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Aqueous exfoliated graphene by amphiphilic nanocellulose and its application in moisture-responsive foldable actuators†

Xuezhu Xu and You-Lo Hsieh *

Graphene is a promising material for diverse applications, such as in composites, optoelectronics, photovoltaic cells, and energy storage devices. However, high-yielding liquid exfoliation of good-quality graphene in high concentrations remains a challenge. In this study, amphiphilic 2,2,6,6-tetramethylpiperidin-1-yl-oxyl (TEMPO)-mediated cellulose nanofibrils (CNFs) were demonstrated in robust aqueous exfoliation of graphite into high quality graphene in high yields and stable dispersions with graphene concentration up to 1 mg mL⁻¹. Over 50% of graphene flakes exfoliated were 3 layers or less, of which ca. 5% were monolayer, and another 47% were multilayers, leaving only 3% as un-exfoliated graphitic platelets. Outstanding yields up to 84.2% were achieved at an optimized 0.2 g g⁻¹ graphite : CNF feed ratio. The dispersed graphitic flakes are stabilized by Coulomb repulsion from the surface bound charged CNFs. Aqueous graphene suspensions stabilized by CNFs were easily vacuum filtered into nanopapers that exhibited rapid moisture triggered motion and spontaneous recovery in the absence of moisture, resembling actions of biological motor cells in “shame plant” leaves. Such unique moisture responsive behavior is attributed to the highly accessible, charged CNF surfaces and the recovery is due to the inherently hydrophobic graphene. This facile aqueous exfoliating approach using amphiphilic CNFs as multi-functional exfoliating, dispersing and structural-forming agents for moisture-responsive graphene nanopaper opens up a large-area of potential applications toward biologically inspired sensors and actuators.

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Introduction

Graphene, composed of a single layer of sp² bonded carbon atoms arranged in a hexagonal lattice, has many outstanding attributes, including extremely high electron carrier mobility (up to 200 000 cm² V⁻¹ s⁻¹),¹ superior tensile modulus (1 TPa),² high specific surface area (2630 m² g⁻¹),³ good thermal conductivity (~5000 W m⁻¹ K⁻¹), and ultra-high optical transmittance (~97.7%).⁴ Typically, graphene can be produced by adhesive tape peeling,⁵ chemical vapor deposition,⁶ solid-state micromechanical cleavage,^{7,8} and liquid phase exfoliation.⁹ For many high performance applications (e.g., electrodes, electronics and conductive coatings), large quantities of graphene in the form of liquid suspensions, inks or dispersions are needed, making liquid phase exfoliation a desirable approach to produce graphene. However, keeping exfoliated graphene dispersed is extremely challenging because the orderly

graphene sheets tend to agglomerate by stacking tightly *via* the abundant van der Waals interactions.

Shearing or sonicating graphite in compatible organic liquids with surface energy very close to that of graphite, *i.e.*, 70–80 mJ m⁻²,¹⁰ guarantees well dispersed graphene products. Successful organic liquids have included *N*-methyl-2-pyrrolidone (NMP),^{7,11} dimethylformamide (DMF),¹² 1,2-dichloroethane (DCE),¹³ *o*-dichlorobenzene,¹⁴ *N*-cyclohexyl-2-pyrrolidone,¹⁵ and dichloromethane.¹⁵ Using NMP, for example, defect-free graphene can be produced with high electron mobility at concentrations as high as 1.2 mg mL⁻¹. However, the use and presence of residual organic liquids require special caution and further filtering or processing.¹⁶

Aqueous dispersants, such as pyrene derivative 1-pyrenebutyrate (PB),¹⁷ dyes,¹⁸ 7,7,8,8-tetracyanoquinodimethane (TCNQ),¹⁹ salts,^{20–22} porphyrins,²³ flavin mononucleotide (FMN),^{24,25} and poly(3,4-ethylene dioxathiophene)/poly(styrene sulfonate) (PEDOT/PSS),^{26,27} have shown to be effective at suspending graphene in water. These dispersants stabilize graphene in water by building up double electrostatic layers on graphene to overcome the van der Waals interactions; however, they most significantly lowered the electrical conductivity of the graphene produced. For example, PB decreased the electri-

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cal conductivity of the obtained graphene down to 2 S cm^{-1} ,¹⁷ much less than that of any pristine graphite (1000 S cm^{-1}).²⁸ In addition, the concentrations of graphene produced were very low, *i.e.*, 0.1 ,¹⁷ 0.02 ,¹⁹ and 0.05 mg mL^{-1} ,²³ from PB, TCNQ, and porphyrin, respectively. Thus, these market-available aqueous dispersants were limited in their ability in exfoliating graphite into graphene.

