Supporting Information

Aqueous Exfoliated Graphene by Amphiphilic Nanocellulose and its Application in Moisture-responsive Foldable Actuators

*Xuezhu Xu, and You-Lo Hsieh**

Fiber and Polymer Science, University of California, Davis, California 95616, United States

*Corresponding Author Professor You-Lo Hsieh, E-mail: ylhsieh@ucdavis.edu; Fax: +1 530 752 7584; Tel. +1 530 752 0843.

S1. Experimental:

S1.1. Preparing cellulose from rice straw

Cellulose was extracted from rice straw (Calrose variety, 2015 harvest in the Sacramento valley in northern California) according to previous procedures.[1] Dried 30 g milled RS powder (Wiley Mini Mill, Thomas Scientific, pass 20-, 40- and 60-mesh consecutively) was loaded into a thimble and fluxed with 200 mL toluene (99.9 %, Fisher Scientific) and 100 mL anhydrous ethanol (Fisher Scientific) in a Soxhlet extractor at 120 ^{o}C for 20 h. The thimble was then left in fume hood for 48 h and 50 ^{o}C oven for 24 h to evaporate toluene/ethanol. To remove hemicellulose and lignin, 7.5 g sodium chlorite (O_2ClNa, 80 % purity, ACROS) in 1000 mL DI water at pH was adjusted to 3-4 by adding acetic acid (99.7 %, Fisher Scientific). Then, it was warmed to 70 ^{o}C so RS powder was added and stirred for 5 h. Obtained slurry was filtrated and washed till pH ~7. Obtained dried RS powder, 30 g potassium hydroxide (KOH, 85 % purity, Sigma-Aldrich) and 600 ml water were mixed (KOH/water 5 %) at 25 ^{o}C for 24 h and at 90 ^{o}C for 2 h. Obtained slurry was washed and filtrated till pH ~7, then frozen by liquid nitrogen dried by lyophilized at −50 °C (FreeZone 1.0L Benchtop Freeze Dry System, Labconco, Kansas City, MO).

S1.2. TEMPO mediated defibrillated CNFs

Cellulose nanofibrils (CNFs) were prepared from RS-based cellulose employing 5 mmol sodium hypochlorite (NaClO, 11.9%, reagent grade, Sigma-Aldrich) per gram of cellulose and mechanical blending at 37,000 rpm for 30 min as reported previously.[2] In detail, 1.0 g cellulose was added into 100 mL water (purified by Milli-Q plus water purification system, Millipore Corporate, Billerica, MA) and stirred for 5 min. 2 mL of an aqueous mixture of 0.016 g 2,2,6,6-tetramethylpyperidine-1-oxyl (TEMPO, 99.9%, Sigma-Aldrich) and 0.1 g sodium bromide (NaBr, NaBr, 99.6%, Sigma-Aldrich) was added and stirred for another 5 min. Oxidation reaction was initiated by adding ~3.436 mL sodium hypochlorite (NaClO, 10-15 % chlorine, Sigma-Aldrich) solution drop-wisely at 20 µm/time to reach 5 mmol NaClO per gram of cellulose. The pH decreased as oxidation proceeded and was adjusted to 10 ± 0.2 with 0.5 M sodium hydroxide (NaOH, Fisher Scientific). The oxidation reaction ended when no acid was produced, or pH ceased to lower, lasting approximately 65 min. The pH was adjusted to 7 with 0.5 M hydrochloric acid (HCl, 1N, Fisher Scientific). The suspension was centrifuged (5000 rpm, 15 min) to get precipitate, it was dialyzed against water till its conductivity was ca. 0.8 mV/cm. With addition of 150 ml water, the TEMPO-treated cellulose was defibrillated for 30 mins using a high-performance blending machine (Vitamix, 5200, Cleveland OH) operated at 37,000 rpm. Obtained TEMPO-CNF was centrifuged (1500 rpm, 15 min) again to obtain the CNF-containing supernatant which was then concentrated using a rotary evaporator. Final aqueous CNF suspension has a concentration of 0.67 wt.%.

