ABSTRACT: Graphene is the strongest known material. However, the challenge of translating that strength from the microscale to the more useful macroscale remains unmet. Preparing solid structures from self-assembled graphene oxide liquid crystals has allowed the creation of paper and fibers with excellent mechanical properties. Conventionally, vacuum filtration, wet spinning, and freeze-drying are used to prepare such structures from graphene oxide liquid crystals. Here, we introduce photocuring as an additional option to create solid structures of self-assembled graphene oxide liquid crystals that allows for thicker samples and other shapes to be realized. The photocured graphene oxide paper prepared here exhibited mechanical properties comparable to those of benchmark samples prepared by vacuum filtration.

1. INTRODUCTION

The discovery of graphene by Nobel laureate Novoselov et al. triggered a frenzy of research and excitement due to its extraordinary properties: physical, mechanical, and electrical. This two-dimensional, one-atom-thin material exhibits a Young’s modulus of 1 TPa and a tensile strength of 130 GPa. Such properties make it the strongest material known, but translating them to a macroscopic scale remains a challenge. The strength of a material fundamentally depends on its structure, not merely on the intrinsic strength of chemical bonds. Thus, the self-assembly of graphene oxide sheets into liquid crystals that can be transformed into solid macroscopic structures is a promising approach to addressing that challenge.

This self-assembly process leads to various kinds of macroscopic structures such as paper and fibers. These solid structures are prepared using various methods, including wet-spinning, freeze-drying, and filtration, which preserve the ordered structure in the liquid crystal phase. Xu et al. used wet spinning to prepare graphene fibers with a 1450 MPa tensile strength following annealing at 3000 °C. Wan et al. used sequential bridging during a stretch-induced biaxial orientation of reduced graphene oxide to produce sheets with an in-plane tensile strength of 1547 MPa at room temperature. In the same study, it was demonstrated that the increasing the alignment between the reduced graphene oxide sheets improves the mechanical and electrical properties. Even defects that may appear as minor wrinkles in the graphene oxide that are commonly formed during the evaporation of dispersants have a major detrimental effect on the final properties. Li et al. demonstrated that plasticizing graphene oxide paper to facilitate the flattening of these wrinkles significantly improves the mechanical and electrical properties.

Dikin et al. prepared graphene oxide paper with a 120 MPa tensile strength and a 32 GPa Young’s modulus using vacuum filtration of aqueous dispersions. It is also possible for graphene oxide to form liquid crystals in multiple organic solvents. Amphiphilic self-assembly, observed in many systems before graphene oxide, is predominantly driven by solvophobic forces in nonaqueous solvents (analogous to hydrophobic effects in water). Here, we introduce photocuring as a technique to prepare solid structures from graphene oxide dispersions. Since water prevents the cationic photocuring reaction of epoxy, we follow Jalili et al. and prepare photocured graphene oxide liquid crystals from dispersions in an alcohol: ethylene glycol and 1-phenylethanol (1-PtOH). While we have previously shown semiconducting nanoparticles to be able to photocure epoxy, we decided to use the commercially available initiator bis(4-methylphenyl) iodonium hexafluorophosphate, because it is commonly used in stereolithography 3D printing resins and in the photocuring literature, as a starting point. Equations 1 and 2, and Figure 1 show an example of a cationic photopolymerization mechanism, described by Yagci et al., where protons open up the epoxide rings and initiate polymerization.
Equations 1 and 2 are reproduced from ref 15.

We demonstrate that the epoxide groups on the basal planes of neighboring graphene oxide sheets form ordered liquid crystals and can “cross-link” into a solid structure with substantial mechanical properties. This introduction of photocuring as a process to transform graphene oxide crystals from a liquid state to a solid state can be exploited by various manufacturing processes using UV light (e.g., stereolithography 3D printing) to make structures of self-assembled graphene oxide that are thicker and more complex than the paper, fibers, and aerogels currently possible.

2. RESULTS AND DISCUSSION

First, we use polarized light microscopy to determine if graphene oxide liquid crystals are formed in the dispersions used in this study (Figure 2). We observe clear birefringence in our benchmark aqueous graphene oxide dispersions (Figure 2a), which indicates the presence of anisotropic ordering of the graphene oxide sheets. This anisotropic ordering is consistent with that of liquid crystals reported in the literature. We observe similar birefringence in the alcohol dispersions: 1-PtOH (Figure 2b) and ethylene glycol (Figure 2c). These polarized light microscope images indicate that graphene oxide liquid crystals are well-dispersed in all cases.