Similarly, aqueous phase exfoliation with ionic surfactants (*e.g.*, ultrasonication with sodium dodecylbenzene sulfonate (SDBS) for 30 min) has worked, but produced an extremely low graphene concentration of only 0.05 mg mL^{-1} at best.⁹ Moreover, the substantial residual surfactant can dramatically decrease the electrical conductivity. Graphene concentration can be substantially improved to 0.3 mg mL^{-1} by using other novel surfactants, such as sodium cholate, but needing an exceedingly long sonication time (up to 400 h).²⁹ Comparatively, FMN has shown to be the only efficient dispersant that yielded aqueous graphene concentrations as high as 0.3 mg mL^{-1} and at as low FMNS/graphene mass ratios as 0.04. Aqueous exfoliation with FMN also allowed the formation of free-standing graphene films that displayed a high electrical conductivity of 520 S m^{-1} without thermal annealing or other post-treatments. However, the most obvious drawback for most of these surfactants is that the accumulated surfactant layers surrounding graphene serve no much beneficial functions.

Nanocelluloses are nanoscale crystalline domains isolated from native cellulose that can carry negative surface charges, such as cellulose nanofibrils (CNFs) from 2,2,6,6-tetramethylpiperidin-1-yl-oxyl (TEMPO)-mediated oxidation first reported by A. Nooy *et al.* in 1995³⁰ and further developed by Isogai and others.^{31–33} We have derived nanocelluloses from agricultural biomass in the forms of cellulose nanocrystals (CNCs) by sulfuric acid hydrolysis³⁴ and CNFs by TEMPO-mediated oxidation, shear force, and a combination of thereof.^{35–37} Nanocelluloses are known for their impressively high intrinsic tensile strength of $1.6\text{--}6.4 \text{ GPa}$ ³⁸ and Young's modulus of up to $78\text{--}114 \text{ GPa}$,^{39–42} the highest among organic materials and closest to those of carbon nanotubes (*e.g.*, *ca.* 30 GPa and $270\text{--}950 \text{ GPa}$ for tensile strength and Young's modulus, respectively).^{43,44} The unique surface-active characteristics of CNFs have enabled their function as emulsifiers⁴⁵ as well as exhibited amphiphilicity when assembled into aerogels.⁴⁹ While biological materials, such as silk fibroin⁵⁰ and lignin,⁵¹ have shown to aid in assembling graphene oxide and carbon nanotubes and CNFs have been used to stabilize conducting materials,⁵² carbon nanomaterials,⁵³ and graphene,⁵⁴ the potential of CNFs in exfoliating or peeling graphene from bulk graphite crystals in aqueous medium had not been reported.

In this study, we exploited amphiphilic CNFs as a novel exfoliating agent and a facile surfactant to produce high quality graphene from graphite in a scalable fashion. Simple high-speed blending was employed to simultaneously exfoliate graphite in the presence of amphiphilic CNFs to disperse graphene in water in a single step. The effectiveness of CNFs for the exfoliation of graphite and the resulting graphene quality (defect degree, layer number), morphologies, structures and

electrical conductivities were evaluated. The obtained aqueous suspensions were fabricated into flexible and light-weight graphene/CNF papers by vacuum filtration and the moisture-responsive behaviors of graphene/CNF papers were evaluated.

Results and discussion

Morphologies and idea of using CNFs as a dispersant for graphite

The CNFs synthesized by TEMPO-mediated oxidation of rice straw cellulose were found to be $1.69 \pm 0.52 \text{ nm}$ thick ($n = 100$) by AFM (Fig. 1a, Fig. S1†), and $2.57 \pm 0.85 \text{ nm}$ wide and $0.99 \pm 0.48 \text{ }\mu\text{m}$ long ($n = 200$) by TEM (Fig. 1b). At $0.67 \text{ wt\%}$, aq. CNFs were highly viscous (Fig. S2†) due to their very fine lateral dimensions and high length to width/thickness aspect ratios (up to 586). All these observations are consistent with our prior work.^{36,55} As both mica used for AFM and glow discharged grid for TEM are hydrophilic, the wider surfaces that preferentially lay on these hydrophilic AFM and TEM sample supports are assumed to be the hydrophilic (110) or ($\bar{1}\bar{1}0$) planes and the smaller surface in the thickness direction to be the hydrophobic (200) plane (Fig. 1d). This is illustrated by viewing the cellulose I β monoclinic unit cell from the z direction where a surface full of H atoms is present on the top and at the bottom in the axial direction (Fig. 1e).⁵⁶ The surface tension (γ) of water (70.4 mN m^{-1}) is inherently high due to the abundance of intermolecular hydrogen bonding among water molecules. In the presence of CNFs, the surface tension (γ) increased very slightly from that of water (70.4 mN m^{-1}) to 71.3 mN m^{-1} at $0.23 \text{ wt\%}$ CNFs, and then decreased to 65.7 mN m^{-1} with further increases in CNF concentrations to $0.86 \text{ wt\%}$ CNFs (Fig. 1c). The very slightly increased surface tension in the presence of $0.23 \text{ wt\%}$ CNFs is unusual and may be associated with the unique ability of CNFs to not only hydrogen bond with water, but also with each other by not only polar, but also hydrophobic interactions. The water surface tension in the presence of CNFs may be linearly extrapolated to as low as 51 mN m^{-1} at $1.5 \text{ wt\%}$ even though aq. CNFs would have become too viscous at such a concentration. Both these observations of aq. CNFs are intriguing, suggesting unique behaviors of CNFs to be further studied. $10 \text{ }\mu\text{L}$ 0.001% graphene/CNF droplets deposited on a 9.9 mm diameter mica disc spread instantaneously and completely cover the surface, indicative of the overall hydrophilic nature of graphene/CNFs. The AFM images clearly showed the association of multiple CNFs with each individual graphene flake (Fig. 1f). The aqueous dispersibility, hydrophilic characteristic of graphene/CNFs, and individual graphene/CNF domains observed are all supportive of the notion that the exfoliation of graphite into graphene by CNFs functions as the hydrophobic 200 plane on CNF surfaces associated with hydrophobic graphite surfaces whereas the hydrophilic 110 or $\bar{1}\bar{1}0$ planes and surface charges on the exposed CNF surfaces help to peel off graphene sheets and keep the exfoliated graphene sheets dispersed (Fig. 1g).