S1.3. Blending speed

We used a Vitamix blender to complete the exfoliation process of bulk 2D graphite powders into graphene sheets. Standard procedure was conducted at a “high” dial setting, which was given a speed of 37,000 rpm from the manual came with the equipment. An average 29,423 rpm was given by the customer support of the manufacturer. Below list the other values as corrected for this blender after their rigorous experiments as well (**Table S1**). Dial settings at 2, 4, 6, 8, 10 & high, corresponding to an average speeds of 4,200, 10,543, 19,317, 24,010, 24,370, 29,423 rpm, respectively, were used in this study. These numbers may be abbreviated into 4.2 k, 10 k, 19 k, 24 k, 25 k, 30 k rpm in this study.

Table S1. Speeds for Vitamix blender (5200, 220V 50hz, S/N: 059184150615293423) measured with no load by Vitamix Customer Support on March 5, 2018.

Dial Setting	Test 1	Test 2	Test 3
1	1,765	740	970
2	5,060	3,090	4,450
3	10,125	4,860	7,510
4	12,975	7,225	11,430
5	16,675	13,160	16,350
6	20,200	18,750	19,000
7	23,400	23,460	22,880
8	23,850	24,380	23,800
9	24,060	24,650	24,140
10	24,080	24,690	24,340
High	29,190	29,890	29,190

S2. Results and discussion

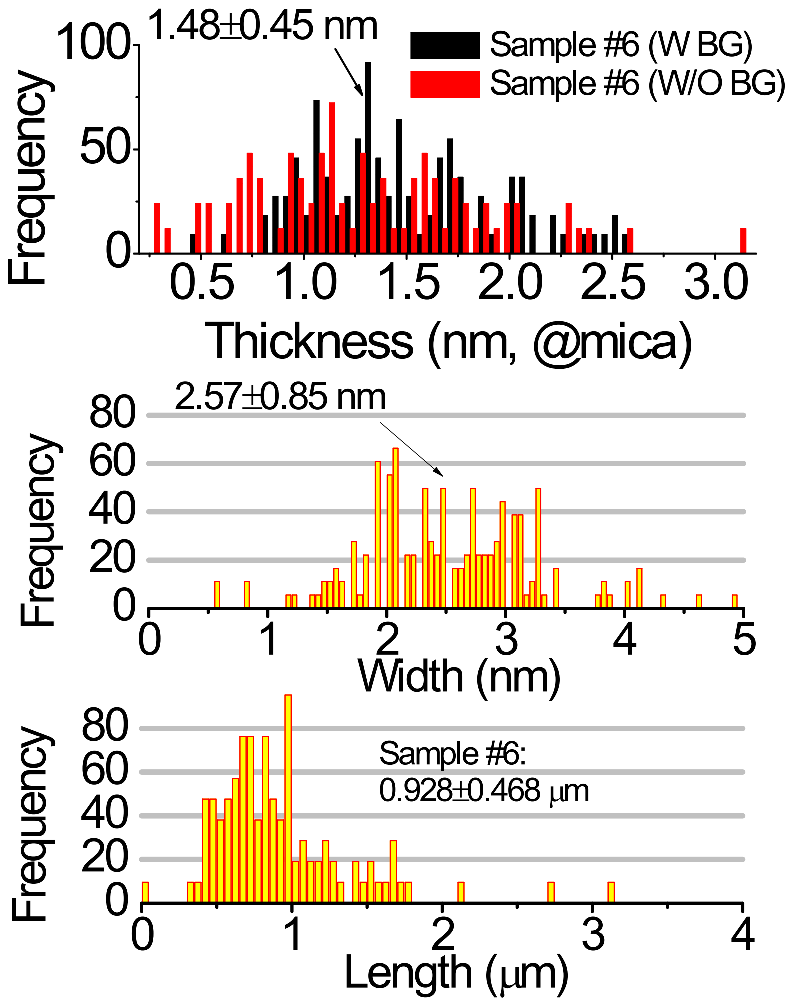

Figure S1. Height, width and length histograms of CNFs.

Figure S2. A viscous aqueous suspension with 0.67 wt.% CNF.