Next, we conduct NMR experiments to determine whether the epoxide groups on the basal plane of graphene oxide undergo a photocuring reaction upon exposure to UV light (Figure 3). In the NMR spectra of raw graphene oxide, we observe shifts at 60, 70, and 130 ppm. We assign those shifts to the carbons on the epoxide group, alcohol, and conjugated double bonds on the graphene oxide’s basal plane, respectively. In the NMR spectra of the photocured graphene oxide in 1-PtOH, we observe an additional shift at 20 ppm, which comes from the photoinitiator. The intensities of shifts corresponding to the carbons on the epoxide and alcohol groups are much weaker in the spectra of the photocured sample in comparison to those in the raw graphene oxide, indicating that the epoxide groups are indeed being consumed in a chemical reaction.

Next, we conduct swell experiments on films of graphene oxide dispersions on glass slides to verify the physical changes expected from a photocuring reaction. We assess that a film is...
“solid” if it does not disperse in either water or alcohol. When photoinitiators are incorporated, films of graphene oxide dispersions in either ethylene glycol or 1-PtOH solidified when they were UV-irradiated for 24 h. On the other hand, the films made from dispersions without photoinitiators did not solidify under any conditions, including when the samples were UV-irradiated for 24 h. Additionally, dispersions did not solidify when they were kept in the dark for 1 month even when they contained photoinitiators. Finally, covering the films prevented solidification under UV radiation for 24 h even when they contained photoinitiators; under these conditions they are exposed to the heat of the photocuring chamber but not the light. These observations indicate that the system undergoes the physical changes expected in a photocuring reaction.

Next, we prepared large samples under various conditions to assess the ordering and mechanical properties. Figure 4 shows a photograph of an example of such a sample where we annealed the graphene oxide paper prepared by photocuring a dispersion in 1-PtOH.

![Photograph of graphene oxide paper, prepared by photocuring a dispersion in 1-PtOH followed by annealing, demonstrating its substantial size and uniformity.](image)

**Figure 4.** Photograph of graphene oxide paper, prepared by photocuring a dispersion in 1-PtOH followed by annealing, demonstrating its substantial size and uniformity. Photograph courtesy of the coauthor Kereles B. Riad. Copyright 2022.

Figure 5 shows SEM images of the fracture surfaces of the graphene oxide papers to examine if the anisotropic ordering of the graphene sheets observed in dispersions (Figure 2) remains after vacuum filtration, photocuring, and annealing. Figure S5f,g shows the fracture surfaces of the literature benchmark graphene oxide paper prepared via vacuum filtration of the aqueous dispersions with and without annealing. In both cases, we clearly observe ordered layers where the graphene oxide sheets are parallel to one another. Figure S5a,d shows the fracture surfaces of graphene oxide paper prepared via vacuum filtration of dispersions in alcohol: 1-PtOH and ethylene glycol, respectively. We observe clear ordered layers in the case of 1-PtOH. Subjectively, there is some ordering when ethylene glycol is used. Similarly to the fracture surfaces of graphene oxide prepared by photocuring, we observe clear ordering when 1-PtOH is used (Figure S5b), while our subjective assessment is that there is some ordering when ethylene glycol is used (Figure S5e). Finally, we observe that the anisotropic state remains after annealing the photocured graphene oxide paper of 1-PtOH dispersions (Figure S5c) and that the relatively large spacing between the graphene oxide sheets decreases dramatically. We analyze XRD and XPS data to discuss the spacing and size of the graphene oxide liquid crystals in the Supporting Information.

The anisotropic nature of the graphene oxide paper studied here makes the mechanical properties directional. Therefore, we use nanoindentation to measure the mechanical properties in the direction normal to the graphene oxide sheets and we use tensile testing to measure the mechanical properties in the direction parallel to the graphene oxide sheets (Table 1). Table S1 presents the values of two-tailed t tests to assess the confidence level in the comparisons. In all cases, we observe substantial stiffness and strength, indicating solid samples.

Consider first the reduced moduli measured by nanoindentation (normal to graphene oxide sheets). We observe an increase after annealing in vacuum-filtered graphene oxide paper prepared using water, from 0.46 to 3.2 GPa. This increase can be explained by the reduction of oxygen-containing groups by annealing, which restores the structural integrity of the sheets more closely to that of the stronger graphene.

