Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C. This journal is © The Royal Society of Chemistry 2016

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C. This journal is © The Royal Society of Chemistry 2016

# **Electronic Supporting Information**

## Formation Mechanism of Graphene Quantum Dots and Its Edge State Conversion Probed by Photoluminescence and Raman Spectroscopy

Gone Rajender<sup>a</sup> and P. K. Giri<sup>a, b,\*</sup>

<sup>a</sup>Department of Physics, Indian Institute of Technology Guwahati, Guwahati 781039, India <sup>b</sup>Centre for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati 781039, India

### SI-1: Synthesis of reduced graphene oxide (rGO)

The rGO is synthesized following a previous report<sup>1</sup>. In brief, GO (50 mg) was mixed with 50 ml of DI water. This mixture was transferred to a ultra-sonication bath and sonicated for 10 min to form uniform solution. Further, 500  $\mu$ L of hydrazine monohydrate (Alfa Aesar, 99%) was then added to the solution and heated in an oil bath at 100 °C for 24 h, over which the reduced GO gradually precipitated out as a black solid. Subsequently, the precipitate was separated from the solution and washed several times with DI water and methanol. Finally, filtered product was dried in an oven to obtain the rGO powder.

#### SI-2: Synthesis of graphene quantum dots (GQDs) from rGO

The synthesis of GQDs using rGO as precursor material is same as described in the synthesis section of GQDs. In brief, 50 mg of rGO powder was mixed with 50 ml of DI water and was sonicated for a few minutes to achieve a uniform dispersion. Next, the mixture was transferred into a Teflon lined autoclave (100 ml) and heated at 200 °C for 12 h.

<sup>\*</sup> Corresponding author: Prof. P. K. Giri; Email: giri@iitg.ernet.in; phone no.: +91 -361- 258 2703.



Fig. S1. TGA profile of OGO sample showing the decomposition temperature of ~200 °C. Inset shows the corresponding DTG curve of OGO.



Fig. S2. TEM images of GO (a) before and (b) after oxidation with  $H_2SO_4$  and  $HNO_3$  mixture; (c) corresponding digital photographs of GO dispersed in water and (d) the photographs of GO after oxidation with  $H_2SO_4$  and  $HNO_3$ . The insets in (a) and (c) show the corresponding SAED patterns, which signify the lattice distortion due to the attachment of functional groups. (e-f) TEM images of few layered rGO sheet and GQDs synthesised using rGO as a precursor material, respectively. The inset in each case shows the corresponding SAED pattern for highly crystalline sp<sup>2</sup> carbon hexagonal structure.



Fig. S3. (a) UV-Vis absorption spectra, and (b) FTIR spectra of OGO and rGO. (c) TGA/ DTG profile of rGO, showing weight loss mostly due the presence of epoxy/C-O (ether), COOH, C=O related functional groups and sp<sup>2</sup> hybridized carbon.



Fig. S4 Raman spectral features of S12, S12H, S12O samples without (left panel) and with (right panel) peak fitting. Note that 632.8 nm laser excitation is used for the Raman measurements. Some of the spectrum are magnified by appropriate factors to enable comparison. The experimental data are shown with symbol and the fitted data are shown with red line. The new Raman bands D1, D2, and D3 correspond to the sp<sup>2</sup>-sp<sup>3</sup> carbon, COOH/C-OH and C=O/C-O edge functional groups, respectively.



Fig. S5 Room temperature steady state PL spectra of various GQDs thin films before and after ( $H_2$  and  $O_2$ ) annealing. (a) Comparison of PL spectra and Gaussian peak fitting for S12, S12H and S1FO GQDs thin films (left panel). (b) Comparison of PL spectra and Gaussian peak fitting for S24F, S24FH and S24FO GQDs thin films (right panel). The PL is excited with 355 nm laser source. Note that P1 and P2 are significant for the zig-zag and armchair edge states, while P3 and P4 signify the COOH/C-OH and C=O/C-O edge functional groups, respectively. All the peak positions are in nm units. The experimental data are shown with symbols and the fitted data are shown with red line in each case.



Fig. S6. Raman spectra of S24 sample before and after annealing in  $H_2$  and  $O_2$ . Note that the 514.5 nm laser excitation is used for the Raman measurement. The vertical dotted lines are guide for the different Raman peaks.

Table T1. Summary of fitting parameters for Raman bands of various GQDs thin films before and after annealing. The new Raman bands, D1, D2 and D3 are fitted with Gaussian peaks, while the well-known D, G and D' bands are fitted with Lorentzian peaks.

Sample	Peak position in cm <sup>-1</sup>						Intensity ratio				
	Dl	D2	D	D3	G	D'	$I_{D1}/I_G$	$I_{D2}/I_G$	$I_D/I_G$	$I_{D3}/I_G$	$I_D / I_G$
S12	1187	1260	1334	1438	1577	1610	0.05	0.13	0.70	0.10	0.33
S12H	1187	1260	1334	1438	1577	1610	0.28	0.36	2.27	0.72	1.18
S12O	1180	1253	1332	1436	1572	1610	0.57	0.28	2.59	1.44	0.48
S12F	1185	1260	1333	1440	1577	1609	0.19	0.22	0.83	0.16	0.19
S12FH	1185	1260	1334	1438	1574	1608	0.25	0.24	1.56	0.35	0.44
S12FO	1185	1260	1333	1440	1573	1610	0.45	0.28	1.08	0.91	0.43
S24	1185	1262	1332	1436	1574	1609	0.20	0.18	1.07	0.39	0.23
S24H	1185	1260	1333	1435	1577	1608	-	0.25	1.75	0.35	0.68
S24O	1185	1260	1333	1438	1577	1610	0.47	0.27	1.62	0.95	0.54
Peak Identity	sp <sup>2</sup> -sp <sup>3</sup> carbon	СООН /С-ОН	Zig-zag/armchair states	<i>C=0/C-0</i>	<i>C=C</i>	Crystalline defects					

Sample		Atomic percentage (%)								
	<i>C</i> = <i>C</i>	Ether (C-O)	C=0	СООН	π-π*	<i>C=C</i>	Ether (C-O)	C=0	СООН	<i>π- π</i> *
S24	284.50	286.14	287.50	290.00	293.70	39	22	10	13	16
S24H	284.50	286.10	287.50	290.00	293.99	52	9	10	12	17
S24O	284.59	286.10	287.60	289.80	293.80	42	7	20	9	22

Table T2. Summary of fitting parameters for core level C1s XPS spectrum of S24, S24H and S24O samples.

### **References:**

1. 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.