Supplementary Information

Modulation of the electrostatic and quantum capacitances of few layered graphenes through plasma processing

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I. Calculation of the space charge capacitance (C_{sc}) and the quantum capacitance (C_Q)

The plasma processing of the few layer graphene (FLG) samples was considered to increase the carrier density of the graphene, giving rise to an increase in measured capacitance from the CV measurements - Table I and Figure 2(a). In order to analytically model this increase, it was necessary to consider the constituent capacitances (all normalized per unit area), *i.e.*, the space-charge capacitance: C_{sc} , and the quantum capacitance: C_Q , in terms of an *equivalent* carrier density.

The measurement for the FLG represents accumulated responses from each of the individual layers. A major influence in accounting for the charge densities of the individual layers is the *screening*, starting from the layer closest to the electrolyte, which shields the internal layers of the FLG from the charges in the electrolyte and implies a diminishing electrical

potential from the outer to the inner layers of the FLG. Consequently, the carrier density in the single layer of graphene closest to the electrolyte is considered to be: $n_{2D,0}$. The carrier density of each subsequent layer would typically be scaled down by an exponential factor $\sim \exp(-x/\lambda)$, where λ is an *appropriate* screening length¹, *e.g.*, a Debye length or a Thomas-Fermi screening length (see Section I. b). The need to consider various types of λ as well as the possibility of *nonlinear screening* in FLG systems has been previously reported².

a. Estimating the carrier density in the layer, closest to the electrolyte: $n_{2d,0}$, and the E_F

A quantitative discussion of $n_{2D,0}$ requires derivation starting from the energy (E) dependent density of states: $D(E)$, of graphene. While the inter-layer interaction in FLG has been implicated in a nonlinear energy dispersion, *e.g.*, a hyperbolic dispersion for bilayer graphene³, we approximate that in the vicinity of the Fermi energy (E_F), a linear energy dispersion relation of the form: $E = \hbar v_F k$, where $\hbar$ is the reduced Planck constant ($=1.05 \times 10^{-34}$ Js), v_F is the Fermi velocity - typically in the range of $c/300$, where c is the velocity of light^{4,5}, and k as the wavevector, could be considered to gain useful insights⁶. Consequently, the two-dimensional DOS would be:

$$D(E)dE = \frac{4}{(2\pi)^2} 2\pi k dk \Rightarrow D(E) = \frac{2}{\pi} \frac{E}{(\hbar v_F)^2} \quad (S1)$$

In our analyses, the v_F has been determined from the Raman analysis (see Figure 3(b) in the main text), and k refers to the wave-vector. We calculate $n_{2D,0}$ from:

$$n_{2D,0} = \int_0^{E_F} f(E) D(E) dE = \int_0^{E_F} D(E) dE = \frac{1}{\pi} \frac{1}{(\hbar v_F)^2} E_F^2 \quad (S2)$$

where $f(E)$ is the Fermi-Dirac function, and is assumed to be unity for the far right hand side of the above relation. Such an assumption is valid if the Fermi energy (E_F) of the first layer is more

than $3k_B T$ away from the Dirac point (denoted by $E = 0$). Indeed, in line with estimates of $n_{2D,0}$ of $\sim 5 \times 10^{12} \text{ cm}^{-2}$, in practical graphene⁷ and graphite⁸, the E_F is of the order of 0.25 eV, which is much greater than $\sim 78 \text{ meV}$ ($=3k_B T$ at 300 K: room temperature, at which the experiments were done). The extension of such SLG based approximations to FLG has been previously noted in literature³.

b. Choice of appropriate screening length and the estimation of the space charge capacitance: C_{sc}

Through the use of Maxwell's equation for the change in the potential ($\Delta\phi$), of the form: $\nabla^2(\Delta\phi) = -\Delta\rho/\epsilon$, where $\Delta\rho$, is the change in the charge density ($= e dn$), with e as the unit of elementary electronic charge due to the change in the number of contributing carriers dn and ϵ being the dielectric permittivity of the graphene ($=5.7 \epsilon_o$) with ϵ_o as the vacuum permittivity ($=8.854 \times 10^{-12} \text{ C}^2/\text{Nm}^2$), one may derive an *effective* screening length (λ), assuming that ϕ varies as $\exp(-x/\lambda)$. Consequently, the solution of the Maxwell equation yields:

$$\lambda = \sqrt{\frac{\epsilon}{e^2} \left(\frac{dE}{dn} \right)} \quad \text{with } dE = e\Delta\phi \quad (\text{S3})$$

