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Hydrolysable Tannin as Enviromentally Friendly Reducer and Stablizer for Graphene Oxide

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Materials

Natural graphite powder (purity of 99.9%) was produced by Qingdao Xinghua Graphite Co., Ltd, China. Tannin acid (TA) was produced by Fuchen Chemical Reagent Factory, Tianjin, China. Other reagents were chemical pure and used as received.

Preparation of graphite oxide

Graphene oxide (GO) was prepared according to the modified Hummers method [1]. Typically, 5 g of natural graphite powder and 2.5 g sodium nitrate were put into 115 ml of concentrated H_2SO_4 in an ice bath. With vigorous stirring, 15 g of potassium permanganate ($KMnO_4$) was slowly added to keep the temperature lower than 5°C. After a stirring for 30 min at about 35 ^{o}C, the suspension above was carefully added into 230 ml of deionized (DI) water and further stirred for about 10min. Successively, 12.5 ml of H_2O_2 aqueous solution (30%) and 700 ml of DI water were added. The obtained brilliant yellow suspension of GO was washed with diluted hydrochloric acid and with plenty of DI water until neutral. The graphite oxide paper was obtained by centrifugation at 8000 rpm and an air dry.

Preparation of reduced graphene oxide (rGO) and its paper

The suspension of graphene oxide (GO) was prepared by dispersing GO into water via sonication. After an addition of tannin acid (400 wt% relative to GO) and a sonication for 30 min, the reduction was performed for 10 h at 80 ^{o}C. Both the GO/tannin acid aqueous solution and the reduced graphene oxide (rGO) were stably dispersed without any aggregates. The paper of rGO was prepared by filtering the suspension through nylon membrane (0.22μm) and was repeatedly washed with deionized water. The dried rGO paper was obtained after peeling off the substrates. The images of rGO paper were shown in Fig S1 with an average thickness of 28 μm.

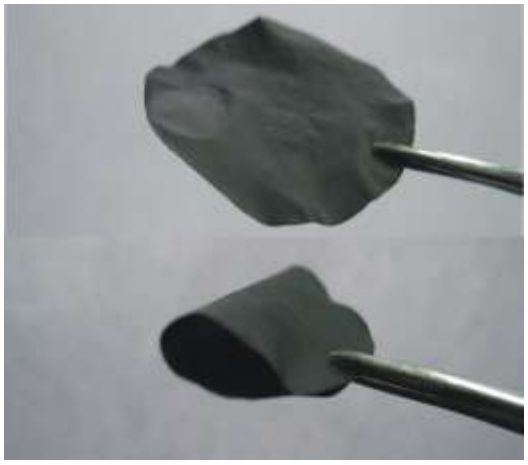

Fig S1 Images of rGO papers

A control experiment was carried out to exclude the effect of thermal treatment. The thermally treated GO (t-GO) was obtained without TA under the same condition (10 h @ 80°C). The good solubility in water and the brown appearance of t-GO (Fig S2a) imply that thermal treatment on reduction is unsuccessful. The X-ray photoelectron spectroscopy (XPS) for t-GO powder was shown in Figure S2b. According to the calculation of the peak area, the ratio of graphic carbon

atoms (CC) to oxygenic carbon atoms (CO_x) for GO, t-GO and rGO were determined to be 0.88, 0.92, and 1.21, respectively. The low CC/CO_x ratio of t-GO strongly indicates that the oxygenic groups on GO could not be effectively removed by simple heating at 80°C. It's worthy of note that the CC/CO_x ratio of rGO was undersstimated for the anchored TA on rGO, which was to be further substantiated by another experiment (Fig S3-S5).

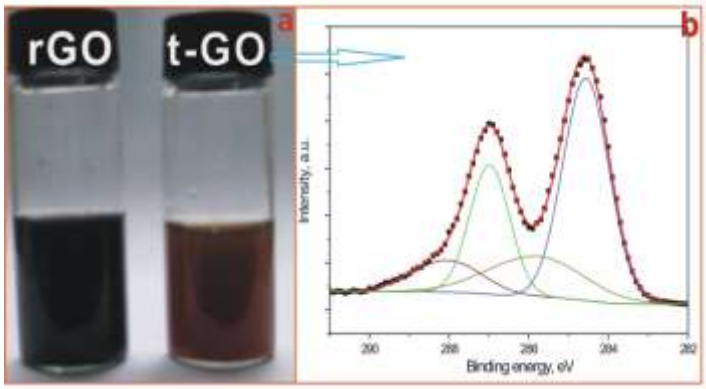

Fig S2 Appearance of suspension of rGO and t-GO (both with a concentration of 0.5 mg/ml, a) and XPS spectroscopy of t-GO (b)