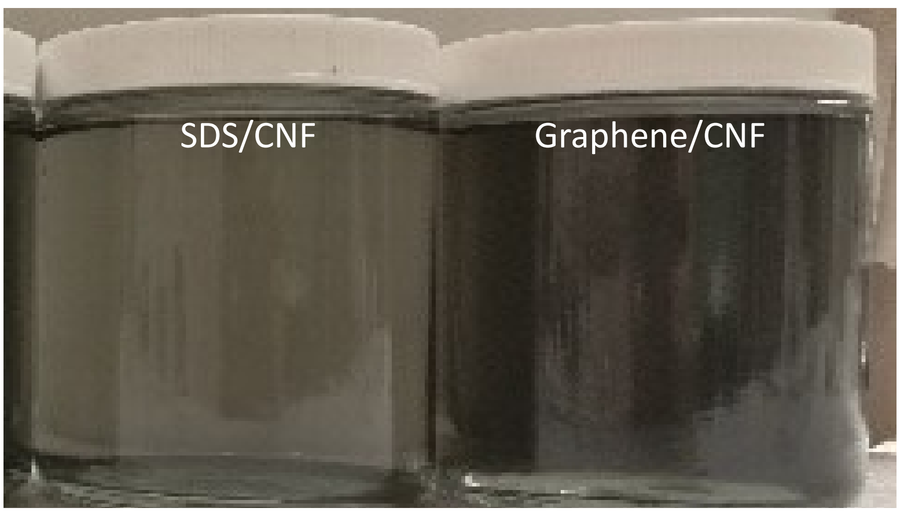

Figure S3. A photo of aq. graphene suspensions prepared under the same condition with SDS surfactant (left) and CNF (right).

Table S2. Raman data of various exfoliated graphene by using different exfoliators.

Sample	D (cm-	D	G (cm-	G	D'	D'	2D	2D	D+D'	D+G

	1)	intensity	1)	intensity	(cm^{-1})	intensity	(cm^{-1})	intensity	(cm^{-1})	intensity
Graphite	1350.0	107.8	1582.4	1875.0	-	-	2727.5	1321.4	-	-
Graphene/CMC	1347.7	4921.1	1580.6	6569.6	1621.4	3234.1	2700.6	6095.9	2943.5	2786.6
Graphene/SDS	1345.0	3730.8	1580.6	3606.9	1622.3	1645.7	2696.7	3240.3	2940.9	1428.0
Graphene/CNF	1349.5	951.5	1581.4	1114.4	1623.1	590.7	2705.4	1076.5	2962.5	476.6

Table S3. Raman data of various exfoliated graphene by using different exfoliators.

Sample	I(D)/A(G)	I(2D)/I(G)	I(2D)/I(D+G)	L_a (nm)	$1/L_a$ (nm^{-1})	$I(D)/I(G)*E_L^4$ (eV^4)
Graphite	0.19126	0.7	0	86.8	0.011521	0.38866
Graphene/CMC	0.43655	0.9	2.2	38.0	0.026298	0.88712
Graphene/SDS	0.49176	0.9	2.3	33.8	0.029623	0.99931
Graphene/CNF	0.48676	1	2.3	34.1	0.029322	0.98916

Table S4. Optimization for exfoliation of graphene by CNFs with varied graphite:CNF loadings at blending speed of 37×10^3 rpm for 30 min.

Sample	a	b	c	d
Graphite:CNF feed ratio ($g\ g^{-1}$)	32.8	6.6	1.0	0.2
Graphene in graphene/CNF (wt.%)[a]	23.1	20.6	17.8	15.2
Graphene in supernatant ($mg\ mL^{-1}$)[b]	0.3	0.6	0.9	1.0
Graphene:CNF ratio ($g\ g^{-1}$)	0.30	0.26	0.22	0.18

Graphene yield (to initial loading, %)	0.5	4.0	24.8	84.2

[a]Values were determined by TGA: residual mass of graphene/CNF (at 500 ^{o}C). [b]Graphene+CNF concentration in water were determined by weighting the mass of 1 mL graphene/CNF suspension before and after drying at 50 ^{o}C for 12 h. Graphene in supernatant were calculated from data in graphene/CNF (wt.%) by 1 mg mL^{-1} = 0.1 wt.%.