Fig. 1 Aq. CNF derived from rice straw cellulose as an exfoliating agent and dispersant to exfoliate graphite into graphene: (a) AFM image of 0.0001% CNFs on mica; (b) TEM image of 0.0001% CNFs on a glow-charged carbon coated copper grid; (c) surface tension (γ) of aq. CNFs at different CNF concentrations; (d) a simplified model showing idealized arrangement of cellulose molecules (each molecule as one grey rectangular block) to expose the (200) hydrophobic planes on the sides and (110) or ($\bar{1}\bar{1}0$) hydrophilic planes on the top and bottom surfaces; the thickness as well as width and lengths in d were experimentally measured by AFM and TEM, respectively; the vertical sides are hydrophobic 200 planes with the presence of all carbon–hydrogen bonds (C–H) where the horizontal sides are the hydrophilic 110 and $\bar{1}\bar{1}0$ planes with hydroxyl groups; (e) cellulose I β monoclinic unit cell viewed from the z-direction, plane (200) is on top of the cell. The model was adopted from the Crystallography Open Database;⁵⁶ dotted box shows where all carbon–hydrogen bonds (C–H) are standing up along this hydrophobic plane; (f) AFM images of 10 μ L 0.001% graphene/CNF on mica. Graphene/CNF exfoliated from 32.8 g g^{−1} graphite : CNF (blending at 37k rpm, supernatant after final centrifugation at 11 000 rpm for 60 min); (g) Scheme of exfoliation of graphite represented by multilayers of 2D graphene sheets into single layer graphene by CNFs.

Quality of exfoliated graphene

The exfoliated graphene sheets had an average 1.15 nm thickness determined by AFM (Fig. 2a, inset) and varied in thickness as shown by the different shades in the TEM images (Fig. 2b). Based on the reported monolayer thickness of 0.335 nm,⁵⁷ approximately 5% of the exfoliated graphene were in monolayer (<0.39 nm), 19% in two layers (0.4–0.6 nm), 26% in triple layers (0.7–0.9 nm), and 47% in multilayers (1.0–10.0 nm). Only 3% graphene has over 10 layers or so called un-exfoliated graphitic platelets. At the same 0.15% aq. dispersant concentration, CNFs exfoliated much more graphene than SDS (Fig. S3†). A selected area electron diffraction

pattern on an arbitrary area in Fig. 2c showed typical graphene crystalline planes, *i.e.*, 0 $\bar{1}10$, $\bar{1}010$, $\bar{2}010$, and $\bar{1}\bar{1}20$.⁴⁶ The diffraction spots on the inner circle are obviously brighter than those on the outer circle, indicating some graphene to be monolayer.⁴⁶ Overall, 50% of the CNF-exfoliated graphene are three layers or less while the remainder is at least four layers.

The D, G and 2D Raman peaks (Fig. 2d–g) change in shape, position and relative intensity with a number of graphene layers. The D peak at ~ 1350 cm^{−1} is from sp² carbon rings near a graphene edge or a defect in the carbon lattice,⁵⁸ the G peak at ~ 1580 cm^{−1} represents an in-plane vibrational mode of the sp² hybridized carbon atoms, and the 2D band at ~ 2700 cm^{−1} is the second order of zone-boundary phonons.⁴⁷

Fig. 2 Evidence of the CNF-aided exfoliated graphene layer structure: (a–b) AFM and TEM images; (c) TEM SAED of graphene obtained from the graphene domain and region marked with a red box in (b); (d) Raman spectra of dried CNF-assisted graphene flakes deposited on alumina; (e) the intensity ratio of 2D/G and D/G values for graphene produced by different exfoliators to identify the exfoliation degree and defect degree; (f) graphitic crystalline size vs. $I(D)/I(G)$ for exfoliated graphene; (g) 2D peak deconvolution corresponding to the CNF, SDS and CMC exfoliated graphene in comparison to pristine crystal graphite.