TGA of rGO and w-rGO

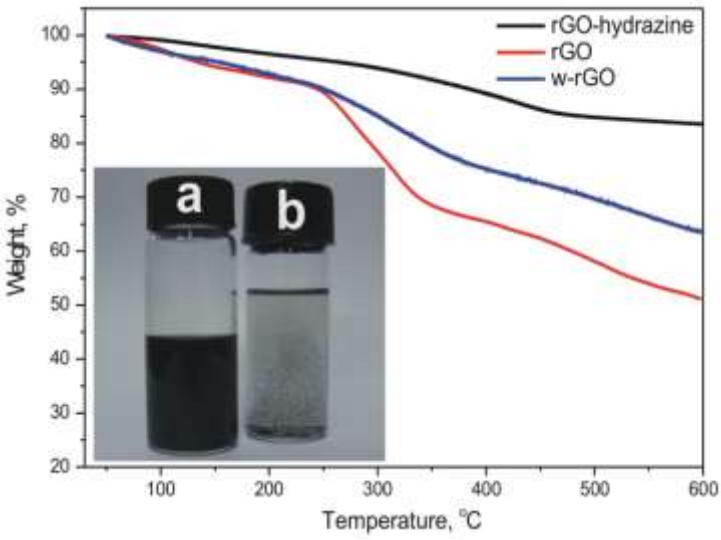

Fig S3 TGA of rGO, w-rGO and rGO-hydrazine and the dispersion of rGO (a) and w-rGO (b) in ethanol

Since the interaction between TA and graphene substantiated, some TA molecules may not be easily removed from rGO. Copious ethanol was utilized to remove TA by re-dispersing rGO paper in ethanol via sonication. The paper of washed rGO (w-rGO) was obtained by filtration and vacuum dry. Thermal gravity analysis (TGA) was conducted to estimate the content of TA in rGO and w-rGO. Comparing with the TGA of reduced graphene oxide by hydrazine (rGO-hydrazine), as shown in Fig S3, the TA content in rGO and w-rGO was estimated to be 33 wt% and 20 wt%, respectively. However, w-rGO could not be re-dispersed in ethanol (FigS3, insert). This indicates that the solubility of rGO was mainly originated from the anchored TA molecules.

Quality comparison of graphene obtained by various methods

The conductivities of reduced graphene oxide reported in the literatures along with preparation conditions, C/O and D/G ratios were summarized in Table S1.

Table S1 Quality comparison with others' results

Reducer	Loading [a]	Condition	C/O	D/G	Conductivity, S/m	Ref.
$NaBH_4$	N/A	N/A	4.78 [b]	1.91	NA	2
		Additional H_2SO_4 treatment	8.57 [b]	1.0	~500	
		Further thermal treatment 15min @1100 °C	>246 [b]	0.82	~2.0×10^4	
Fe / HCl	N/A	6h @ room temperature	7.9 [c]	0.32	2300	3
Flash		0.1-2J/cm^2	4.23 [b]	N/A	~10^3	4
HBr	>10	24h @ 110°C	3.9 [c]	0.89	0.023	5
Hydrazine	10	24h @ 100°C	10.3 [b]	N/A	200	6
Thermal treatment	N/A	1050 °C	10 [c]	N/A	1000-2300	7
KOH and hydrazine	N/A	2h @ room temperature and then reduced by 12.5wt% hydrazine	3.1 [b]	N/A	687	8
Vitamin C	50	24h @ 80°C	N/A	1.75	14.1	9
Vitamin C	10	48h @ ~23 °C	N/A	N/A	800	10
Alcohols	100	5 days @ 100°C	4.0-30.0 [b]	1.1-1.3	10^{-5}-10^3	11
TA	4	10h @ 80°C, washed by water	1.21 [c]	1.18	424.3	Present work
		Further washed by ethanol	2.44 [c]	1.15	656.7	

Note: a, weight ratio of reducer/GO; b, elemental analysis; c, by XPS.

XPS and Raman spectra of TA

To assign the oxygenic carbons in XPS spectra of rGO, the XPS spectra for TA was also recorded (Fig S4a). To exclude the effects of TA on the red shift and the calculation of D/G ratio, the Raman signal of TA was collected. In Raman scanning, a damped laser density to avoid its strong fluorescent effect (Fig S4b).