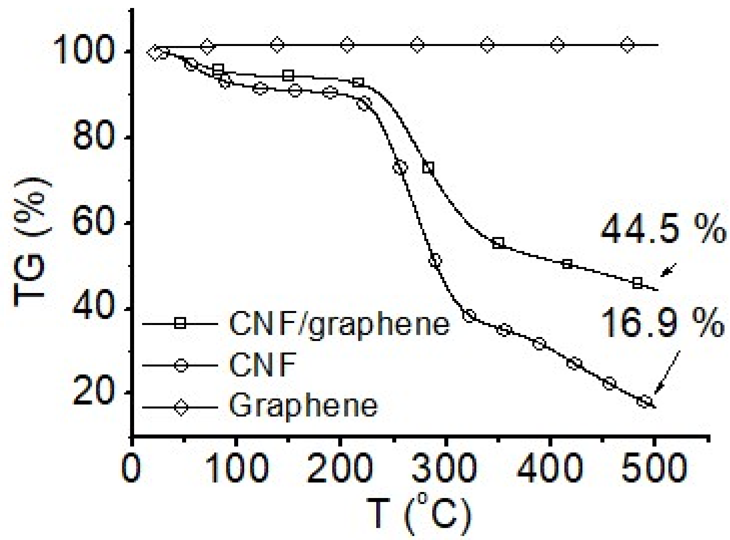

Figure S4. TGA curves of CNF/graphene nanopaper prepared as sample (a). CNF nanopaper and Graphene ones were measured to caculate the content of graphene in sample (a).

Table S5. Graphene and other sheet materials exfoliated by different dispersants.

Dispersants, additives[a] [year]	time, h	Graphene concentration, mg/mL^{-1}	Ref. title
NMP, G, soni, [2010]	1000	1.20	High-concentration solvent exfoliation of graphene [3]
SDBS+water, G [2009]	0.5	0.05	Liquid phase production of graphene by exfoliation of graphite in surfactant/water Solutions liquid phase production of graphene by exfoliation of graphite in surfactant/water

			Solutions [4]
Sodium Cholate+water, TMDs [2011]	0.5	0.06	Large-Scale Exfoliation of Inorganic Layered Compounds in Aqueous Surfactant Solutions [5]
Sodium cholate+water, G, [2010]	500	0.30	High-concentration, surfactant-stabilized graphene dispersions [6]
Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)+water, G [2012]	17.0	15	Highly concentrated aqueous suspensions of graphene through ultrasonic exfoliation with continuous surfactant addition [7]
100% H_2SO_4, CNT [2004]	3.0	0.24	Water-soluble, exfoliated, nonroping single-wall carbon nanotubes [8]
NMP, G, blending [2014]	0.5	0.10	Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids [9]
CNC+water, G, [2014]	4.0	0.20	High-concentration aqueous dispersions of graphene produced by exfoliation of graphite using cellulose nanocrystals [10]

[a] G is the graphene, CNT denotes carbon nanotubes, TMDs means transition metal dichalcogenides.

Table S6. Electrical conductivity of various CNF/graphene films prepared by blending graphite at 32.8 g g^{-1} graphite:CNF feed ratio for 30 min. V2-10 denotes variation in blending speed. V11 = 37 × 10^3 rpm.

Dial at blending	Sheet resistance （kohm sq^{-1}）	std.	Conductivity （S m^{-1}）	std.
v2[a]	6.73	0.40	5.96	0.36
v4	4.43	0.29	11.50	0.78
v6	3.57	0.15	12.76	0.55
v8	2.87	0.35	17.33	2.18
v10	1.90	0.36	38.46	6.88
v11	1.03	0.12	94.49	11.29

[a] V2-11 denotes dial settings which corresponds to .2 k, 10 k, 19 k, 24 k, 25 k, 30 k in Table S1.

S3. References

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