Further, we observe a reduced modulus in vacuum-filtered graphene oxide paper prepared from 1-PtOH dispersions (2.3 GPa) that is almost 1 order of magnitude higher than that of graphene oxide paper prepared from ethylene glycol dispersions (2.8 GPa). This can be explained by the fact that ethylene glycol reduces the functional groups on the graphene oxide sheets so significantly that the ordering is reduced (visible in Figure S5c,d) and the mechanical properties are compromised. Similarly, we observe a higher reduced modulus in photocured graphene oxide paper prepared from 1-PtOH dispersions (1.9 GPa) in comparison to that of photocured graphene oxide paper prepared using ethylene glycol dispersions (1.2 GPa). We have been unable to observe any statistically significant difference in the reduced modulus due to annealing the photocured graphene oxide paper prepared from 1-PtOH dispersions. Unlike the case for vacuum-filtered graphene oxide paper, the functional groups in photocured graphene oxide paper are already utilized in the photocured samples in the forms of cross-links and are unaffected by annealing. Notably, all of the photocured samples are weaker than those prepared via vacuum filtration from the dispersions using the same alcohol. This is likely because the vacuum forces lead to better packing in comparison to our photocuring procedure. Finally, we note that the reduced moduli of photocured graphene oxide paper prepared from 1-PtOH dispersions (1.9 GPa unannealed and 2 GPa annealed) are comparable to those of our benchmark samples prepared using vacuum filtration of aqueous dispersions common in the literature (0.46 GPa unannealed and 3.2 GPa annealed).

Next, we consider the tensile strength and Young’s modulus measured by tensile testing (parallel to the graphene oxide sheets). First, we note that the benchmark graphene oxide paper we prepared by vacuum filtering aqueous dispersions has lower tensile strength and Young’s modulus (4 MPa and 1.1 GPa respectively) in comparison to those prepared by Dikin et al. (120 MPa strength and 32 GPa Young’s modulus). This is likely because of the difference in the properties of the starting graphene oxide such as the lateral size and degree of oxidation; both are known factors directly affecting the formation of liquid crystals and the resulting mechanical properties. Figure S1 shows that the lateral size of our starting graphene oxide is 4.11 μm, which is much smaller than the ~30 μm
commonly found in the graphene oxide liquid crystal literature.\textsuperscript{23}

Annealing the graphene oxide paper prepared by vacuum filtering aqueous dispersions increases both the tensile strength (from 4 to 6 MPa) and Young’s modulus (from 0.8 to 1.1 GPa). Additionally, graphene oxide paper prepared by vacuum filtering 1-PtOH dispersions has a higher tensile strength (5 MPa) and Young’s modulus (2 GPa) in comparison to those prepared by vacuum filtering ethylene glycol dispersions (1.3 MPa strength and 0.5 GPa modulus). This increase is likely due to the reduction of the oxygen-containing groups by ethylene glycol compromising both the ordering of graphene oxide sheets and bonding as discussed earlier. Similarly, graphene oxide paper prepared by photocuring 1-PtOH dispersions has a higher tensile strength (1.7 MPa) and Young’s modulus (0.5 GPa) in comparison to those prepared by photocuring ethylene glycol dispersions (1 MPa strength and 0.3 GPa modulus). Finally, unlike the case with the nanoindentation observations, annealing of photocured graphene oxide paper prepared from 1-PtOH dispersions significantly improves the mechanical properties: tensile strength (from 1.7 to 4 MPa) and Young’s modulus (from 0.5 to 1.5 GPa). Annealing removes a significant amount of the remaining dispersant, bringing the graphene oxide sheets closer together, as observed in SEM (Figure 5c,d). This closer packing leads to stronger bonds between the graphene oxide sheets that improves the mechanical properties in the direction parallel to the graphene sheets but does not affect those normal to the graphene sheets. Nonetheless, the tensile strengths and Young’s moduli of all photocured samples are smaller than those of the papers prepared using vacuum filtration of the same dispersant, indicating that there remains room for improvement in the photocured sample preparation procedure.

