

## ***Supporting Information***

### **Multifunctional textured graphene-based coatings on elastomeric gloves for chemical protection**

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#### **Supplemental Methods**

##### Graphene oxide synthesis procedure

Graphite oxide (GO) was synthesized using a modified Hummers' method with a pre-intercalation treatment. Concentrated  $\text{H}_2\text{SO}_4$  (100 mL) was heated to 80 °C in a 500 mL Erlenmeyer flask.  $\text{K}_2\text{S}_2\text{O}_8$  (10 g) and  $\text{P}_2\text{O}_5$  (10 g) were added to the acid and stirred until fully dissolved. Graphite powder (14 g, Bay Carbon Inc. SP-1 grade) was added to the solution and kept at 80 °C for 5 hrs. The mixture was then cooled and placed in an iced bath, followed with slow dilution by 200 mL deionized (DI) water. The solid sample was filtered using a vacuum filtration unit (47 mm diameter, 0.2  $\mu\text{m}$  pore size), further rinsed with 1 L DI water and then dried in air for overnight. Concentrated  $\text{H}_2\text{SO}_4$  (500 mL),  $\text{NaNO}_3$  (10 g) and the pre-oxidized graphite powder were transferred into a 2 L Erlenmeyer flask in an ice bath, then  $\text{KMnO}_4$  (70 g) was slowly added to the mixture while stirring (temperature was controlled within 10 °C during the complete process). The flask was moved to a 40 °C water bath and left for 3 hrs, and then transferred back into the ice bath. DI water (1 L) was slowly added to the flask while stirring, taking caution that the temperature did not rise above 55 °C. After dilution, 60 mL of a 30%  $\text{H}_2\text{O}_2$  solution was added to the mixture dropwise. The color of the solution turned from dark brown to bright yellow. This mixture was left under stirring overnight to consume the  $\text{H}_2\text{O}_2$ . The washing process included 5 rounds of acid washing using 1M HCl to remove residual salts (centrifugation at 4000 rpm for 30 min), and 4 rounds of acetone washing (centrifugation at 4000 for 30 min). After thorough washing, the resulting wet solid was collected and dried in air for 72 hrs. To harvest GO suspensions, approximately 4 g dried sample was fully dispersed in 1 L DI water and bath sonicated for 40 min. The suspension was centrifuged at slow speed (around 1000 rpm) for 5 min, then the supernatant was carefully collected by a pipette. After 3 rounds of centrifugation and supernatant collection, the final GO suspension was obtained for use.

Figures S1-4 and text below give additional information related to the fabrication of planar films, wrinkled films, and surface treatments, as well as the gravimetric permeation experiments.

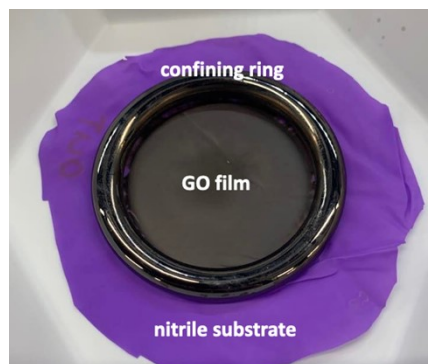


Figure S1. Ring method to create defined-area graphene-based films on elastomer (nitrile) substrates by solution casting.