Defects increase the D peak intensity and cause a concomitant increase in a D/G peak intensity $I(D)/I(G)$, comparing CNF-dispersed graphene and the bulk graphite as shown in Fig. 2d. Specifically, $I(D)/I(G)$ is 0.48 for graphene exfoliated by CNFs (Fig. 2e), indicating a low defect level similar to graphene exfoliated by NMP⁷ and far lower than the high 0.98 ratio for defective oxidized graphene.⁴⁸

Meanwhile, the ratio of $I(2D)/I(G)$ is used to determine the layer number of graphene. It is reported that a value of 3–4 indicates monolayers, a value of less than 0.5 indicates few layers, and a value of one is for bilayers.²¹ In this study, CNF-exfoliated graphene has an intensity ratio of one (Table S3†), suggesting the presence of a large amount of bilayers. $I(2D)/I(D + D')$ (D' is the minor peak on the right shoulder at the G peak) relates to the level of electrical conductivity. From these data, it is predicted that graphene exfoliated by CNFs has a lower intrinsic electrical conductivity compared to graphite due to the defects (edges) generated by the aggressive exfoliation process.

The $I(D)/I(G)$ ratio was used to show the average in-plane size (L_a) of the carbon sp^2 domain (internal area without

edges, foreign atoms or defective holes) and is expressed by the Tuinstra-Koenig relation:⁴⁹

$$\frac{I(D)}{I(G)} = C(E_l)/L_a$$

where the empirical constant $C(E_l)$ depends on the energy of the laser. Here a 514.5 nm laser was used so that $E_l = 2.41$ eV.⁴⁷ Cancado *et al.* deduced an empirical equation between L_a and the integrated intensity:⁴⁷

$$L_a(\text{nm}) = \frac{560}{E_l^4} \left(\frac{I(D)}{I(G)} \right)^{-1}$$

We plotted $I(D)/I(G) \times EL^4$ (eV^4) vs. $1/L_a$ as shown in Fig. 2f. The respective crystalline sizes of graphene exfoliated by CNFs and SDS were 34.1 nm and 33.8 nm, showing similar sp^2 crystalline domains (Table S3†), and correspond to their $I(D)/I(G)$ results shown in Fig. 2e. The intensity ratio of D to G peaks for graphene may be used to calculate the nanosheet length as:⁵⁰

$$L = \frac{0.094}{(I_D/I_G)_{\text{G'ene}} - (I_D/I_G)_{\text{G'ite}}}$$

where L is the length in μm , I_D/I_G denotes the intensity ratio, and the suffixes “ene” and “ite” denote graphene and graphite, respectively. Accordingly, the respective graphene sheet lengths exfoliated by CMC, SDS and CNF aqueous dispersants were 138, 96 and 119 nm. Even though the equation used is empirical with a relative error of $\sim 20\%$, the CNF-blended graphene sheets were imaged and measured by AFM having an average lateral dimension of 248 ± 121 nm that agrees well with the theoretical prediction, meanwhile, these length values indicate that the CNF exfoliated graphene prepared by vigorous blending has comparable lateral lengths.

Lastly, Fig. 2g shows a significant change in the shape (*i.e.*, $2D_1$, $2D_2$) and intensity (relative intensity to G peak) of the $2D$ peak of graphene compared to bulk graphite. Single-layer graphene was reported to have a single, sharp $2D$ peak, roughly four times more intense than the G peak. In this study, the $2D$ peak in graphite consists of two components $2D_1$ and $2D_2$, roughly $3/10$ and $2/10$ of the G peak at 2706.9 and 2737.6 cm^{-1} , respectively. For graphene exfoliated by CNFs, the highest $2D_1$ peak increased its intensity up to $7/10$ of the G peak and the $2D_2$ component almost disappeared. The full $2D$ peak of graphene exfoliated by CNFs upshifted by *ca.* 25 cm^{-1} as compared to graphite. These evidence attest that the CNF exfoliates graphite into graphene efficiently but not all in single layers, which are consistent with the AFM and TEM results. Therefore, the CNF works as a

dispersant with similar exfoliation effects to surfactant SDS, but better.

