Supporting Information

Understanding enhanced electrical property of free-standing graphene paper: Synergistic effect of iodide adsorption into graphene

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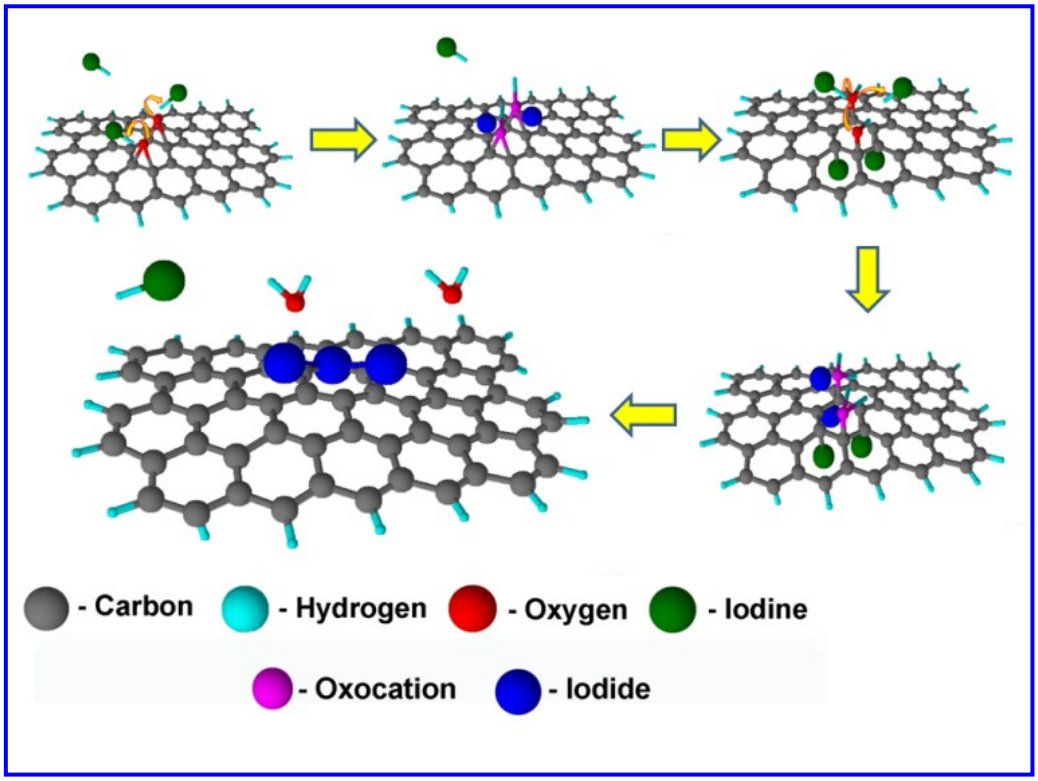

Scheme S1: Schematic diagram for reduction mechanism of graphene oxide in hydroiodic acid.

Reduction time (hr)	Thickness of FSG (µm)	Sheet resistance (Ω/□)
0.5	2	180
	3	120
	10	123
1	2	23.5
	3	8.8
	10	9.1
24	2	24.1
	3	9.3
	10	10.4

Table S1: Effect of sheet resistance w.r.t thickness of FSG and concentration of GO colloids.

Measurement of sheet resistance by four-probe technique:

The current source were applied at outer probes, in the meantime, the voltage were measured byinner two probes. Since the spacing between the probes is at equal distance, the surfaceresistivity can be obtained directly [1].The FSG was sliced with thedimension of 1 x 1 cm^2 and determined the sheet resistance using the following equation (1);

$$R_S = 4.53\left(\frac{V}{I}\right) \text{.....(1)}$$

The factor 4.53 arises, as the thickness of the film is lower than the probe distance.Thus by applying 4.53 mA, the sheet resistance is equivalant to the voltage exerted by the FSG paper.