We also note that the annealed photocured graphene oxide paper prepared using 1-PtOH has a tensile strength and Young’s modulus (4 MPa and 1.5 GPa respectively) comparable to those of our benchmark samples prepared using vacuum filtration of aqueous dispersions common in the literature (unannealed, 4 MPa and 0.8 GPa, respectively; annealed, 6 MPa and 1.1 GPa, respectively). Finally, we prepared a 0.632 mm thick sample by photocuring additional layers of the 1-PtOH dispersions, which is about 3 times thicker than the sample we obtained by vacuum filtering aqueous dispersions as is common in the literature.

Table 1. Mechanical Properties of Graphene Oxide Papers

| graphene oxide paper | nanoindentation ($n = 25$) Er (GPa) | tensile testing ($n \geq 5$) |
|----------------------|-----------------------------------|--------------------------|
|                      | average 90% confidence interval*  | average 90% confidence interval* |
| vacuum-filtered water| 0.46 0.02                          | 4 2                                    | 0.8 0.2                  |
| vacuum-filtered water + annealing| 3.2 0.4                        | 6 3                                    | 1.1 0.5                  |
| vacuum-filtered ethylene glycol| 2.8 0.5                          | 1.3 0.5                                | 0.5 0.1                  |
| vacuum-filtered 1-PtOH| 23 4                             | 5 4                                    | 2 1                      |
| photocured ethylene glycol| 1.2 0.2                          | 1.0 0.8                                | 0.3 0.2                  |
| photocured 1-PtOH| 1.9 0.6                          | 1.7 0.6                                | 0.5 0.3                  |
| photocured 1-PtOH + annealing| 2.0 0.4                        | 4 1                                    | 1.5 0.7                  |

Figure 5. SEM images of fracture surfaces of various graphene oxide papers showing the degree of anisotropic ordering between graphene oxide sheets in samples prepared with different conditions. Scale bars are 50 μm.
3. CONCLUSIONS

We demonstrate that it is possible to photocure graphene oxide liquid crystals. The photocured graphene oxide paper we prepared has mechanical properties comparable to those of benchmark graphene oxide paper prepared by vacuum filtering aqueous dispersions in both directions relative to the graphene oxide sheets: normal (reduced modulus measured by nanoindentation) and parallel (Young’s modulus and tensile strength measured by tensile tests). Photocuring graphene oxide liquid crystals allows for thicker and perhaps more complicated structures than what is possible with current methods such as vacuum filtering or wet spinning.

4. EXPERIMENTAL SECTION

Graphene oxide (S Method, product no. GNOS0010) powder was purchased from ACS materials and used as is. Ethylene glycol (99.5%), 1-phenylethanol (98%), and bis(4-methylphenyl)iodonium hexafluorophosphate (photoinitiator, 98%) were purchased from Sigma-Aldrich and used as is.

4.1. Sample Preparation for SEM and Mechanical Testing. Benchmark samples of graphene paper from aqueous dispersions were prepared following a procedure adapted from that of Dikin et al.10 Graphene oxide aqueous dispersions at a concentration of 3 mg/mL were prepared using deionized water. Batches of 40 mL were sonicated and then vacuum-filtered for 3 h. This process was repeated to make two layers. The sample was then peeled from the filter paper. Some samples were then annealed at 120 °C for 2 h.

Graphene oxide paper prepared using alcohol dispersions follow a similar procedure but with a concentration of 12 mg/mL and a batch volume of 25 mL, and the samples were dried under room temperature and pressure.

As shown in Scheme 1, photocured samples were prepared by first preparing a 2 wt% solution of photocuring initiator in an alcohol. Batches consisting of 9 g of those solutions and 0.12 g of graphene oxide were sonicated. Those dispersions were poured onto a filter paper and left to dry for 4 h followed by photocuring under a benchtop UVA lamp (Model UVP XX-15 L, peak emission 365 nm, light intensity at sample surface 2 mW/cm²). Samples prepared from ethylene glycol dispersions were photocured until solid (72 h per layer) and consisted of four layers. Samples prepared from 1-PtOH dispersions were photocured until solid (24 h per layer) and consisted of two layers. Samples were then peeled from the filter paper. Some of the samples prepared from 1-PtOH dispersions were annealed at 190 °C for 2 h. Note that the number of layers is different for the two systems because the samples prepared with ethylene glycol were too fragile to remove from the filter paper with fewer than four layers. This is consistent with the differences in mechanical properties observed (Table 1), which would have been amplified had they had the same number of layers.

