously (Video S1). In addition, due to the difference in humidity gradient and the strong interlayer interaction, the hGC/PAMAM film can even curl and tumble on the water surface (Video S2). Similarly, the hGC/PAMAM film bends downward when the finger approaches from above, as shown in Figure 6B. When water droplet is added in the middle of the hGC/PAMAM strip (with a length of 40 mm and a width of 15 mm), the strip quickly bends

Figure 6. Moisture deformation response of hGC/PAMAM film

(A) The rapid deformation of the hGC/PAMAM film when put on the palm. Inset shows the film on the palm but wearing a glove.
(B) Bending downward of the hGC/PAMAM film once a fingertip approaching.
(C) The hGC/PAMAM strip (length: 40 mm, width: 15 mm) bend rapidly at the water drop and then partially recover.
(D) Reproducible droplet-driven curl-straightening of the hGC/PAMAM film in Figure (C).
(E) Schematic diagram of the response mechanism of the hGC/PAMAM film to humidity.
(F and G) The strain and deformation of the hGC/PAMAM film exposure to moisture gradients monitored by Vic3D, respectively.
about 94° at the water droplet, and gradually returns to 45°, during which the water droplet does not slide (Figure 6C and Video S3). The hGC/PAMAM strip returns to a flat state when the droplet is completely dry, this droplet-driven curling-straightening phenomenon can be repeated for more than 10 cycles (Figure 6D). In addition, we investigate the time-dependent bending angle of hGC films of different thicknesses during bending (on) at 60% relative humidity and during recovery (off) at ambient conditions (Figure S8). The results show that the maximum bending angle decreases with the enhancement of film thickness, and the duration of the recovery of the original shape is short for the film with low thicknesses.

When hGC/PAMAM film is exposed to water gradient vapors, the hydrophilic part of the hGC/PAMAM film at the bottom swells due to water absorption, forming strong intermolecular hydrogen bonding interaction, and resulting in corresponding compressive stress on the low-humidity side. The difference in swelling along the transverse and vertical directions causes this compressive stress to expand toward the lower humidity side and cause bending deformation of the hGC/PAMAM film, as shown in Figure 6E. The dynamic strain and deformation process of the hGC/PAMAM film under the moisture can be monitored by Video Image Correlation in 3D (Vic3D). As shown in Figure 6F, when the hGC/PAMAM film is placed above the humidity source (Figure S9), and the RH difference is 80%, the film produces a high strain region on the high humidity gradient side and expands rapidly to the low humidity side within 0.5 s. It is worth noting that with the gradient migration of strain, the original high strain region produces a reverse high strain, which is likely due to the shrinkage of the expanded hGC sheets with the infiltration and overflow of water vapor. At the same time, as shown in Figure 6G (Video S4), the high humidity gradient region of the hGC/PAMAM film swells and expands to both sides. The displacement on one side of the low humidity gradient gradually increased from 0.83 mm to 6.60 mm within 1 s. The above phenomena indicate that the difference in humidity gradient causes the in situ gradient expansion of hGC/PAMAM film in the lateral and vertical directions. The hGC/PAMAM film generates high stress in the high humidity area, and the macroscopic deformation is caused as the stress migrates to the low humidity area.

For the layer-by-layer hGC/PAMAM film, compared with nanopores, the presence of oxygen-containing functional groups plays a great role in the interlayer and in-plane transport of water molecules. The groups (for instance, C-O, C-OH, and so forth) attached to the hGO sheets result in a relatively large d-spacing. Due to hydrogen bonding and a narrower space available for diffusion, water molecules have low mobility in the oxidized regions that are randomly covered with C-O, C-OH. Importantly, such groups tend to clump together and leave infiltrated regions of bulk unoxidized graphene sheets. These unoxidized regions realize the rapid penetration of water molecules between GO layers under the control of a certain d-spacing. Notably, larger d-spacing impairs the fast transport of water molecules between GO layers s. In this article, PAMAM bridging-enhanced carboxylated hGO films are able to suppress the increase of d-spacing under high humidity (Figure 5C), enabling fast transport of water molecules between layers. This enables hGC/PAMAM films to exhibit a higher humidity deformation response. This is consistent with the latest research conclusions in this field. The presence of functional groups plays a large part in enabling fast water transport, and higher in-plane pore density does not necessarily lead to higher water permeability.

Table 1 shows a comparison of the reported moisture deformation response works of GO-based materials. Compared with the conventional bilayer structure, the homogenized GO films exhibited higher sensitivity to humidity and showed fast and continuous motion. In addition, the hGC/PAMAM mentioned in this work exhibits better interlayer bonding strength, can work stably under high humidity conditions, and can maintain structural stability even if it is continuously immersed in water. Thanks to the capability of fast and sensitive moisture deformation response, the hGC/PAMAM film is promising for fabricating smart actuation devices.

