

Supplementary Information

Synthesis and spectral measurements of sulphonated graphene: some anomalous observations

Susmita Maiti, Somashree Kundu, Debasmita Ghosh, Somrita Mondal, Chandra Nath Roy and
Abhijit Saha*

UGC-DAE Consortium for Scientific Research, Kolkata Centre, III/LB-8 Bidhannagar,
Kolkata 700098, India; E-mail: abhijit@alpha.iuc.res.in

The FTIR spectrum of graphite oxide and sulphonated graphene is shown in Fig. S1. The spectrum for GO shows the presence of C-O (ν_{C-O} at 1097 cm^{-1}), C-O-C (ν_{C-O-C} at 1284 cm^{-1}), C-OH (ν_{C-OH} at 1401 cm^{-1}) and C=O in carboxylic acid and carbonyl moieties ($\nu_{C=O}$ at 1715 cm^{-1}).¹⁻⁴ The peak at 1613 cm^{-1} may be from skeletal vibrations of un-oxidized graphitic domains. After pre-reduction and sulphonation, SG shows the peaks at 1162 cm^{-1} , 1126 cm^{-1} , and 1035 cm^{-1} (two ν_{S-O} and one $\nu_{S-phenyl}$) confirm the presence of a sulphonic acid group, and the peaks at 1005 cm^{-1} (ν_{C-H} in-plane bending) and 830 cm^{-1} (out-of-plane hydrogen wagging) are characteristic vibrations of a *p*-disubstituted phenyl group.³

The x-ray diffraction (XRD) analysis for graphite oxide and SG are shown in Fig.S2. A typical peak near $2\theta = 9.83^\circ$ with a full width at half maximum (FWHM) of $\sim 0.93^\circ$ observed in GO corresponds to layer to layer distance (d spacing) of $\sim 0.71\text{ nm}$ and these results are consistent with the earlier reported values.^{5,6} However, compared to the starting material, GO, a significant shift of the peak to higher 2θ angles ($\sim 23.85^\circ$) with decreased d-spacing of $\sim 0.37\text{ nm}$ was observed in XRD of SG. This reduction in the d-spacing clearly indicates a more compact well ordered two-dimensional structure.^{7,8}

Fig. S3 shows the typical Raman spectra for graphene oxide (GO) and SG. The Raman spectrum of GO exhibits two prominent peaks at 1335 and 1585 cm^{-1} , which are assigned to the D band (related to the disorder induced phonon mode of vibrations of sp^3 carbon atoms) and G band (associated with the first-order scattering of E_{2g} mode for sp^2 carbon lattice of graphitic domain), respectively.⁹ SG exhibits two peaks at 1356 and 1599 cm^{-1} because of the D and G bands, respectively. Empirically, the band position can be correlated to the number of atomic layers present by the following relation.¹⁰

$$\omega_G = 1581.6 + \frac{11}{(1 + n^{1.6})}$$

where, ω_G is the position of G band in wave number and n is the number of layers present in the material. So, the number of layers present in GO and SG are about 4 and 3, respectively. Usually, the I_D/I_G intensity ratio of graphene is very useful to evaluate the structural changes during the chemical processing. In our study, the I_D/I_G intensity ratio of sulphonated graphene is 1.24 which is slightly higher than that of the graphene oxide 1.13 (Fig. S3). The observed higher ratio in SG may be attributed to the introduction of $-\text{SO}_3\text{H}$ groups to the sp^2 carbon network. Further, G band of graphene oxide shifts from 1585 cm^{-1} to 1599 cm^{-1} on sulphonation. The higher energy shift of D and G band in SG may be attributed to the anchoring of aryl sulphonic acid group to the graphene sheets causing a difficulty in the lattice vibration of sp^2 carbon.^{11,12} Thus, the Raman spectrum of SG reveals successful attachment of $-\text{SO}_3\text{H}$ groups onto the graphene surface which is in good agreement with the previous report.^{13,14} The presence of $-\text{SO}_3\text{H}$ group was also revealed through FTIR spectral measurements as described above. In addition, the observed energy dispersive spectrum (EDS) of SG (Fig.S4) confirms the presence of sulphur in the synthesized sulphonated graphene.

TEM images of GO and SG are shown in Fig. S5 (a,b). TEM images of SG and GO are transparent. It is evident that the microstructure of sulphonated graphene remains unaltered on reduction as well as sulphonation of GO. The TEM images are folded over on one edge with isolated small fragments of graphene on its surface. Also the folding at the edges is directly visible from high resolution TEM analysis. Edges or folding of layers is dominated by dark lines as they are parallel to the electron beam.¹² Insets of Fig. S5 show the wrinkles within the layers having the folded edges.