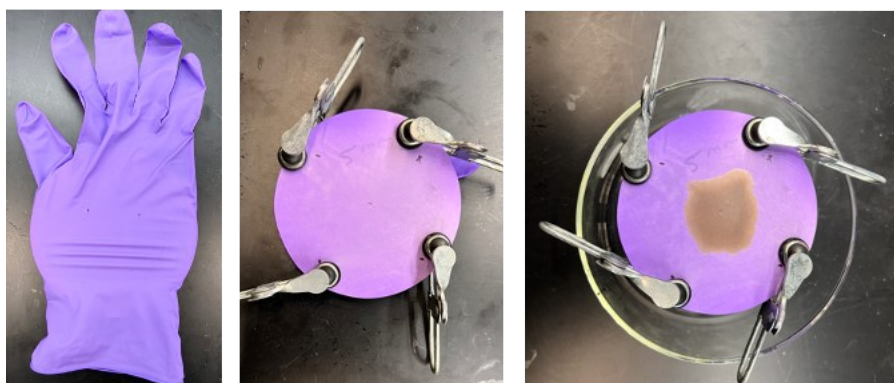


Figure S2. Mechanical frame method for creating well-defined stretched states of glove-derived nitrile films, which are key to creating wrinkled, stretchable graphene-based films. Left: whole gloves are stretched over an aluminum disk frame, then Center: clamped and trimmed. Four points in a rectangle are marked prior to stretching and measured after stretching to determine the strain percentage and strain uniformity in 2D. Right: a small graphene oxide test film after deposition on the stretched nitrile.

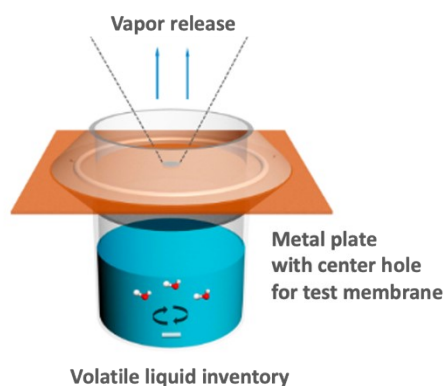


Figure S3. A schematic representation of the batch permeability test apparatus, adapted from Liu et al.[29]. Test films were supported on the metal plate and adhere over the 2-cm diameter using epoxy. A leak tight environment was created by clamping the metal plate in between the two-piece glass apparatus by O-rings. 150 ml water was added to 200 ml vessel for water permeation test, and 35 ml hexane was added to 45 ml vessel for the hexane permeation test.

### Protocol for applying PFAS-free antiwetting agents to film surfaces

Manufacturer's directions on the product containers were used to guide the delivery of the antiwetting coating to the graphene film and textured graphene film surfaces.

Product "*Nanoman*" was applied after shaking the bottle well, then using 2-3 pumps from its trigger spray valve at 20-30 cm from the surface. The films were left to dry in the laboratory room air for 24 hrs.

Product "*Protect Me*" was applied using 2-3 pumps from the trigger spray valve from 20 cm distance from the surface. The films were left to dry in the laboratory air for 24 hrs. (The manufacture recommends a minimum of 12 hrs and 24 hrs for temperatures below 64 F).

Product "*Detrapel*" was applied through approximately 5 seconds of continuous spraying from the aerosol delivery valve until a continuous film formed on the surface. The films were left to dry in room air for 24 hrs.

All antiwetting coatings were applied one time only, and excess liquid was not wiped or otherwise removed from the surface.