Measurement of sheet resistance and electrical properties by Hall-effect measurement setup:

Van der pauw method was utilized to measure the sheet resistance and electrical properties. The samples were prepared by applying silver paste at the corners of fabricated FSG papers for an electrical contact. Four consecutive measurements were performed by applying current at two adjacent corners and the voltage was measured repeatedly at other corners to ensure the uniform resistivity. The sheet resistance was measured by the following equation;

$$R_s = \frac{\pi R_{(AD,BC,AB,CD)}}{In\ 2} \text{.....(2)}$$

The bulk carrier concentration and hall co-efficient was calculated by applying 0.5 Tesla of magnetic field (B) perpendicularly to the FSG sample and simultaneously 1 mA of dc current (I) is also applied.

$$n_s = \frac{8 \times 10^{-8} IB}{q(V_{AD,BC,AB,CD})}$$

$$Bulk\ carrier\ concentration\ (N_c) = \frac{n_s}{t} \text{.....(3)}$$

$$V_H = \frac{I \times B}{n \times e \times t}$$

$$Hall\ Co-efficient\ (R_H) = \frac{V_H \times t}{I \times B}$$

$$R_H = \frac{1}{n \times e} \text{.....(4)}$$

Raman spectra of FSG:

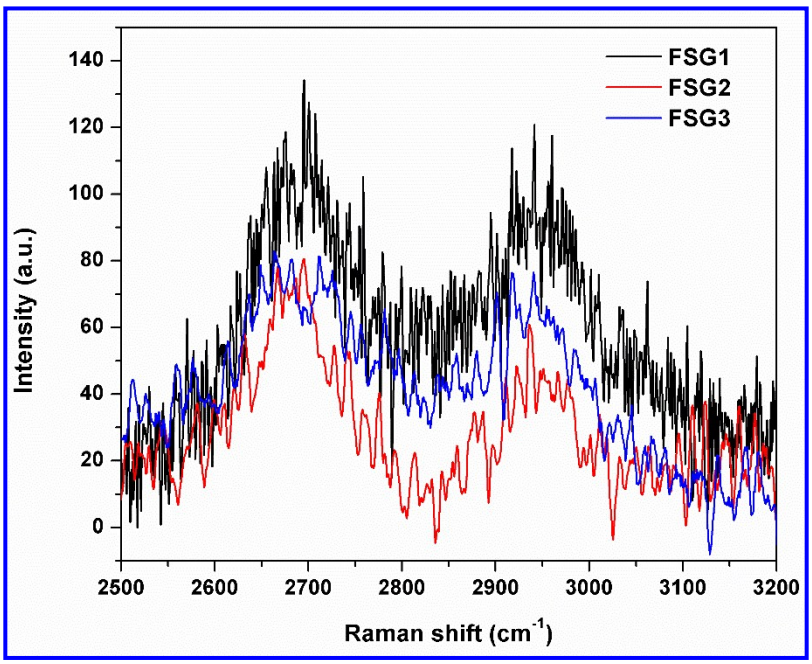

Figure S1: Raman spectra of FSG samples (2D and D+G bands).

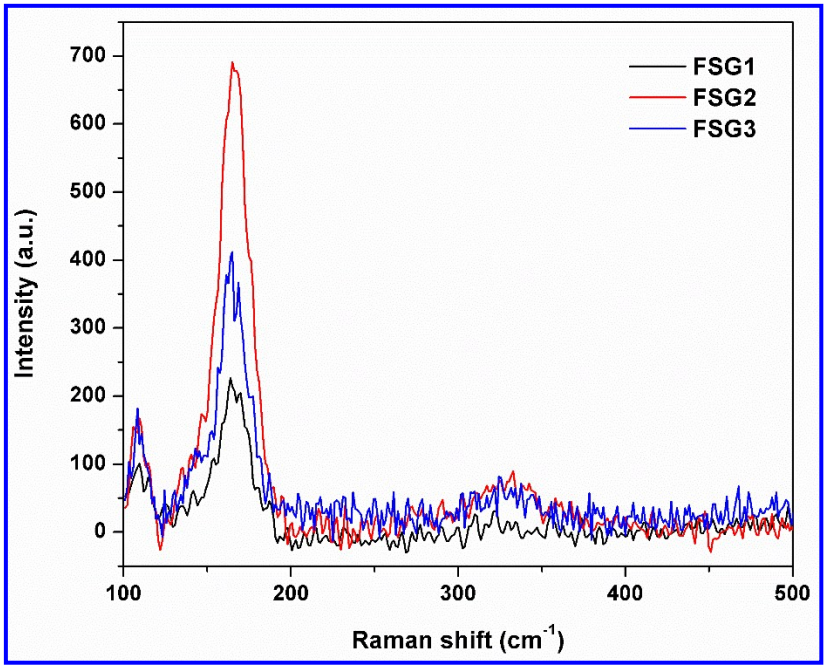

Figure S2: Raman spectra of FSG samples (iodide peaks).