**Conclusion**

In this study, a facile solution method was developed to self-assemble the homogeneous hGC/PAMAM film with water resistance and moisture deformation response. A series of test characterizations and MD simulations showed that the N-C=O covalent bonds formed between PAMAM and hGC sheets inhibited the slippage of the sheets. The uniformly abundant nanochannels in the plane allowed the rapid penetration of water vapor, resulting in gradient strain of the film in the axial and transverse directions, while the strong interlayer bonding limited its excessive expansion under high relative humidity difference. The above synergistic effect enabled hGC/PAMAM film to have better water resistance, which was not re-dispersed even after sonication for 1 h and exhibited efficient and controllable bending deformation.
This work provides a new idea for solving the problem of poor water resistance of GO-based humidity-responsive materials, further expanding the application potential of GO in the field of humidity-sensing devices.

Limitations of the study
In this article, we fabricated the hGO sheets with abundant in-plane nanopores by etching GO sheets with H2O2. The density and size of the pores within the hGO sheets layer are sensitive to the etching time of H2O2. It is worth noting that a higher in-plane pore density does not necessarily lead to higher water permeability, but rather weakens the mechanical properties of the film. In addition, the GC/PAMAM films did not exhibit deformation response to humidity. This was mainly because it is difficult to achieve uniform dispersion of macromolecules in GO dispersions, the stacking of GO sheets leads to a large number of randomly distributed wrinkles inside GO/PAMAM film (Figure S5).

STAR METHODS
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SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.105496.

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AUTHOR CONTRIBUTIONS
H.F. T. supervised the project. Y. Z., and F. W. performed experimental and mechanistic studies. Y.F. Z. helped with the MD simulation. B. J. conducted the tensile tests. W.X. L. conducted the Vic3D measurements. C. W., and C. S., conceived the project. All authors analyzed the results and approved the current version of the article.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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STAR METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Chemicals, peptides, and recombinant proteins | Macklin (Shanghai, China) | Cat#G810361; CAS no. 7782-42-5 |
| Potassium permanganate (≥99.0%) | Sigma-Aldrich | Cat#Z23468; CAS no. 7722-64-7 |
| phosphorus pentoxide, ≥99.0% (NT) | Sigma-Aldrich | Cat#71359; CAS no. 1314-56-3 |
| Concentrated sulfuric acid, ≥99.0% | Sigma-Aldrich | Cat#339741; CAS no. 7664-93-9 |
| Potassium sulfate (≥99.0%) | Sigma-Aldrich | Cat#P0772; CAS no. 7778-80-5 |
| hydrogen peroxide (34.5–36.5%) | Sigma-Aldrich | Cat#18304; CAS no. 7722-84-1 |
| Sodium hydroxide (≥98%) | Sigma-Aldrich | Cat#SS881; CAS No. 1310-73-2 |
| Chloroacetic acid (≥99.0%) | Sigma-Aldrich | Cat# 402923; CAS No. 79-11-8 |
| Hydrochloric acid, 1 M | Sigma-Aldrich | Cat# 150696; CAS No. 7647-01-0 |
| Ethylenediamine core (PAMAM), generation 0.0 solution, 20 wt % | Sigma-Aldrich | Cat# 412368; CAS No. 155773-72-1 |
| PVDF Hydrophilic Membrane Filters, 0.22 μm, 47 mm | Scientificfilters.com/Tisch Scientific | SF15024 |

Software and algorithms

- Origin 8 Origin Lab https://www.originlab.com/
- LAMMPS LAMMPS website https://www.lammps.org/

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Huifeng Tan (tanhf@hit.edu.cn).

Material availability
Materials are available up on request.

Data and code availability
- Data reported in this article will be shared by the lead contact on request.
- There is no dataset or code associated with this work.
- Any additional information required to reanalyse the data reported in this study is available from the lead contact upon request.