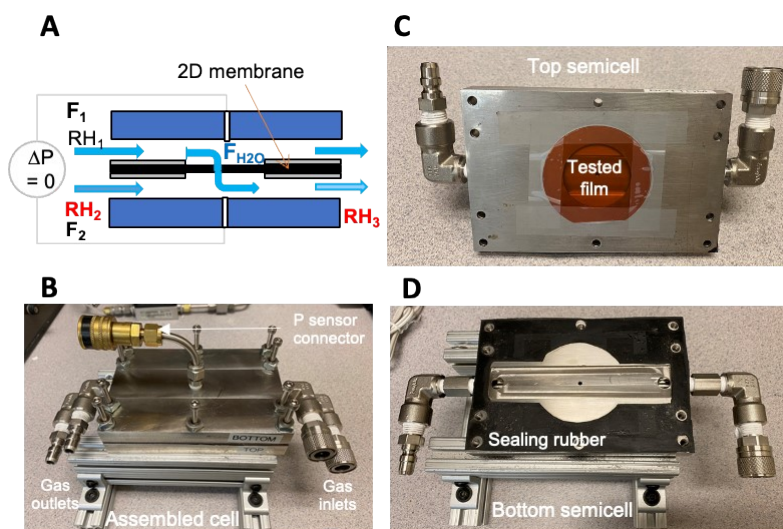


Figure S4: Dynamic water-vapor permeation cell. A: Schematic representation highlighting the wet and dry  $N_2$  streams that contact the top and bottom surface of the 2D membrane film, respectively. The flow rate of permeated water vapor,  $F_{H_2O}$ , is quantified from the difference in the relative humidity of the drier stream, as  $F_2 \times (RH_3 - RH_2)$ .  $F$  = flow rate,  $RH$  = and relative humidity. B: Full permeation cell consisting of the top and bottom semicells displayed in panels C and D, respectively, where the location of the test sample (here, a Kapton film as impermeable control) and sealing rubber are displayed.

### Supplemental Results

For the initial screening phase, the fabricated film formulations were subjected to a fold test and a tensile test. The fold test involved creasing dried films once in each direction and inspecting

for visible cracking or persistent creases. The tensile test consisted of attaching a 50-gram weight to a film ~4 cm in diameter suspended in air and recording the film's ability to support the weight (mass of the weight was chosen as a threshold weight, which unmodified GO cannot support). Note the tensile test was only performed on free standing films, not the films supported on elastomer substrates, where the substrate is expected to carry the mechanical load.

**Table S1. Promising formulations from the screening phase**

Polymer Additive	Cross-linking Agent	Material Architecture	Fabrication Method	Fold Test	Tensile Test	Wet Mechanical Stability Test
None	None	Unmodified GO	Vacuum Filtration	Crease	Failure	Degradation
			Drop cast on nitrile	Crease	N/A*	Degradation
Methylcellulose	Glutaraldehyde	Nacre	Vacuum Filtration	Pass	Pass	Stability
			Drop cast on nitrile	Pass	N/A	Stability
Polyallylamine	Glutaraldehyde	Nacre	Vacuum Filtration	Crease	Failure**	Stability
			Drop cast on nitrile	Crease	N/A	Stability
Polyurethane***	Carbodiimide	Sandwich (nitrile substrate)	GO drop cast; Top film drop cast or brushed	Pass	N/A	Stability
Styrene Butadiene Rubber A***	Carbodiimide	Sandwich (nitrile substrate)	GO drop cast; Top film drop cast	Pass	N/A	Stability
Styrene Butadiene Rubber B***	Carbodiimide	Sandwich (nitrile substrate)	GO drop cast; Top film drop cast	Pass	N/A	Stability
Ames Blue Max***	Proprietary	Sandwich (nitrile substrate)	GO drop cast; Top film brush coated	Pass	N/A	Stability
Plastidip*** (elastomer coating)	Proprietary	Sandwich (nitrile substrate)	GO drop cast; Top film sprayed	Pass	N/A	Stability
Flex Seal*** (elastomer coating)	Proprietary	Sandwich (nitrile substrate)	GO drop cast; Top film drop cast	Pass	N/A	Stability

**Table S2. Summary of unsuccessful nacre formulations. These formulations either degraded during wet mechanical stability tests or failed both the fold and tensile tests.**

Polymer Additive	Cross-linking Agent	Material Architecture	Fabrication Method	Fold Test	Tensile Test	Wet Mechanical Stability Test
Polyallylamine	None	Nacre	Vacuum Filtration	Crease	Failure	Degradation
Polyallylamine	EDAC	Nacre	Vacuum Filtration	Failure	Failure	Stability
Polyallylamine	Citric Acid	Nacre	Vacuum Filtration	Failure	Failure	Stability
Polyallylamine	Ascorbic Acid	Nacre	Vacuum Filtration	Failure	Failure	Degradation
Methylcellulose	None	Nacre	Vacuum Filtration	Pass	Pass	Degradation
Methylcellulose	Citric Acid	Nacre	Vacuum Filtration	Pass	Pass	Degradation
Polyethyleneimine	EDAC	Nacre	Vacuum Filtration	Failure	Failure	Stability
Carboxy methyl cellulose	None	Nacre	Vacuum Filtration	Pass	Pass	Degradation
Polyurethane*	Carbodiimide	Nacre	Vacuum Filtration	Pass	Pass	Degradation
Epoxy Ester*	Carbodiimide	Nacre	Vacuum Filtration	Pass	Pass	Degradation