Optimizing exfoliation conditions and attributes of graphene/CNFs

The CNF-aided exfoliation of graphite into graphene was further optimized by varying the blending speed and initial graphite to the CNF feed ratio. Blending was applied at speeds from 5 k to 37 k rpm to the initial protocol, *i.e.*, 50 mg mL^{-1} aq. graphite and 32.8 g g^{-1} graphite : CNF feed ratio. Graphene concentrations (C_G , excluding CNFs, in mg mL^{-1}) in the supernatant from settling for 24 h and centrifugation at 1.5 k rpm and then at 11 k rpm were compared (Fig. 3a). At a fixed initial graphite : CNF feed ratio of 32.8 g g^{-1} , graphene C_G exfoliated increased nearly linearly with blending speed, peaked at 0.5 mg mL^{-1} graphene concentration at 37 k rpm, except at 12 k rpm. The graphene exfoliated C_G values were similar, except for the least blended, between the two levels of centrifugations, indicating settling for 24 h and one round of 15 min centrifugation at 1.5 k rpm was sufficient to precipitate larger graphene. The electrical conductivity of vacuum-filtered graphene/CNF nanopaper from blending at 5 k – 25 k rpm remained low at 0.1 S cm^{-1} (Fig. 3b black line), but that blended at 37 k rpm significantly increased to 0.94 S cm^{-1} , corresponding to a sheet resistance of 1.03 ± 0.12 $\text{k}\Omega \text{ sq}^{-1}$ (Fig. 3b red line, Table S6†). Since there is no significant difference in the con-

Fig. 3 Parameter optimization in CNF exfoliation of graphite into graphene: (a–c) effect of blending speed (5 – 37×10^3 rpm, 30 min) at a fixed 32.8 g g^{-1} graphite : CNF feed ratio: (a) graphene concentration C_G ; (b) electrical conductivity of nanopaper by vacuum filtration of aq. graphene/CNF; right Y-axis in red plots sheet resistance versus blending speed for the above-mentioned graphene/CNF films; (c) graphene lateral dimension; (d–f) effect of the graphite : CNF feed ratio at a fixed 37×10^3 rpm: (d) graphene concentration with the highest marked by a red star; (e) graphene yield defined as final graphene mass over the initial graphite feed, with the highest marked by a red star; (f) colloidal stability of aq. CNF-assisted exfoliated graphene (graphite : CNF feed ratio: 32.8 g g^{-1} , blending speed: 37×10^3 rpm) evaluated by absorbance at 450 nm of UV-vis spectra. Inset figure is the UV-Vis spectra of diluted graphene/CNF aq. suspensions measured from 250 to 600 nm wavelength at the initial stage and after 60 h.

centrations of graphene C_G , the increased conductivity is believed to be associated with graphene attributes, *i.e.*, sizes and layers. The lateral dimensions of the exfoliated graphene reduced drastically with the initial increases in blending speeds, lowering from 3 μm at 5k rpm, 1.4 μm at 12k rpm, to 0.7 μm at the maxima at 37×10^3 rpm (Fig. 3c). The 0.7 μm lateral size was comparable to the 0.5 μm value reported for graphene exfoliated by surfactant SDBS.⁵¹ Therefore, CNF exfoliated more efficiently into graphene whose lateral dimensions reduced with increasing blending speed. The electrical conductivity of the resulting graphene was only improved with the 0.7 μm size exfoliated at 37k rpm. Even the most conductive graphene/CNF nanopaper is far less conductive compared to graphite (3000 S cm^{-1}), which is expected due to the presence of insulating CNFs (Fig. 4b).

The effect of the initial graphite : CNF feed ratio was then varied from 32.8 to 0.2 g g^{-1} at the optimal blending speed of 37k rpm for 30 min (Table S4†). With decreasing graphite : CNF feed ratios or increasing CNFs in the initial suspensions, graphene concentration C_G increased from 0.3 to 1.0 mg mL^{-1} (Fig. 3d), showing the positive effect of the CNF

exfoliating agent. Higher graphene concentration is advantageous for handling, processing and applications. In the meantime, graphene yield, defined as the final graphene mass over the initial graphite feed, increased to 84.2% with increasing CNFs in the feed or reducing graphite : CNF ratio at 0.2 g g^{-1} (Fig. 3e). These data show that the graphene exfoliated into aqueous media C_G is dependent on the graphite : CNF feed ratio $\phi_{\text{G:CNF}}$ according to $C_G \sim \phi_{\text{G:CNF}}^x$, where $x \approx -0.187$. This processing showed a high tunability in product qualities, *i.e.*, conductivity (graphene) or strength/film forming ability (CNFs).

Aq. graphene absorbed strongly within the UV range (Fig. 3f inset).⁵² The stability of the exfoliated graphene/CNFs over time was monitored by the optical absorbance at 450 nm. The graphene suspensions blended at 37×10^3 rpm for 30 min remained stable and did not settle for at least 60 h (Fig. 3f). In general, having a stable graphene dispersion is crucial for facile processing into free-standing films.