Figure S3 shows the presence of polyiodides in FSG paper after reduction treatment. The peak at 112 cm-1 assigned to the symmetrical stretching modes of triiodies and peak at 160 cm-1 resembles the symmetric stretch of iodine molecules combined with tri-iodides to form polyiodides [2].

Electronic Band structure

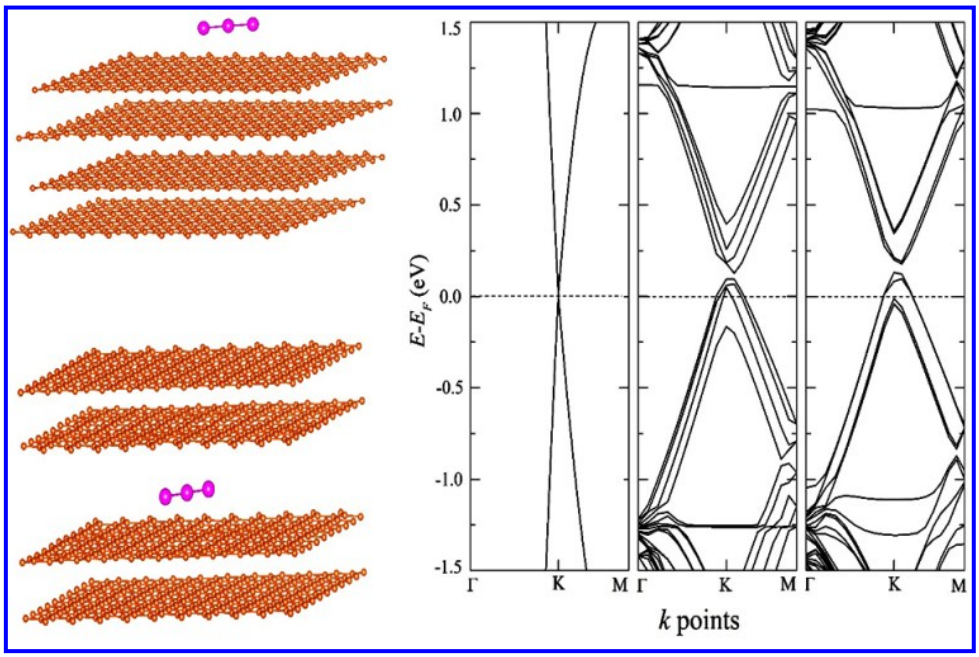

Figure S3:DFT analysis of triiodide adsorbed 5×5 supercell of graphene with four-layer thickness

It is well understood by structural analysis that HI treated GO paper reduced to sp^2 carbon by leaving polyiodide species in FSG and provides good electrical conductivity. Further to understand the interaction between the polyiodides and graphene sheets, DFT analysis was performed as shown in Figure S3. First principles calculations on triiodide adsorbed 5×5 supercell of graphenewith four-layer thickness are performed to understand and explain the experimental observations. Within the considered structure model, two different triiodide adsorptions namely, on the surface and between the interlayer are chosen as shown in Figure S1. Optimized structures disclose that the distances between the triiodide and graphene layer are 3.9 and 3.42 Å fortriiodide adsorbed at surface and interlayers, respectively. This results that triiodide molecule at the surface is interacted withweekVan der Waals force than that in the interlayers. At the same time, ground state energy values of these two structures show that 18.7 meV is greater for triiodide intercalated structure than the surface.