\* Proprietary polymer-based dispersions

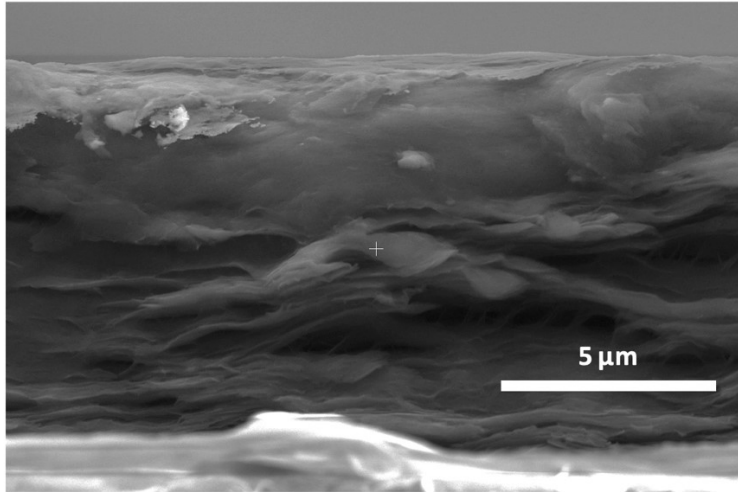


Figure S5. Cross-sectional SEM of GO-MC-GA film on PVDF substrate showing the layered microstructure.

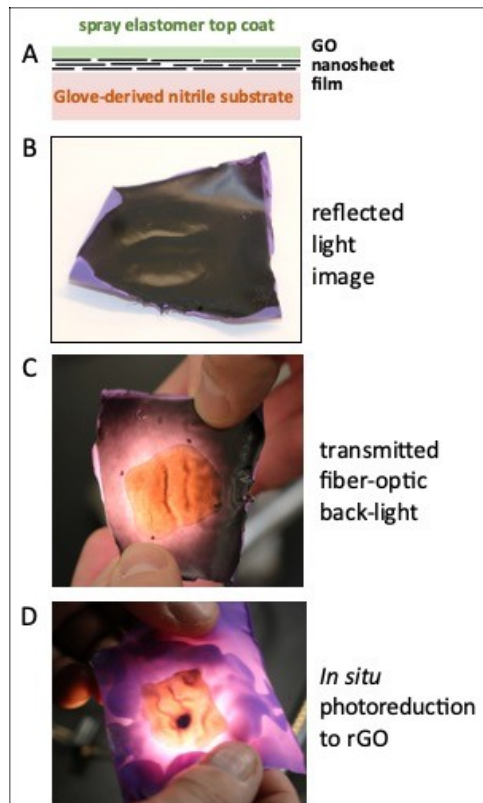


Figure S6. Structure of sandwich barrier films. A: Sketch of GO film on nitrile substrates with polymer top-coats for solvent stability. B: Optical image of the top surface of a sandwich barrier architecture based on *Plastidip* top coat. D: The structures of the imbedded GO films can be seen using fiber optical back lighting, D: focused fiber optic light at high intensity can locally reduce the GO to rGO photothermally.