References

1. C. H. Lucas, A. J. L. Peinado, J. D. D. L. Gonzalez, M. L. R. Cervantes and R. M. M. Aranda, *Carbon*, 1995, **33**, 1585–1592
2. G. I. Titelman, V. Gelman, S. Bron, R. L. Khalfin, Y. Cohen and H. Bianco-Peled, *Carbon* 2005, **43**, 641–649.
3. N. B. Colthup, L. H. Daly, S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3rd ed.; Academic Press: London, 1990.
4. S. Stankovich, R. D. Piner, S. T. Nguyen and R. S. Ruoff, *Carbon*, 2006, **44**, 3342–3347.
5. D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii and Z. Sun, *ACS Nano*, 2010, **4**, 4806–4814.
6. H. Y. Jeong, J. Y. Kim, J. W. Kim, J. O. Hwang, J. E. Kim, J. Y. Lee, T. H. Yoon, B. J. Cho, S. O. Kim, R. S. Ruoff and S. Y. Choi, *Nano Lett.*, 2010, **10**, 4381–4386.
7. I. K. Moon, J. Lee, R. S. Ruoff and H. Lee, *Nat. Commun.*, 2010, **1**, 73.
8. K. S. B. D. Silva, S. Gambhir, X. L. Wang, X. Xu, W. X. Li, D. L. Officer, D. Wexler, G. G. Wallace and S. X. Dou, *J. Matter. Chem.*, 2012, **22**, 13941-13946.

9. A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, A. K. Geim, *Phys. Rev. Lett.* 2006, **97**, 187401 (1–4).
10. H. Wang, Y. Wang, X. Cao, M. Feng and G. Lan, *J. Raman Spectrosc.*, 2009, **40**, 1791–1796.
11. K. N. Kudin, B. Ozbas, H. C. Schniepp, R. K. P. homme, I. A. Aksay and R. Car, *Nano Lett.* 2008, **8**, 36–41.
12. M. Lazzeri and F. Mauri, *Phys. Rev. Lett.* 2006, **97**, 266407 (1–4).
13. A. Kundu, S. Nandi, R. K. Layek and A. K. Nandi, *ACS Appl. Mater. Interfaces.*, 2013, **5**, 7392–7399.
14. J. Ji, G. Zhang, H. Chen, S. Wang, G. Zhang, F. Zhang and X. Fan, *Chem. Sci.*, 2011, **2**, 484–487