A Boltzmann approximation, whereby the volumetric charge density: $n = n \exp(E/k_B T)$ and $dn/dE = n/k_B T$, yields the Debye screening length (λ_D). However, in graphene, with $n_{2D,0} \sim E_F^2$ the (dn/dE) evaluated at $E=E_F$ is equal to $(2n/E_F)$ and results in an alternative screening length of the Thomas-Fermi form: λ_{TF} .

$$\lambda_{TF} = \sqrt{\frac{\epsilon}{e^2} \frac{E_F}{2n}}, \text{ with } C_{sc} = \frac{\epsilon}{\lambda_{TF}} \quad (\text{S4})$$

where n is set to be equal to $(n_{2D,0})^{3/2}$. Consequently, the C_{sc} is estimated to ϵ/λ_{TF} .

c. Estimation of the quantum capacitance: C_Q

The implication of the λ_{TF} is that the charge on any subsequent (say, l^{th}) layer (counted from the outermost graphene layer, facing the electrolyte, with carrier concentration: $n_{2d,0}$ into the current collector) would be:

$$n_{2d,l} = n_{2D,0} \exp(-lx/\lambda_{TF}) \quad (S5a)$$

Figure S1: While the constituent charge (Q) in the individual layers of the FLG is discrete, the carrier concentration from the outermost layer into the current collector was modeled through a continuous exponential decay.

The “ x ” was obtained from the experimentally determined spacing between the layers, through Atomic Force Microscopy (AFM) measurements and was estimated to be ~ 1 nm: Figure S2.

Figure S2: Atomic Force Microscopy (AFM) indicating the typical thickness of the investigated FLG samples. The figure on the right indicates a 5+-1 layer FLG as has also been corroborated through electron diffraction studies (unpublished data).

Schematically, the magnitude of the charge in the layers of our FLG films would be as indicated in Figure S1. The sum of the net *discrete* charge on the individual layers, *i.e.*, $\sum_{i=0}^N n_{2D,i}$

would contribute to the quantum capacitance, through:

$$C_Q = d \left(= e \sum_{i=0}^N n_{2D,i} \right) / dV = e^2 D(E_F) \quad (\text{S5b})$$

d. The variation of $n_{2D,0}$ for fitting the experimental values to C_Q and C_{sc}

For fitting the experimental values of the experimentally measured capacitance (C_{meas}) to C_Q and C_{sc} , we varied n_{2D0} for each plasma power until the combined series capacitances, estimated from Eqns. (4) and (5) match the experimental values. It is found that the values of n_{2D0} begin at $4.5 \times 10^{12}/\text{cm}^2$, which is in good agreement with contemporary literature on carrier concentrations in intrinsic graphene^{6,7,9} as well as through interpolation from bulk graphite⁸.

Table S1. The values of the two-dimensional carrier density ($n_{2D,0}$), the Thomas-Fermi screening length (λ_{TF}) the sum of sum of the net *discrete* charge on the individual layers ($\sum n_{2D,i}$) and the volumetric charge density (n) were fit to the measured capacitance (C_{meas}) at a given plasma power (P) to yield the space-charge capacitance (C_{sc}) and the quantum capacitance (C_Q) through using Eqns. (1), (2), and (3) in the main text incorporating the relations in Eqns. S4 and S5.