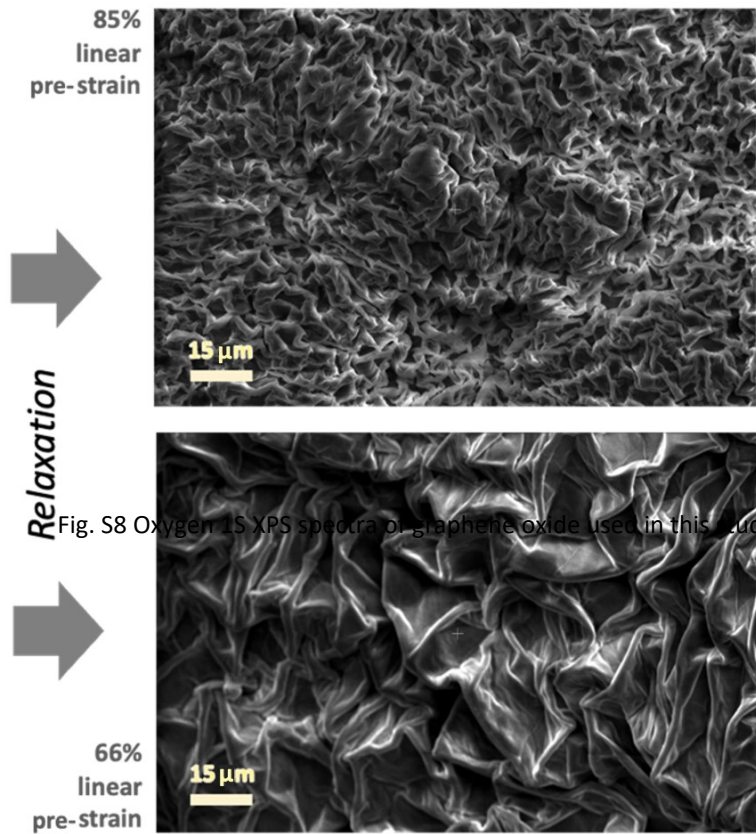


Fig. S8 Oxygen 1S XPS spectra of graphene oxide used in this study.

Figure S7. Morphologies and structural characterization of textured graphene oxide films on glove-derived nitrile. A. Film fabricated by the glove inflation method; B: film fabricated by the mechanical stretch method.

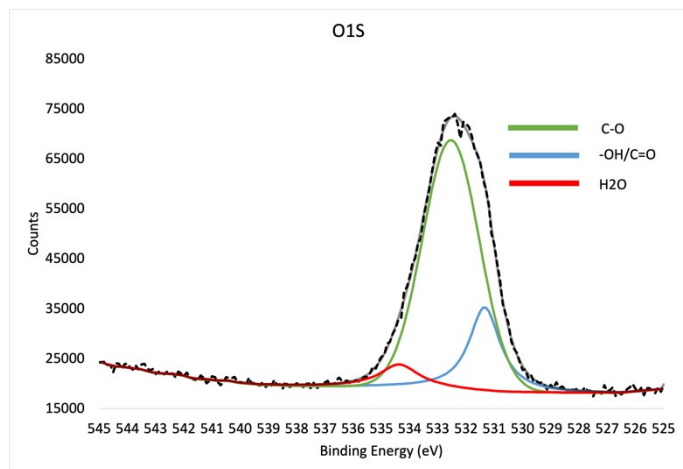


Fig. S8 Oxygen 1S XPS spectra of graphene oxide used in this study.