The gained energy in this structure is due the stronger interaction of iodide molecule in the interlayers. But the value of gains energy is small as compared to the room temperature.Therefore, it suggests that triiodide molecules can be simultaneously adsorbed at both surface as well as at the interlayers of the graphene sheets with small external triggering. Electronic band structures reveal that edges of the valence band of graphene in both structure models move toward the conduction band when compared to pristine graphene and it leads to the generation of holes at the edges of the valence band. Also, graphene sheets with iodide molecules at the interlayer produce more hole-carriers than the iodide molecules at the surface. Therefore, these calculations infer that the iodide molecule intercalated graphene sheets generates p-type charge carries to show the higher conductivity.

Estimation of Optical band gap:

The correlation between the absorption coefficient of allowed indirect and direct transition opticalband gap can be determined by the equation

$$\alpha E \approx A(E - E_{gap})^{1/2} \text{ Indirect transition}$$

$$\alpha E \approx A(E - E_{gap})^{2} \text{ Direct transition}$$

where, E = hν (photon energy) and A is constant.

$$Kubelka - Munk\ [F(R)] = \frac{(1-R)^2}{2R} = \frac{k}{s} \quad \text{.....(5)}$$

where, F(R) is the Kubelka−Munk function, R is the experimentally obtained reflectance of the sample, k is the molar absorptioncoefficient, and s is the scattering coefficient. Using the relationship of the above equations;

$$[h\nu\, F(R)]^{1/2} = A[h\nu - E_{gap}] \quad \text{.....(6)}$$

$$[h\nu\, F(R)]^{2} = A[h\nu - E_{gap}] \quad \text{.....(7)}$$

By extrapolating the linear fiiting of the tauc plot for the abovesaid equation, the indirect and direct allowed transition optical band gap was determined by the equation (6) and (7) respectively.

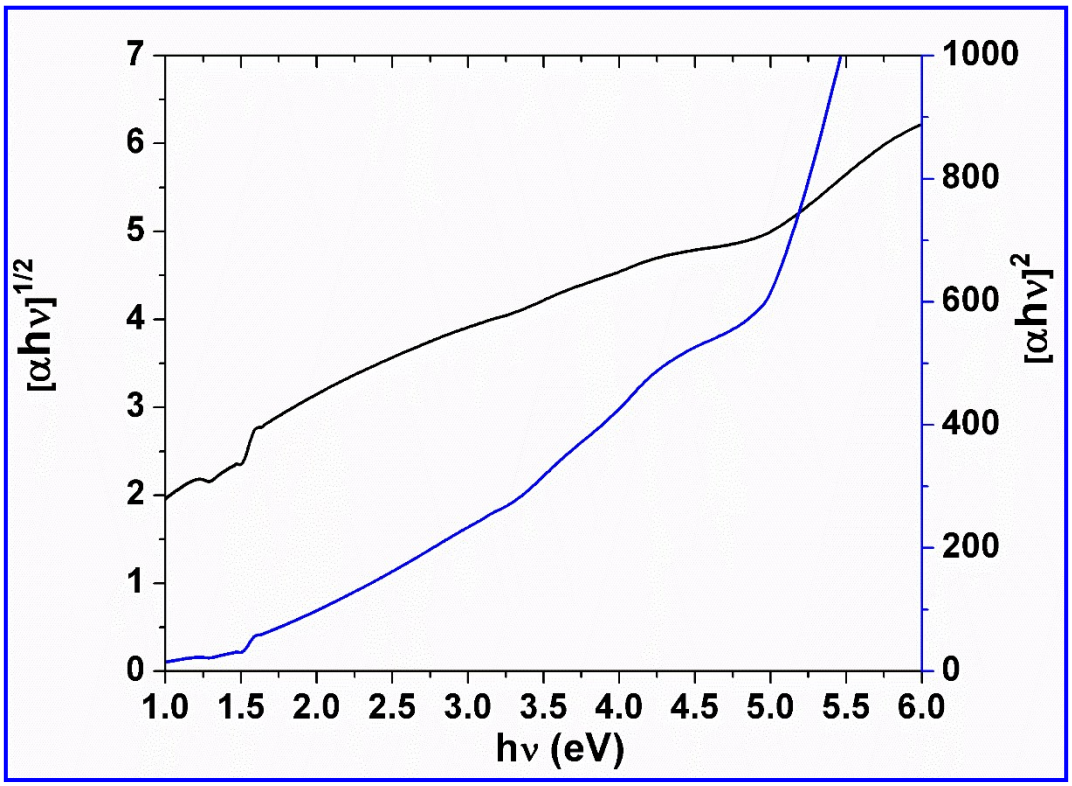

Figure S4: Tauc plot of GO paper in both the transition state (indirect and direct allowed transition)