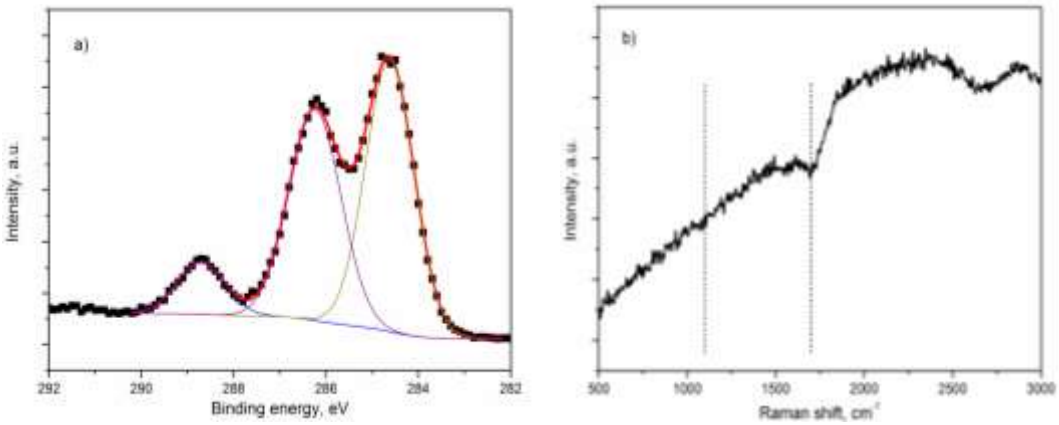

Fig S4 XPS (a) and Raman (b) of TA

Preparation of oxidized TA (o-TA)

The suspension of GO/TA (5/1, w/w) was stirred for 10 h at 80 ^{o}C. The powder of oxidized TA (o-TA) was obtained after a filtration through nylon membrane and a vacuum evaporation to remove water. Another control experiment was performed to exclude the thermal influence. The product of TA in control treatment (c-TA) was similarly obtained but without GO. Both o-TA and c-TA were characterized by Fourier transform infrared (FTIR) and XPS spectroscopy and the corresponding results were shown in Figure S5.

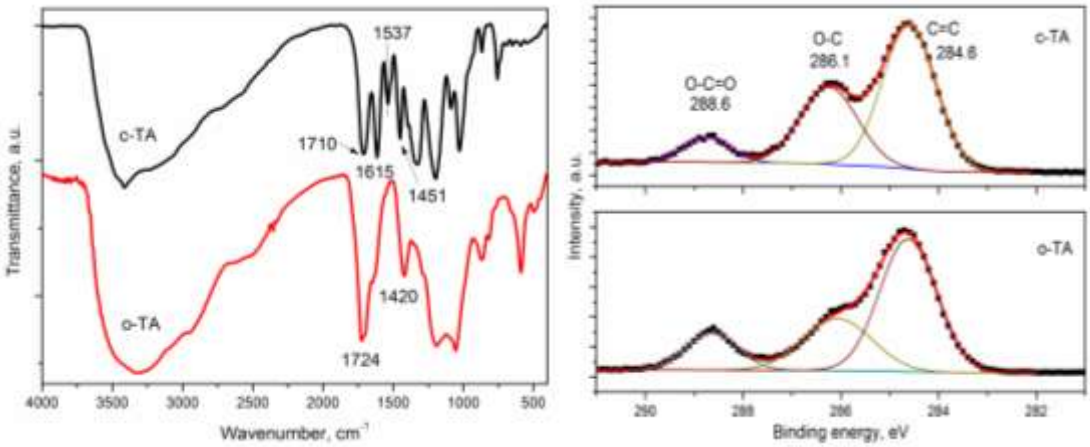

Fig. S5 FTIR (left) and XPS (right) spectra of c-TA and o-TA

Comparing with the others' FTIR results, there is no practical difference between c-TA and the pristine TA [12-14]. The absorption at 1710 cm^{-1} was related to C=O. The unsaturated aromatic bonds were located at 1615, 1537 and 1451 cm^{-1} [12, 14]. Thus, we proposed that TA molecules cannot be oxide or reduce themselves under the condition for the preparation of o-TA. According to the FTIR spectroscopy of o-TA in Fig S5a, those three characteristic aromatic bonds were changed substantially. Only an unsaturated bond at 1420 cm^{-1} was observed. The carboxyl bond at 1724 cm^{-1} was highly intensified. From their XPS spectra (Fig S5b), the content of the phenol groups was decreased from 33.5% for c-TA to 27.4 % for o-TA, indicating that phenol groups are partially consumed. According to these results, the conversion of phenols of TA into quinones by GO is convictive. Consequently, the authors strongly propose that the reducing ability of TA towards GO is originated from the phenol groups, which are converted into quinone during the reaction. The conjugated aromatic structure was broken for the o-TA molecules. Our proposed mechanism was elucidated in Scheme 1.