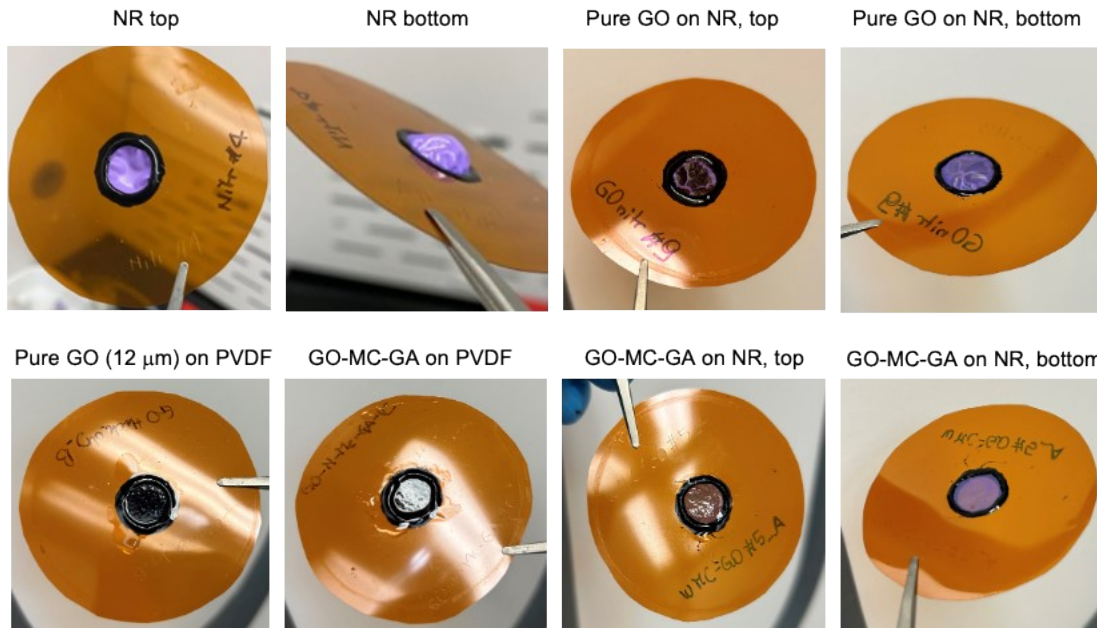


Figure S9: Photographs of top and/or bottom surfaces of GO-based films after liquid DCP permeation testing. Bare nitrile (NR) films, which are poor barriers to liquid DCP, swell and deform dramatically in contact with DCP liquid (top left). Pure GO coatings do not suppress the nitrile swelling and this leads to cracking of the GO top film (top right). Thick GO and all GO-MC-GA composite films suppress nitrile swelling and deformation (bottom row). Note also that these images collected after overnight contact show that the top surfaces of each of the effective-barrier films (GO-MC-GA and thick pure GO) are still fully wetted by a liquid pool of DCP. This confirms that the test films were in continuous contact with liquid DCP throughout the experiment, and the presence of bulk residual liquid is an independent confirmation of the effective barrier performance.

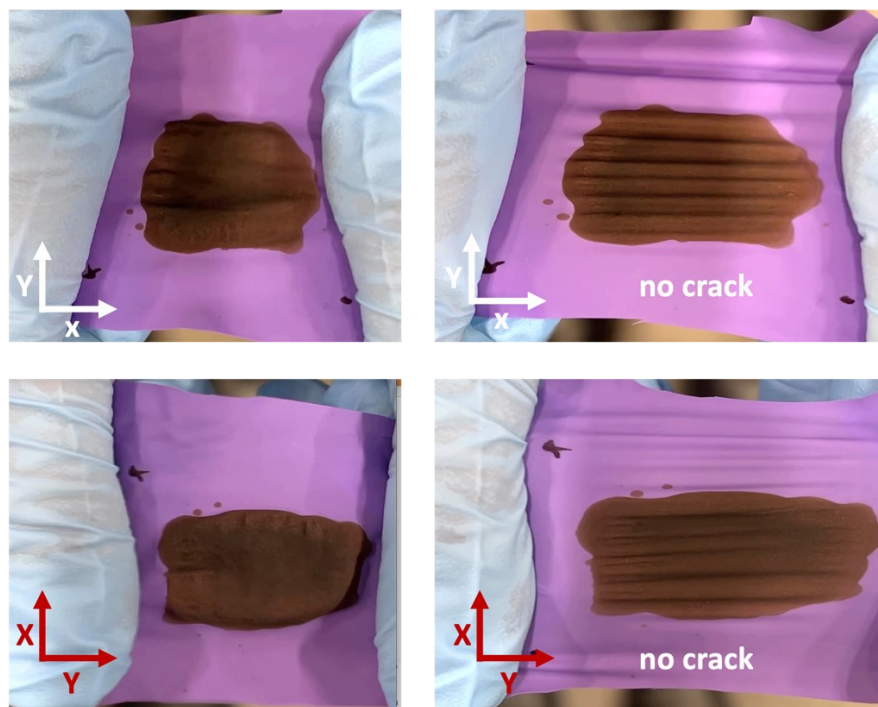


Figure S10. Evidence that the stable stretchability of crumpled graphene is isotropic: Top: reversible, crack-free X-directional stretching. Bottom: reversible crack-free Y-directional stretching of the same sample. All images are from the same sample and experiment as shown in Fig. 6 in the main text and the associated video.