Electrocatalytic activity of FSG:

The electrocatalytic activity towards triiodide reduction is an important factor in dye-sensitzed solar cells. In commercial, platinised FTO is used as counter electrode and further, the graphene based electrodes replaced it. Specifically, the heteroatom doped graphene as counter electrode enhance the performance of DSSC due to the excellent catalytic behaviour. Generally, the doped graphene has better electrocatalytic behaviour than the pristine graphene [3]. The adsorption of triiodide is higher in the case of pristine graphene and thus the poor performance. Based on this, the iodide adsorbed graphene shows p-type character and hence it should function triiodide reduction effectively. Herein，we conducted cyclic voltammetry for bare FSG and platinised FSG to understand the triiodide interaction. Figure S5 shows the cyclic

voltammetry of bare FSG and Pt/FSG electrodes in triiodide redox couple electrolyte that consist of 0.1 M $LiClO_4$, 10 mM LiI_2 and 1 mM of I_2.

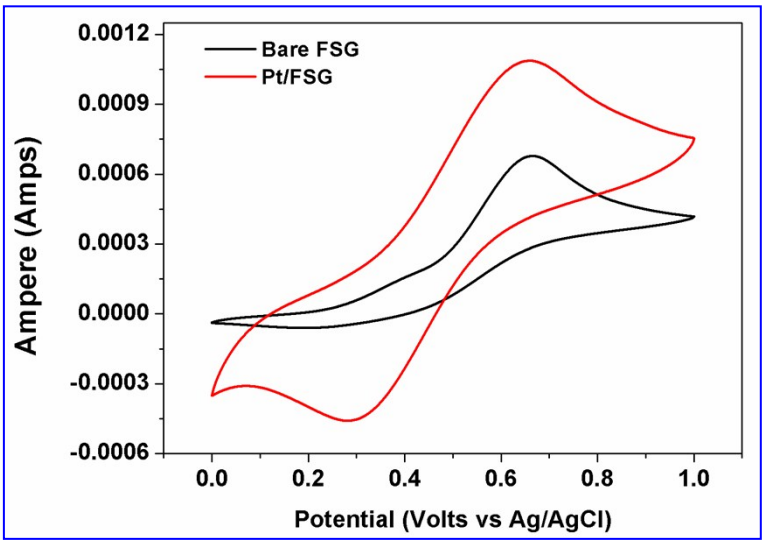

Figure S5: Cyclic voltammogram of FSG and Pt/FSG in triiodide/iodide redox couple electrolyte with scan rate of 50 mV/s.

The triiodide redox couple is assigned to the redox reaction of I^-/I_3^- at 0.6 V vs Ag/AgCl and I_3^-/I^- at 0.28 V vs Ag/AgCl. But the triiodide reduction reaction of bare FSG is not found and it may due to the adsorption of triiodide and hinders to charge transfer. This result is well correlated with other characterization and it confirms a triggering between the iodides and graphene.

Reference:

[1] Yoshiyuki S, Toshiya O, Mineharu S, Tomoyasu K, Shigeo K. Development of fine-pitch four point probe for high spatial resolution of sheet resistance measurement. J. Surf. Anal. 2004;11:58-61.

[2] Jing XL, Jun L,Ji-Fei F, Bahar K, JianL,Rong C. Iodine uptake and enhanced electrical conductivity in a porous coordination polymer based on cucurbit[6]uril. Inorg. Chem. Front., 2016;3:1393-7.

[3] Shaocong H, Xin C, Hongwei W, Xiao Yu, Ming P, Kai Y, Dechun Z. Nitrogen-doped graphene for dye-sensitized solar cells and the role of nitrogen states in triiodide reduction. Energy Environ. Sci., 2013;6:3356-62.