4.2. Characterization. POM images of crystals suspended in water were captured on a Nikon Ti microscope equipped with a 10x Plan Apo objective lens (NA 0.45), crossed linear polarizers, and a Nikon DSRi2 color camera.

All NMR spectra were recorded on a Bruker Avance III HD spectrometer operating at a field of 9.4 T with corresponding 13C and 1H Larmor frequencies of 100.60 and 400.07 MHz, respectively, using a triple-resonance 1.9 mm MAS probe in double-resonance mode. Spectra were recorded under magic-angle spinning conditions at a frequency of 35 kHz using a 1.5 ms long ramped 1H to 13C cross-polarization. A 50 kHz spectral width was used, and 8192 transients were added with a 15 ms acquisition time and a recycle delay of 5 s. High-power 1H decoupling was applied during the acquisition using spin-alignment. The applied radio frequency fields were 65 and 100 kHz for 13C (cross-polarization) and 1H (cross-polarization and decoupling), respectively. All spectra were externally referenced to TMS (0 ppm) by setting the unshielded CH2 resonance of adamantane to 38.48 ppm.

SEM was conducted with a Hitachi S-3400N scanning electron microscope using a secondary electron detector under high vacuum. The sample preparation procedure was described above. In the case of the image shown in Figure S1, raw graphene oxide was dispersed in ethanol and was drop-casted on the SEM stage.

Nanoindentation was used to provide the thin-film mechanical properties24 and was conducted using an STM microscope (Multimode 8 AFM) for imaging and a Hysitron Triboscope equipped with a Berkovich tip for the indentation. The maximum indentation force was 25 μN with a 5 s hold period. We calculated the reduced modulus following the method of Cheng and Cheng25 and conducted 25 repeats at different locations on the specimen. The largest indentation depth observed was ~100 nm, which is much smaller than 10% of the thickness of the thinnest sample (0.07 mm), indicating that we could ignore the influence of the substrate.26 We note that the modulus calculations used in nanoindentation apply to isotropic materials, while our graphene oxide paper is anisotropic. However, Hay et al.27 demonstrated that, for the Berkovich pyramid indenters used in this work, the indentation modulus is usually strongly biased toward the Young’s modulus and provides a useful first-order approximation of it.

Tensile testing was conducted on razor-cut ~40 × 12 mm rectangular samples using a Z5 Tensile machine from Hoskin Scientific with a preload of 0.2 N and a strain rate of 1 mm/min. The length and width of the sample were measured using a ruler with a 1 mm resolution. The sample thickness, measured by a micrometer, varied from 0.07 to 0.68 mm depending on the preparation procedure used. The graphene oxide paper samples were glued on Garolite bars that were clamped on during the test, as shown in Figure 6b. The gage length (between the two Garolite sticks) was 20 mm, with the rest of the sample being glued to the Garolite sticks (~10 mm for each side) to allow for gripping. The machine controlled the applied force and measured the change in length. The strain was then calculated by dividing the change in length, as measured by the cross-head movement of the machine, by the initial sample length (~20 mm). The tensile strength corresponded to the maximum stress obtained, and the
Young’s modulus corresponded to the slope of the linear region in the stress–strain curve (an example is shown in Figure 6a). At least five repeats were conducted. We also note that the small thickness of the graphene oxide paper involved in this study leads to many challenges in the sample preparation for tensile testing, which led to large error bars relative to those in nanoindentation. This source of error makes it more difficult to determine statistically significant differences in key comparisons with a confidence level similar to what we can achieve in comparing nanoindentation data.

XRD was conducted using a D8 Advance instrument from Bruker AXS Inc. with a Cu (1.5418 Å) source using a voltage of 40 kV and a current of 40 mA. Measurements were performed with the Bragg–Brentano geometry mode, in 0.02° increments and with 1 s integration time.

X-ray photoelectron spectroscopy (XPS) spectra were collected using a ThermoScientific K-Alpha spectrometer with an aluminum Kα, 1486.6 eV, source. An X-ray beam size of Φ400 μm wasis used. To minimize the effect of possible charge on the sample surface, the flood-gun-generated, low-energy electrons (plus Ar+ ions) were utilized to compensate for charging. Survey scanning, to provide the information on element percentage (atom %) for all possible atoms on the sample surface, was set up at a full energy scale, with a pass energy of 200 eV, a scanning step size of 1 eV, and a dwell time of 50 μs, for an average of five scans. The high-resolution scanning to provide the chemical state (bond) information for individual elements C and O was set up at a specific energy scale (C 1s, 274.5–298.5 eV; O 1s, 524.8–544.8 eV), with a pass energy of 50 eV, a scanning step size of 0.1 eV, and a dwell time of 50 μs, and was an average of 10 scans.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02084.