Characterizations

The electric conductivity of rGO paper was determined by the four-probe method using a Keithley 2635A system sourcemeter, USA. The microstructure of prepared papers of GO and rGO were directly characterized by Raman, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The t-GO sample was subjected to XPS. The Raman spectra are recorded by LabRAM Aramis of HORIBA Jobin Yvon, France. A He-Ne ion laser with an excitation wavelength of 532.8 nm is used as the illumination resource. X-ray diffraction (XRD) patterns of GO and rGO papers were recorded using a Rigaku D/max IIIA X-ray diffractometer (Japan) with Cu K_{α} radiation (λ = 1.54Å). XPS analysis was carried out on the Kratos Axis Ultra DLD X-ray photoelectron spectrometer (England) with a monochromated Aluminum Kα source

(1486.6 eV). All the XPS spectra of the samples are calibrated to the reference graphitic carbon (binding energy, 284.6 eV)[15]. AFM was conducted on a Veeco Multimode V scanning probe microscope in a tapping mode. The TGA was scanned from 50 to 600°C at 10°C/min on a TA Q5000 thermogravimetric analyzer under nitrogen atmosphere. The FTIR spectrum was collected on a Bruker Vector 33 spectrometer. The interaction between TA and rGO was characterized by UV-vis spectroscopy. The UV-vis spectra of the suspension of TA, GO, TA/GO and TA-rGO were collected on a Scinco S-3150 spectrometer, Korea.

The dispersity of re-dispersed rGO in various solvents was checked. The concentration of as-prepared rGO aqueous and the re-dispersed rGO suspensions in ethanol, DMF and DMSO were 0.5 mg/ml. The morphology of the re-dispersed rGO was further investigated by transmission electron microscopy (TEM). The suspension of the re-dispersed rGO in ethanol was diluted to 5mg/L and deposited on a cupper grid. After a vacuum dry, the observation was performed on a JEOL JEM-2010HR Transmission Electron Microscope (Japan) with an accelerating voltage of 200 kV.

References:

1. W. Hummers Jr and R. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-1339.
2. W. Gao, L. B. Alemany, L. J. Ci and P. M. Ajayan, *Nature Chemistry*, 2009, **1**, 403-408.
3. Z. J. Fan, W. Kai, J. Yan, T. Wei, L. J. Zhi, J. Feng, Y. M. Ren, L. P. Song and F. Wei, *ACS Nano*, 2010, **5**, 191-198.
4. L. J. Cote, R. Cruz-Silva and J. X. Huang, *J. Am. Chem. Soc.*, 2009, **131**, 11027-11032.
5. Y. Chen, X. Zhang, D. Zhang, P. Yu and Y. Ma, *Carbon*, 2011, **49**, 573-580.
6. S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon*, 2007, **45**, 1558-1565.
7. H. C. Schniepp, J. L. Li, M. J. McAllister, H. Sai, M. Herrera-Alonso, D. H. Adamson, R. K. Prud'homme, R. Car, D. A. Saville and I. A. Aksay, *J. Phys. Chem. B*, 2006, **110**, 8535-8539.
8. S. Park, J. An, R. D. Piner, I. Jung, D. Yang, A. Velamakanni, S. T. Nguyen and R. S. Ruoff, *Chem. Mater.*, 2008, **20**, 6592-6594.
9. J. Gao, F. Liu, Y. L. Liu, N. Ma, Z. Q. Wang and X. Zhang, *Chem. Mater.*, 2010, **22**, 2213-2218.
10. J. L. Zhang, H. J. Yang, G. X. Shen, P. Cheng, J. Y. Zhang and S. W. Guo, *Chem. Commun.*, 2010, **46**, 1112-1114.
11. D. R. Dreyer, S. Murali, Y. Zhu, R. S. Ruoff and C. W. Bielawski, *J. Mater. Chem.*, 2011.
12. M. Jastrzebska, J. Zalewska-Rejdak, R. Wrzalik, A. Kocot, I. Mroz, B. Barwinski, A. Turek and B. Cwalina, *J. Biomed. Mater. Res. Part A*, 2006, **78A**, 148-156.
13. J. Iglesias, E. G. De Saldana and J. A. Jaen, *Hyperfine Interact.*, 2001, **134**, 109-114.
14. S. Cowen and H. A. Al-Abadleh, *Phys. Chem. Chem. Phys.*, 2009, **11**, 7838-7847.
15. J. I. B. Wilson, J. S. Walton and G. Beamson, *J. Electron Spectrosc. Relat. Phenom.*, 2001, **121**, 183-201.