METHOD DETAILS

Preparation of GO dispersion
The GO was synthesized from pure natural graphite by improved Hummers’ method.47,48 3 mL H2SO4 (18.4 M) was placed in a beaker and heat to 80°C, then 1 g K2S2O8 and 1 g P2O5 were added in turn and stirred continuously until dissolved completely. 2 g Graphite powder was added to the above mixed solution. Then the mixture was further reacted at 80°C for 8 h and then cooled to room temperature. After which the mixture was washed in deionized water and filtered to obtain pre-graphite oxide, which was left at 50°C for at least 12 h under ambient conditions. The as-obtained pre-graphite oxide and 6 g KMnO4 were added slowly to 46 mL H2SO4 (98%) in an ice bath, stirred continuously for 0.5 h to dissolve completely. The reaction temperature was controlled at about 4°C, and the system temperature was raised to 35°C for 3
After the reaction is completed, 380 mL deionized water was slowly added to the mixture, then 5 mL hydrogen peroxide (H₂O₂) was added while stirring until the solution turns golden yellow. Then the mixed solution was filtered and washed with HCl (10% v/v) and deionized water in sequence until the pH value is close to 7. The obtained GO was dispersed in water, ultrasonic for 30 min to obtain a homogeneous dispersion of 2 mg/mL.

**Preparation of hGO dispersion**

Here, we prepared the hGO sheets with abundant in-plane nanopores via a convenient mild defect-etching reaction. Briefly, 5 mL, 30% H₂O₂ was added to as-synthesized 50 mL, 2 mg/mL GO dispersion, then heated at 100°C for 3.5 h under stirring. The above mixture was purified by centrifuging and washing to remove residual H₂O₂, and then re-dispersed in water by vibration or ultrasonication for a few tens of seconds to produce a homogeneous hGO aqueous dispersion with a concentration of 2 mg/mL.

**Carboxyl functionalization of hGO (hGC)**

The hGC was prepared according to a reported method. Briefly, NaOH (95%, 12.8 g) and ClCH₂COOH (10 g) were added into the as-synthesized aqueous hGO suspension (~2 mg/mL, 50 mL), and stirred for 3 h under ice bath to assure the conversion of the -OH into -COOH moieties. 10% HCl was used to neutralize and remove the residual NaOH. The above mixture was purified by centrifuging and washing to remove residual reactant, and then re-dispersed in water by ultrasonication for 3 h to obtain a homogeneous hGC aqueous dispersion with a concentration of 2 mg/mL, which has more carboxylic acid groups available for subsequent conjugation.

**Preparation of hGC/PAMAM film**

Here, we developed a facile solution method for synthesizing the hGC/PAMAM film (Figure 1A). Firstly, 0.4 mg, 0.6 mg, 0.8 mg PAMAM were added into 25 mL, 2 mg/mL hGC solution, respectively, and then stirred for 1 h. The wet hGC/PAMAM films can be obtained by a filtering process, with using the PVDF membrane (pore size is ~0.22 μm). Subsequently, the as-received films were dried at room temperature for 48 h. For a comparison, the hGO films without PAMAM were also prepared using similar procedure.

**Instruments for characterization**

The morphologies of films were characterized by SEM (HELIOS Nano Lab 600i, America), AFM (Bruker, Dimension Fastscan, Germany) and TEM (Tecnai T20, America). Raman spectra was recorded on an RM 2000 Microscopic confocal Raman spectrometer (Renishaw, Britain) using a 514 nm laser beam. The d-spacing of the films were measured by XRD (D8 Advance, Bruker, Holland) with Cu Kα radiation (λ = 1.5418 Å). XPS for surface analysis was from Thermofisher ESCALAB 250Xi. FTIR (America) spectrum was from Bruker Tensor Germany spectrometer in the range from 400 cm⁻¹ to 4000 cm⁻¹. A quasi-static tensile testing for different types of film samples was carried out by a micromechanical tester equipped with a 2 kN load cell (Gatan Deben). The loading speed was set as 2 mm/min. The typical gauge length and width of samples were cut into 20 and 5 mm, respectively. The dynamic deformation of hGC/PAMAM film under humidity was measured using the VIC-3D system. Before test, the surface of hGC/PAMAM film was painted with white spray paint to obtain a randomly distributed, high contrast and fine white dot pattern.

**MD simulation**

The large-scale atomic/molecular massively parallel simulator (LAMMPS) was utilized to run all MD simulations. The ReaxFF potential was employed to describe the interactions among C, H, and O atoms, which has been successfully applied in various GO-based nanomaterials. The NVE (constant number of atoms N, constant volume V, and constant energy E) ensemble was used for the dynamics simulation with a time step of 0.1 fs. The non-periodic conditions were applied. To achieve stretching simulations, the length and width of hGC sheets were set to be 100 Å and 60 Å, respectively. The ratio of the elements in hGC/PAMAM was C:O:H:N = 4636:422:294:20. The initial distance between these bilayer sheets was set 6 Å with a 3 m/s stretching velocity. The configurations were fully sufficiently relaxed and optimized before tensile test.