P	C_{meas}	C_{sc}	C_Q	$n_{2D,0}$	n	λ_{TF}	$\sum n_{2D,i}$
W	$\mu\text{F}/\text{cm}^2$	$\mu\text{F}/\text{cm}^2$	$\mu\text{F}/\text{cm}^2$	$(\times 10^{12})\text{cm}^{-2}$	$(\times 10^{19})\text{cm}^{-3}$	nm	cm^{-2}
0	1.9 ± 0.7	2.5	9.1	4.5	1.0	2.0	11
5	2.3 ± 0.3	3.2	11.0	7.1	1.9	1.6	15
10	4.3 ± 0.7	7.3	20.3	37	22	0.7	48
20	4.7 ± 0.7	8.4	23.1	43	29	0.6	54
35	4 ± 0.3	6.6	19.6	28	15	0.8	38
50	3.1 ± 0.5	5.0	14.2	19	8.5	1.0	31

e. Experimental indication of enhanced capacitance in SLG due to the plasma processing

We have also considered plasma processing of SLG (single layer graphene) to further delineate the capacitance contributions. The SLG film would not be expected to have contributions to the measured capacitance from the C_{SC} and any increase of the measured capacitance may be attributed solely to an enhanced C_Q : from Eqn. (3). Indeed, we have observed a concomitant increase in the capacitance of the SLG: Figure S3.

Figure S3 Cyclic Voltammetry (CV) scans on (i) untreated/*pristine*, and (ii) plasma processed (@ 5 W) single layer graphene (SLG). The increase in the measured capacitance, from $\sim 2.0 \mu\text{F}/\text{cm}^2$ to $\sim 5.9 \mu\text{F}/\text{cm}^2$ may solely be attributed to an enhanced quantum capacitance (C_Q).

We may then conclude, with much more confidence, the effectiveness of the plasma processing treatment in enhancing the overall capacitance, as discussed originally in the paper.

II. Estimation of the charge-correlation length: L_d

We have noted a charge correlation length: $L_d \sim \frac{1}{\sqrt{n_{2D,0}}}$ as noted in Table I, which may

be understood as the average distance between the charged defects (that could have arisen due to the plasma induced charges) that contribute to the C_Q as well as the C_{SC} . It was observed through simulations, that with an applied electrode bias (~ -100 V) and an ion density¹⁰ of the order of $10^{11} / \text{cm}^3$, the average ion penetration depth would be ~ 0.8 nm, which implies that only the first

layer of the FLG would be affected through the plasma processing. Consequently, only the $n_{2d,0}$ is being considered for the L_d .

III. XPS (x-ray photoelectron spectroscopy) analysis of samples subject to argon and hydrogen plasma processing treatment

Through a preliminary XPS study, we have found that there is very little evidence of the contribution of the surface functional groups, and we have also safely ruled out any substantial contribution to the net capacitance.

Previous plasma treatment work, involving, for example, the treatment of activated fibers with *oxygen* plasma¹¹, has found the substantial presence of quinone groups (involving C=O bonds), that may contribute to additional redox capacitance. To circumvent such complications, we have initially considered only *Ar based plasma*, specifically chosen due to the inherently simple plasma chemistry (where only Ar^+ ions are involved) and *avoids* quinone group formation. Consequently, in our data/study, there are absolutely no redox capacitance associated phenomena (as there is no associated peaks in the CV scan): see Figure 2(a).

Figure S3 (a) Carbon associated peaks, indicating the pristine graphene – *control*, argon irradiated FLG – *Ar*, which was subsequently treated with hydrogen plasma – *H₂*. There is no

evidence of quinone functionality (no peak at 287.6 eV) in the *Ar* and the H_2 plasma modified samples. **(b)** The increased oxygen content (as seen through the peak at ~ 532.4 eV in the *Ar* and the H_2 samples) is indicative of saturated C-O bonds.

Additionally, while XPS analyses on the Ar plasma irradiated samples did indicate an enhanced oxygen content, there was *absolutely* no evidence of quinone functionality (C=O related peaks). The increased oxygen content may have occurred due to exposure to ambient and it was noted that the oxygen is bound up in a C-O saturated bond and *not* in a unsaturated C=O configuration.

We also note from the XPS measurements before and after the hydrogen plasma treatment (Figure S2) that the oxygen content seems to have been *reduced* due to the treatment – see Figure S2(b). A concomitant increase (/decrease) of the C 1s (/O 1s) peak intensity was observed due to the hydrogen plasma treatment, which indicates the partial effectiveness of the hydrogen treatment, as noted originally.

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