Aq. graphene suspensions produced by CNF-aided exfoliation of graphite were in concentrations of up to 1 mg mL^{-1} , much higher than those aided by ionic surfactants, *i.e.*,

Fig. 4 Properties of CNF exfoliated graphene: (a) graphene concentrations *versus* exfoliation time plot including data reported in this work and from the literature;^{7,16,29,51,55–57} (b) recent advances in electrical properties of conductive CNFs; (c) tensile strengths of pure CNF and graphene/CNF nanopaper, print paper was also tested for comparison; (d) contact angles of nanopapers from pure CNF and graphene/CNF in various ratios, insets were two representative images of a 10 μL water droplet on CNFs (left) and graphene/CNF nanopapers (right).

0.05 mg mL⁻¹ by SDBS,⁵¹ 0.3 mg mL⁻¹ by NaC²⁹ and very close to the highest 1.2 mg mL⁻¹ value reported using NMP,⁷ that required exceedingly long 460 h sonication (23 W).¹⁶ Therefore, this simple, short (only 30 min) and aq. based CNF-aided exfoliation approach not only produces a high concentration of graphene (1 mg mL⁻¹), but also high quality graphene (50% 3 layers of less, average 7 μ m size) in high yield (84.2%), which is higher than most of the reported values (Fig. 4a, Table S4†).

The tensile properties of both CNF and graphene/CNF (0.3 g g⁻¹ graphene:CNF ratio) nanopapers were measured and compared to a paper (Fig. 4c). The tensile stress of CNF and graphene/CNF nanopaper was similar at 47 MPa and 45 MPa, respectively, and the strain was a slightly higher 1.5% for the graphene/CNF nanopaper than the 1% for the CNF nanopaper. In fact, the lower Young's modulus of 1.6 ± 0.16 GPa for the graphene/CNF nanopaper than 3.6 ± 0.11 GPa for the CNF

nanopaper makes it more pliable and foldable. The water wetting contact angles (CAs) of 10 μ L water droplets on CNF nanopaper showed a CA of 45.7°, consistent with cellulose materials in general, which increased to 54.3° with increasing graphene at the graphene:CNF ratio: 0.3 g g⁻¹. While graphene/CNF nanopaper became slightly less hydrophilic, the overall hydrophilic nature of this nanopaper surface is consistent with the role of CNFs as the matrix that enables such nanopaper formation.

Application of graphene/CNF nanopaper in soft robots

CNF and graphene/CNF nanopaper was prepared *via* vacuum filtration of aq. graphene/CNF with 0, 15.2, 20.6 and 23.1% graphene contents in 90 mm diameter and 8 to 23 μ m thickness (Fig. 5a). These graphene/CNF papers appeared homogeneous and isotropic. CNF defibrillated by TEMPO mediation oxidation and blending carried a 1.33 mmol g⁻¹ surface

Fig. 5 Graphene/CNF nanopaper and application in soft robots; (a) image of graphene/CNF papers with 0, 15.2, 20.6 and 23.1% graphene contents; (b) carboxylate ($-\text{COO}^-$) charge on CNFs titrated with NaOH; (c) cyclic bending and recovery of a 90 mm diameter and 23 μ m thick graphene/CNF nanopaper (15.2% graphene) upon exposure to two human breaths at 0 and 127 s. (d) Proposed folding mechanism of graphene/CNF nanopaper. Graphene flakes and CNFs in the nanopaper are held together by hydrophobic interactions among graphene flakes and hydrophilic and hydrogen bonding among CNFs. Upon exposure to moisture, the distances between CNF–CNF expand as hydrophilic and charge surface groups on CNFs become ionized by water.

charge as determined by NaOH titration (Fig. 5b), indicative of the highly hygroscopic properties of graphene/CNF nanopaper. Graphene/CNF nanopaper bends away instantaneously upon exposure to moisture, then flattens and restores within one second to the original flat form once the moisture is removed. The spontaneous moisture triggered bending and instantaneous recovering could be repeated tens of times (Movie S1†). These motions are similar to but much more rapid than the shame plant, *Mimosa pudica*, native in South and Central America, whose compounded leaves (Fig. S5†) fold inward and droop when touched or shaken physically as a defensive response and then re-open minutes later.⁵³ Further explanations are provided in the ESI.†

Fig. 5c shows two repeatable cycles without noticeable changes in the morphology of graphene/CNF paper. Meanwhile, the recovering time from bended to the original flat form was only one second as shown in Movie S1.† This is highly desirable as the actuation or response time is very important to sensors and actuators, the faster the better. The fast response is attributed to the high moisture-acceptor factors, *i.e.*, the highly charged CNF surfaces and the highly accessible, inherently porous microstructure that has been reported to be as high as 13.3% for an all-CNF based nanopaper.⁵⁴ The hydrophobic graphene on the other hand is expected to be non-responsive to moisture. Therefore, the CNF is particularly useful if aimed for applications in moisture or vapor sensors/actuators. It should be noted that paper made of CNF alone also exhibited some bending/recovery responsive behaviors towards water vapor, but deformed upon multiple exposures, hindering practical applications as sensors and actuators.