Figures

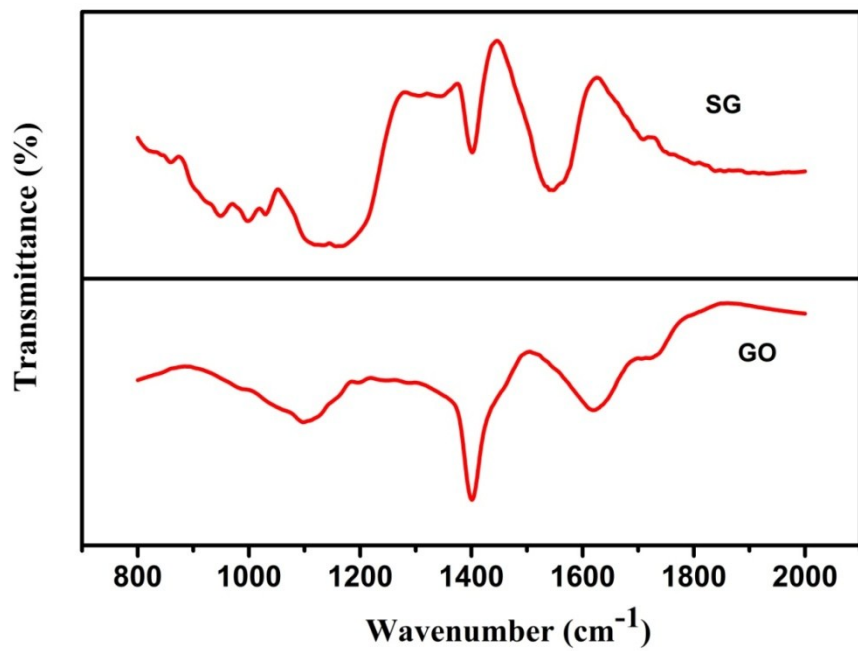


Fig. S1 FTIR spectra of GO and SG

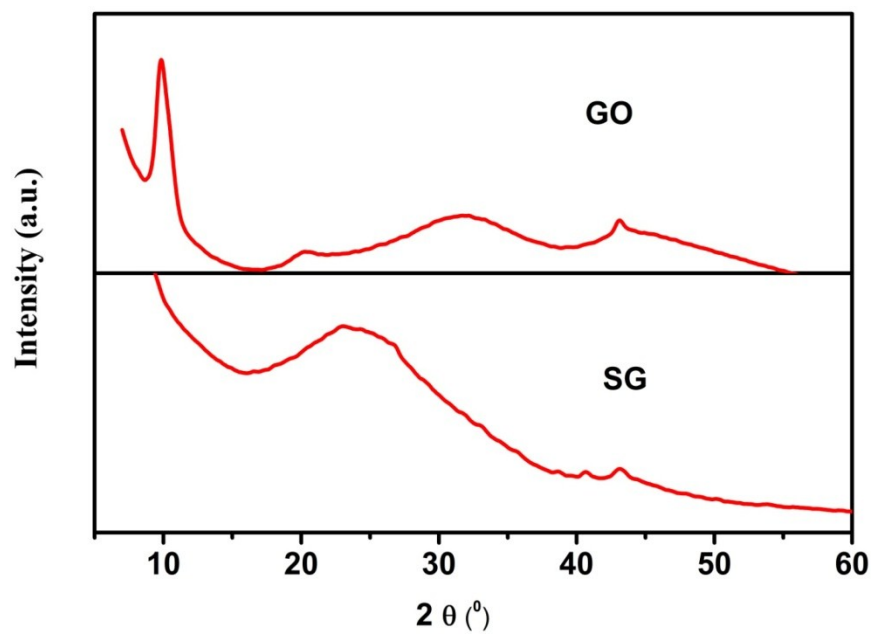


Fig. S2 XRD pattern of GO and SG samples.