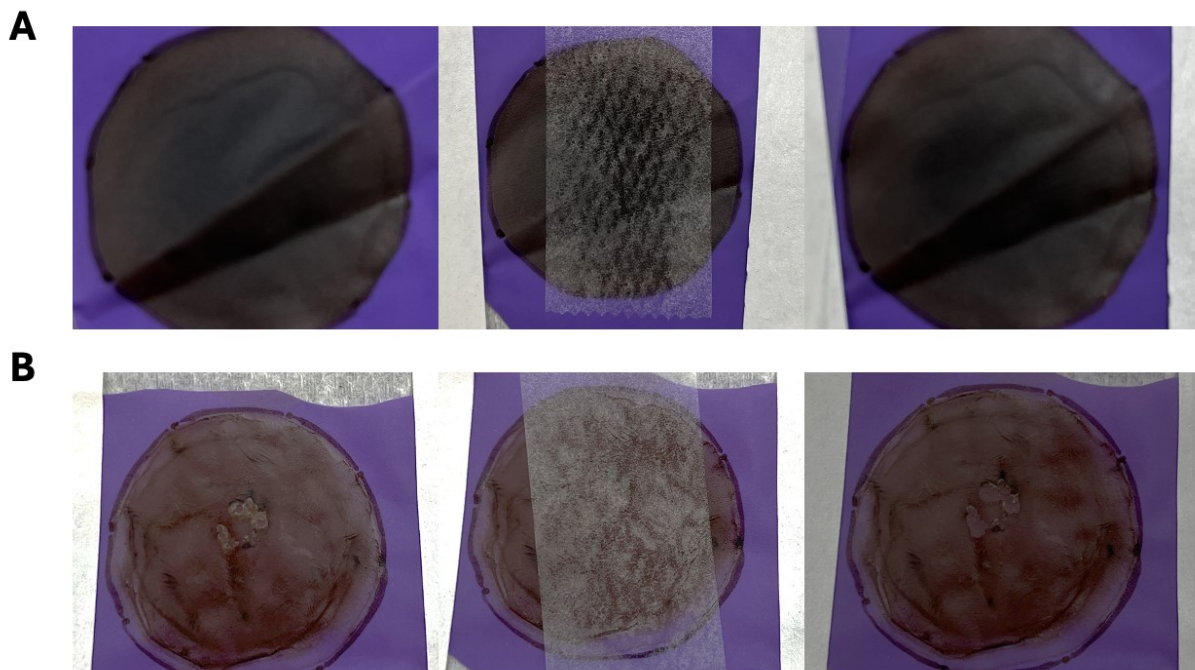
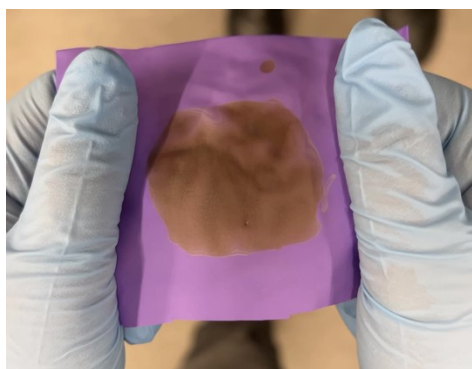


Figure S11. Scotch tape test of GO film and GO-MC film on nitrile. A) Planar GO film before and after scotch tape test showing no observable changes after tape removal and no residual graphene material on the tape (not shown). B) Scotch tape test of GO-MC film as above. Only superficial surface textures associated with bubbles were removed by the tape, and the base film itself is intact after the test.



Supplementary videos. Left: Video S1 shows the re-stretching processes for the planar film with crack formation. Right: Video S2 shows the re-stretching process for a textured film made with 66% biaxial pre-strain. Stretching shown in both X and Y directions.