A simple model is proposed and shown in the side view of a flat nanopaper whose initial top and bottom layers have the same dimension (Fig. 5d). Upon absorbing moisture from the bottom, the lower layer expands dramatically to bend upward pushing the upper part inward. The hydrophobic planes of CNFs associate with the graphene surface through hydrophobic interactions in the dry state. Upon exposure to moisture, the water vapor diffuses in between CNFs to the hydrogen bond with CNF surface hydroxyls and carboxylates to enlarge the inter-CNF spacings, causing volume expansion of the exposed layer and exerting bending action. The rigid and non-absorbing graphene adhered to the hydrophobic surface of CNFs is thought to be responsible for the shape recovery of the nanopaper upon losing moisture from the hydrophilic CNF surfaces and interfaces. The moisture-triggered motions such as a box being opened and reopened repeatedly, or as a folded strip soft robot being able to crawl when activated by a human finger placed above are demonstrated in Fig. S6.†

Conclusions

Aqueous exfoliation using amphiphilic cellulose nanofibrils (CNFs) under high shearing forces provided by blending is shown to be highly efficient at producing high quality, few

defect graphene. This method has the benefits of being a simple, widely accessible and scalable technology. Amphiphilic CNFs work efficiently by associating with graphite *via* hydrophobic interactions, whereas the hydrophilic surfaces help to disperse CNF-bound graphene in aqueous media and the charged carboxylates stabilize the CNF-bound graphene dispersions in water through Coulomb repulsion. A graphene concentration of up to 1 mg mL⁻¹ and a graphene yield of 84.2% have been achieved on graphene/CNF suspension, superseding values reported in protocols using surfactants, and approaching those utilizing the organic solvent NMP. Graphene/CNF nanopaper containing 15.2 to 23.1% graphene with thicknesses of 8 to 23 μ m has demonstrated moisture responsive motions. Particularly, graphene/CNF nanopapers exhibit swift deformation or bending motions to the presence and instantaneous recovery from the absence of moisture stimuli, mimicking the closing-opening behavior of the shame plant or motion of soft robots. For the first time to our knowledge, amphiphilic CNFs prepared by coupled TEMPO-mediated oxidation and blending have shown to be robust exfoliating and dispersing agents while also responsible for moisture responsive stimulus-acceptor characteristics. As producing large quantities of high-quality graphene is necessary for a wide range of applications and commercialization, liquid-phase and in particular aqueous exfoliated graphene is particularly attractive as it allows for facile solution processing *via* filtration, casting, ink-jet printing and roll-to-roll manufacturing. Hence, this bodes well for the scalability of the technology for future industrial applications. Highly robust aqueous exfoliation to fabricate high-quality graphene using a biologically derived nanocellulose is a significant green technology in that direction.

Experimental

Materials

Graphite flakes (49 μ m particle size, Sigma-Aldrich), toluene (99.9%, Fisher Scientific), anhydrous ethanol (Fisher Scientific), sodium chlorite (NaClO₂, 80%, ACROS), acetic acid (99.7%, Fisher Scientific), potassium hydroxide (KOH, 85%, Sigma-Aldrich), sodium hypochlorite (NaClO, 11.9%, reagent grade, Sigma-Aldrich), 2,2,6,6-tetramethylpyperidine-1-oxyl (TEMPO, 99.9%, Sigma-Aldrich), sodium bromide (NaBr, 99.6%, Sigma-Aldrich), sodium hydroxide (NaOH, Fisher Scientific), and hydrochloric acid (HCl, 1N, Fisher Scientific) were used as received. Other exfoliators including carboxymethyl cellulose (CMC, M_w = 250 kDa, SD = 1.2, ACROS) and sodium dodecyl sulfate (SDS, J. T. Baker) were used as received. Water was purified by using a Milli-Q plus water purification system (Millipore Corporate, Billerica, MA).

Cellulose was extracted from rice straw (RS, Calrose variety, 2015 harvest in the Sacramento Valley in northern California) by a three-step procedure³⁶ involving 2 : 1 v/v toluene-ethanol extraction, NaClO₂ leaching of lignin and NaOH removal of hemicellulose with a 31.4% yield. Cellulose nanofibrils (CNFs)

Table 1 Exfoliation of graphite by CNFs at varied graphite : CNF feeds, mass ratios and total concentration at constant blending (37×10^3 rpm, 30 min)

Sample	a	b	C	d
Graphite : CNF feed ^a	5 g : 0.1524 g	1 g : 0.1524 g	0.3 g : 0.3049 g	0.1 g : 0.4572 g
Graphite : CNF ratio (g g ⁻¹)	32.8	6.6	1.0	0.2
Aq. (CNF + graphene) concentration (wt%)	0.14	0.16	0.26	0.31

^a Dry mass of CNF from aq. CNF (0.67 wt%).