SEM of a graphene oxide sheet showing a lateral size of 4.11 μm, XRD patterns of graphene oxide papers of various controls, XPS spectra of raw graphene oxide, annealed graphene oxide paper vacuum filtered from aqueous dispersion, and graphene oxide paper vacuum filtered from ethylene glycol dispersions, P-values* for mechanical properties (two-tailed t test), and XRD data (PDF).

### AUTHOR INFORMATION

#### Corresponding Author

Paula M. Wood-Adams — Laboratory for the Physics of Advanced Materials, Department of Chemical and Material Engineering, Concordia University, Montreal, Quebec, Canada H3G 2J2; orcid.org/0000-0003-1562-3924; Email: Paula.Wood-Adams@concordia.ca

#### Authors

Keroles B. Riad — Laboratory for the Physics of Advanced Materials, Department of Chemical and Material Engineering, Concordia University, Montreal, Quebec, Canada H3G 2J2; orcid.org/0000-0002-2739-1000

Suong V. Hoa — Concordia Center for Composites, Department of Mechanical, Industrial and Aerospace Engineering, Concordia University, Montreal, Quebec, Canada H3G 2J2

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c02084

#### Author Contributions

All authors contributed to the research and manuscript preparation. All authors have given approval to the final version of the manuscript.

#### Funding

We gratefully acknowledge the NSERC and Concordia University for funding.

#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

From Concordia University, we thank Dr. Daniel Rosca for his help with tensile testing, Mr. Mazen Samara and Dr. Dmytro Kevorkov for their help with the SEM images, and Mr. Heng Wang and Mr. Rémi Ehounou for their help with nanoindentation. From Université du Québec à Montréal, we thank Dr. Alexandre Arnold for his help with NMR and Dr. Gwénaël...
Chamoulaud for his help with XRD. From McGill University, we thank Dr. Lihong Shang for her help with XPS.