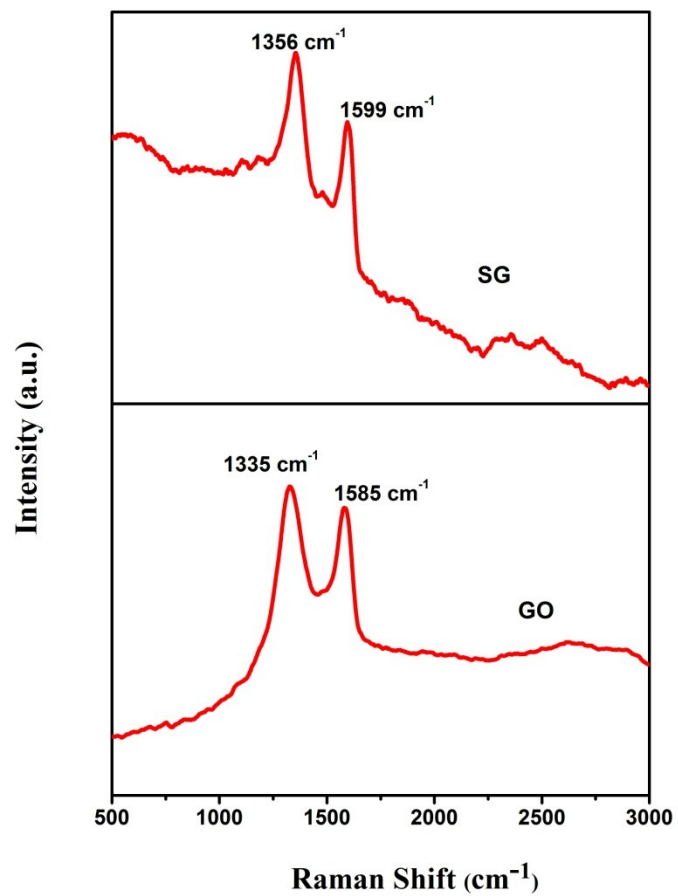


Fig. S3 Raman spectra of GO and SG

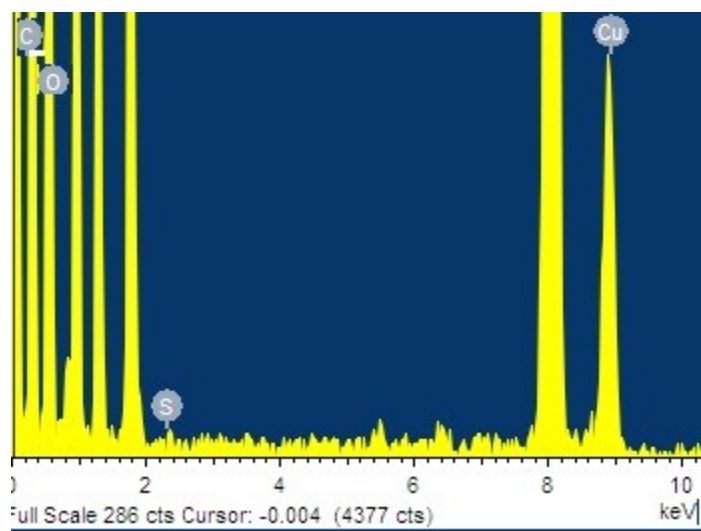


Fig. S4 EDS spectrum of SG

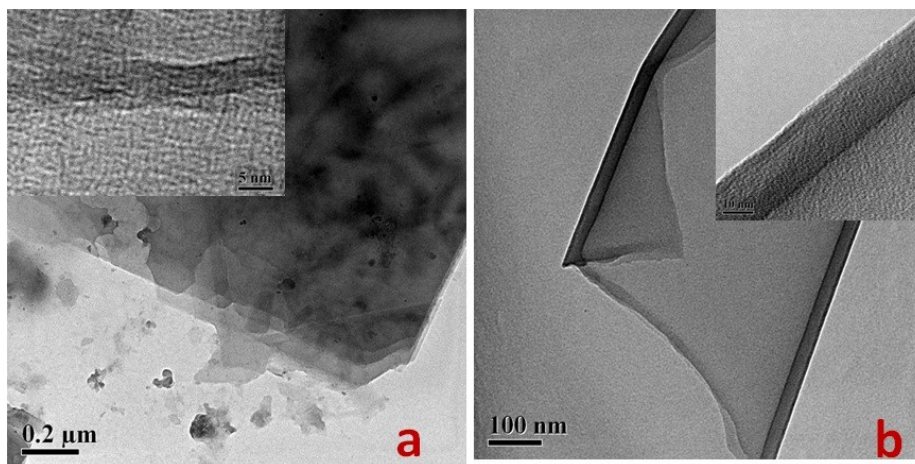


Fig. S5 TEM images of GO (a) and SG (b). High resolution images (wrinkle within the layer) of folded edge are shown in inset of (a) and (b).

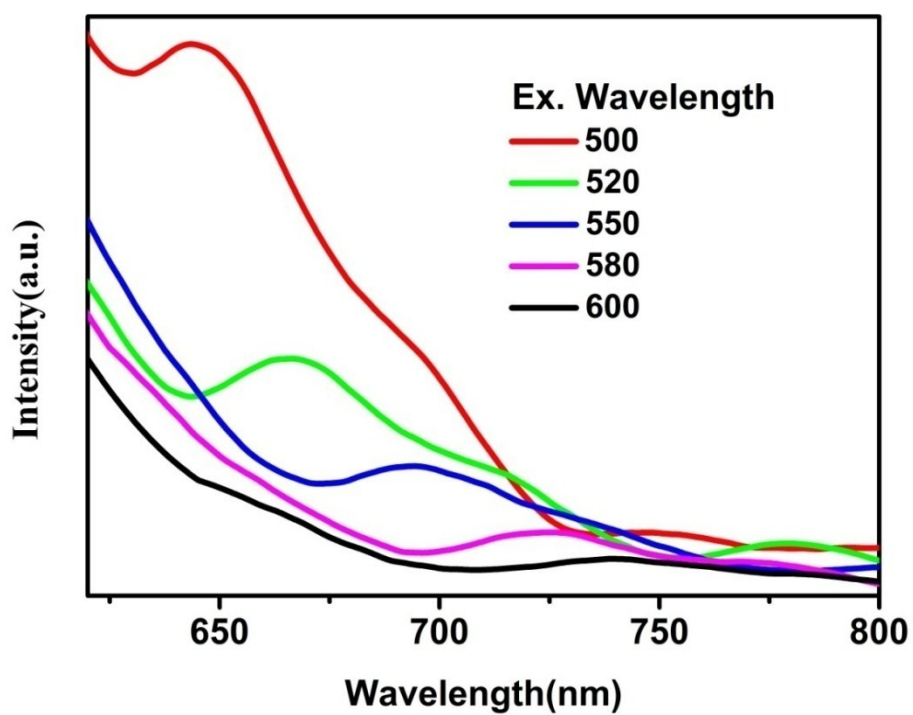


Fig. S6 Photoluminescence spectra of GO in water with excitation wavelengths in the range of 500-600 nm.