were produced as 0.67 wt% aq. suspension by 2,2,6,6-tetramethylpiperidin-1-yl-oxyl (TEMPO)-mediated oxidation (5 mmol g⁻¹ NaClO/cellulose) followed by blending (37k rpm, 30 min), also reported previously.³⁷ Details on measuring the blending speeds are shown in Table S1.†

Exfoliation by nanocellulose

Aq. CNF suspension (0.67 wt%, 22.75 g) was mixed with graphite flakes (5 g, 100-mesh, Sigma Aldrich) and additional water (77 g) to prepare 50 mg mL⁻¹ (5 wt%) aq. graphite suspension and then blended using a high-speed blender (Vitamix 5200, Cleveland OH) for 5 to 60 min. Upon being settled for 24 h, the supernatant was centrifuged (Eppendorf, Centrifuge 5804 R) at 1.5k rpm for 15 min and then at 11k rpm for 60 min to collect the exfoliated graphene in the final aq. supernatant. For comparison, graphite flakes were also exfoliated using carboxymethyl cellulose (CMC) and sodium dodecyl sulfate (SDS) following the same procedures described above. To optimize the graphene yield, the blending speed and CNF:graphite feed ratio were varied, one at a time. First, original aq. graphite–CNF suspension, 5g:0.1524 g CNF:graphite ratio, was blended at varying speeds from 5k to 37k rpm. Then, the CNF : graphite feed ratios were reduced from 32.8 to 0.2 by lowering graphite while increasing CNF concentrations from 5 g : 0.1524 g to 0.1 g : 0.4572 g and blended at 37k rpm for 30 min (Table 1).

Fabrication of graphene/CNF nanopaper

Aq. graphene/CNF suspension (0.1%, 98 g) with 0.098 g graphene/CNF solid mass weight was vacuum-filtered for 24 h through a 90 mm diameter polycarbonate filter with a 0.2 μm pore size membrane (Wheaton) attached to Wheaton 90 mm filtration assemblies.

Characterization

The height of CNFs was imaged by atomic force microscopy (AFM). Aq. CNF suspension (10 μL, 0.0005%) was deposited onto a freshly cleaved hydrophilic mica surface, air-dried, and scanned (Asylum-Research MFP-3D) in air under ambient conditions using tapping mode with OMCL-AC160TS standard silicon probes. The scan rate was set to 1 Hz, and the image resolution is 512 × 512 pixels. The height images and profiles were processed with Igor Pro 6.21 loaded with MFP3D 090909 + 1409, and the thickness was determined from *ca.* 100 individual nanofibrils and the mean and standard deviation were reported.

The width and length of CNFs were imaged by transmission electron microscopy (TEM) on a JEOL2100F electron microscope (JEOL). Aq. CNF suspension (5 μL, 0.0001 wt%) was deposited onto glow-discharged carbon-coated TEM grids (300-mesh copper, formvar-carbon, Ted Pella Inc., Redding, CA) with the excess liquid being removed by blotting with filter paper after 10 min. The specimens were then negatively stained with 2% phosphotungstic acid (PTA) solution 5 times for 2 s, each time blotting with filter paper from the grid bottom to remove excess staining solution and allowed to dry at 50 °C for 10 s. The samples were observed at a 40 or 80 kV accelerating voltage. The widths and lengths of CNFs were measured from *ca.* 200 individual nanofibrils using an image analyzer (ImageJ, NIH, USA) to calculate the mean and standard deviation.

Raman spectra were collected on an RM1000 Raman spectrometer (Renishaw plc) using a 514.5 nm argon ion laser. The stability of aqueous suspensions was characterized by UV-vis spectra on a UV-vis spectrophotometer (Evolution 600, Thermo Scientific). The surface tension (γ) values of aq. CNF suspensions were measured by the Wilhelmy plate method using a platinum plate on a K10 Kruss tensiometer and derived using the equation below, where F is the force in mN m⁻¹ and L is the wetted length of the measuring plate. The γ values of aq. CNF suspensions at different CNF concentrations were calculated from wetting forces (F) measured using a platinum plate with an interfacial length (L) and zero contact angle (θ). The platinum plate was cleaned by burning off residual CNF after each measurement using a Bunsen burner.

$$\gamma = \frac{F}{L \cdot \cos \theta} \quad (\theta = 0^\circ)$$

CNF/graphene compositions were determined by heating the dried CNF and graphene/CNF films at 10 °C min⁻¹ to 500 °C in a thermogravimetric analyzer (TGA-50, Shimadzu Company). Graphene contents in graphene/CNF films were determined by subtracting the residual mass of graphene/CNF by the residual mass of CNF, both at 500 °C. The tensile strengths of CNF and graphene/CNF nanopapers (0.5 cm wide × 2 cm long) were measured at a 1 cm gauge length and constant 1 cm min⁻¹ elongation rate on an Instron tensile tester (Model 5566, Instron).

Conflicts of interest

There are no conflicts to declare.

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