REFERENCES
(1) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric field effect in atomically thin carbon films. Science 2004, 306, 666.
(2) Lee, C.; Wei, X.; Kyser, J. W.; Hone, J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. Science 2008, 321, 385.
(3) Griffith, A. A. The phenomena of rupture and flow in solids. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 1920, 221, 163.
(4) Riad, K. B.; Schmidt, R.; Arnold, A. A.; Wuthrich, R.; Wood-Adams, P. M. Characterizing the structural formation of epoxy-amine networks: The effect of monomer geometry. Polymer 2016, 104, 83.
(5) Wu, D.; Zhang, F.; Liang, H.; Feng, X. Nanocomposites and macroscopic materials: assembly of chemically modified graphene sheets. Chem. Soc. Rev. 2012, 41, 6160.
(6) Xu, Z.; Liu, Y.; Zhao, X.; Peng, L.; Sun, H.; Xu, Y.; Ren, X.; Jin, C.; Xu, P.; Wang, M.; Gao, C. Ultrastiff and strong graphene fibers via full-scale synergetic defect engineering. Adv. Mater. 2016, 28, 6449.
(7) Wan, S.; Chen, Y.; Fang, S.; Wang, S.; Xu, Z.; Jiang, L.; Baughman, R. H.; Cheng, Q. High-strength scalable graphene sheets by freezing stretch-induced alignment. Nat. Mater. 2021, 20, 624.
(8) Li, P.; Yang, M.; Liu, Y.; Qin, H.; Liu, J.; Xu, Z.; Liu, Y.; Meng, F.; Lin, J.; Want, F.; Gao, C. Continuous crystalline graphene papers with gigapascal strength by intercalation modulated plasticization. Nat. Commun. 2020, 11, 2645.
(9) Li, P.; Liu, Y.; Shi, S.; Xu, Z.; Ma, W.; Wang, Z.; Liu, S.; Gao, C. Highly crystalline graphene fibers with superior strength and conductivity by plasticization spinning. Adv. Funct. Mater. 2020, 30, 2006584.
(10) Dikin, D. A.; Stankovich, S.; Zimney, E. J.; Piner, R. D.; Dommett, G. H.; Evmenenko, G.; Nguyen, S. T.; Ruoff, R. S. Preparation and Characterization of graphene oxide paper. Nature 2007, 448, 457.
(11) Jalili, R.; Aboutaleibi, S. H.; Esrafilzadeh, D.; Konstantinov, K.; Moulton, S. E.; Razal, J. M.; Wallace, G. G. Organic solvent-based graphene oxide liquid crystals: A facile route toward the next generation of self-assembled layer-by-layer multifunctional 3D architectures. ACS Nano 2013, 7, 3981.
(12) Du, W.; Wu, H.; Chen, H.; Xu, G.; Li, C. Graphene oxide in aqueous and nonaqueous media: dispersion behaviour and solution chemistry. Carbon 2020, 158, 568.
(13) Greaves, T. L.; Weerawardena, A.; Fong, C.; Drummond, C. J. Many protic ionic liquid mediator hydrocarbon-solvent interactions and promote amphiphile self-assembly. Langmuir 2007, 23, 402.
(14) Riad, K. B.; Arnold, A. A.; Claverie, J. P.; Hoa, S. V.; Wood-Adams, P. M. Photopolymerization using metal oxide semiconducting nanoparticles for epoxy-based coatings and patterned films. ACS Applied Nano Materials 2020, 3, 2875.
(15) Yagci, Y.; Jockusch, S.; Turro, N. Photosensitive polymerization: advances, challenges, and opportunities. Macromolecules. 2010, 43, 6245.
(16) Crivello, J.; Liu, S. Photoinitiated cationic polymerization of epoxy alcohol monomers. J. Polym. Sci., Part A: Polym. Chem. 2000, 38, 389.
(17) Morelli, D.; Bondioli, F.; Sangermano, M.; Messori, M. Photo-cured epoxy networks reinforced with TiO2 in-situ generated by means of non-hydrolytic sol-gel process. Polymer 2012, 53, 283.
(18) Lerf, A.; He, H.; Forster, M.; Kılıçowski, J. Structure of graphene oxide revisited. J. Phys. Chem. B 1998, 102, 4477.
(19) Vacchi, I. A.; Spinato, C.; Raja, J.; Bianco, A.; Menard-Moyon, C. Chemical reactivity of graphene oxide towards amines elucidated by solid-state NMR. Nanoscale 2016, 8, 13714.
(20) Jeong, H.; Lee, Y. P.; Jin, M. H.; Kim, E. S.; Bae, J. J.; Lee, Y. H. Thermal stability of graphite oxide. Chem. Phys. Lett. 2009, 470, 255.
(21) Aboutaleibi, S. H.; Gudarzi, M. M.; Zheng, Q. B.; Kim, J. K. Spontaneous formation of liquid crystals in ultralarge graphene oxide dispersions. Adv. Funct. Mater. 2011, 21, 2978.
(22) Oh, J. Y.; Park, J.; Jeong, Y. C.; Kim, J. H.; Seung, J. Y.; Park, C. R. Secondary interactions of graphene oxide on liquid crystal formation and stability. Part. Part. Sys. Charact. 2017, 34, 1600383.
(23) Zhang, Y.; Li, Y.; Ming, P.; Zhang, Q.; Liu, T.; Jiang, L.; Cheng, Q. Ultrastrong bioinspired graphene-based fibers via synergistic toughening. Adv. Mater. 2016, 28, 2834.
(24) Saha, R.; Nix, W. D. Effects of the Substrate on the Determination of Thin Film Mechanical Properties by Nanoindentation. Acta Mater. 2002, 50, 23.
(25) Cheng, Y. T.; Cheng, C. M. General relationship between contact stiffness, contact depth and mechanical properties for indentation in linear viscoelastic solids using axisymmetric indenters of arbitrary profiles. Appl. Phys. Lett. 2005, 87, 119114.
(26) Wang, M.; Liechti, K. M.; White, J. M.; Winter, R. M. Nanoindentation of polymeric thin films with an interfacial force microscope. Int. J. Mech. Phys. Sol. 2004, 52, 2329.
(27) Hay, J. C.; Sun, E. Y.; Pharr, G. M.; Becher, P. F.; Alexander, K. B. Elastic anisotropy of β-silicon nitride whiskers. J. Am. Ceram. Soc. 1998, 81, 2661.