

Supplementary Information for
Heterogeneous Charge Transfer at the Amorphous Carbon/Solution Interface: Effect on the
Spontaneous Attachment of Aryldiazonium Salts

Deirdre M. Murphy, Ronan J. Cullen, Dilushan R. Jayasundara, Richard L. Doyle, Michael E.G. Lyons
and Paula E. Colavita *

School of Chemistry, University of Dublin Trinity College, College Green, Dublin 2, Ireland.

Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), University of Dublin
Trinity College, Dublin 2, Ireland

Bulk characterization of amorphous carbon films via Raman spectroscopy

The bulk properties of our various carbon materials were characterized using Raman spectroscopy. Spectra were fitted using a combination of a Breit-Wigner-Fano and a Lorentzian peak as proposed by Ferrari et al. The sp^2 content was estimated from the height ratio of the D and G peaks (I_D/I_G) according to the three stage model of Raman spectra of amorphous carbon proposed by Robertson and coworkers.¹⁶

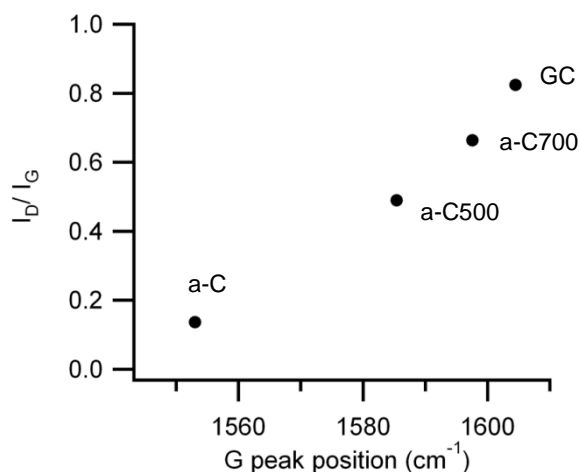


Figure S11. Plot of peak height ratios I_D/I_G ratios vs. G peak position of as prepared amorphous carbon (a-C), amorphous carbon after annealing at 500 °C (a-C500) and 700 °C (a-C700) for 1 h, and of glassy carbon (GC).

Optical characterization of amorphous carbon films

The Tauc bandgap of amorphous carbons is a useful parameter in order to characterize amorphous carbon films; we used UV-Vis absorption measurements in order to obtain this value, following methods previously described.¹² The absorbance of carbon films was recorded from 200-890 nm in order to calculate the absorptivity a ; Tauc plots of $(\alpha h\nu)^{1/2}$ vs. photon energy ($E=h\nu$) were then used as shown in Figure SI.2 in order to calculate the intercept at the energy axis, yielding the Tauc bandgap value.

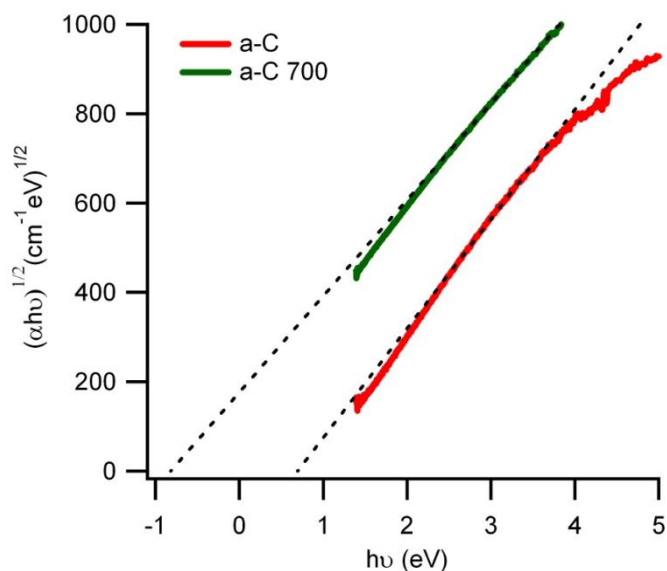


Figure SI.2: Typical Tauc plots of as prepared amorphous carbon films (a-C) and after annealing at 700 °C (a-C700).

Intercalation measurements using 4NBA

Figure SI.3 shows characteristic CVs of glassy carbon (GC) and annealed a-C700 electrodes following 4NBA intercalation, carried out in 0.1 M H₂SO₄ at 0.2 V s⁻¹. The integrated charge associated with Ar-NO₂ reduction (approximately -0.4 V vs. ref.) and Ar-NHOH oxidation peaks (approximately 0.3 V vs. ref) were integrated to obtain the estimated surface coverage for intercalated 4NBA. Values of surface coverage (Γ_{NBA}) of $(19.5 \pm 1.8) \times 10^{-10}$ mol cm⁻² and $(6.2 \pm 1.7) \times 10^{-10}$ mol cm⁻² (95% C.I.) were obtained for annealed a-C700 and GC electrodes, respectively.

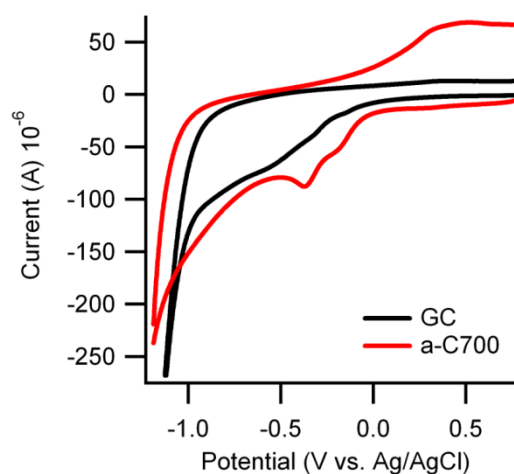


Figure SI.3: Cyclic voltammetry of annealed a-C700 and GC electrodes modified via partial intercalation of 4NBA in acetonitrile solution, measured in 0.1 M H₂SO₄ at 0.2 V s⁻¹.

Atomic Force Characterization of bare and modified carbon samples

We carried out AFM characterization of bare and functionalized carbon samples in order to identify differences in surface morphology among these surfaces. Root-mean-square (RMS) roughness values for bare and aryldiazonium modified surfaces are given below in Table SI.1. Substrates were modified *via* immersion in 0.1 mM aqueous solutions of the aryldiazonium salts for 1 h and subsequently rinsed gently with water. A decrease in roughness is expected upon modification with aryldiazonium salts as previously reported.²¹

	RMS roughness (nm)		
	bare	4NND	5NND
a-C	1.40 ± 0.07	1.01 ± 0.03	0.98 ± 0.06
a-C700	1.31 ± 0.13	1.01 ± 0.06	1.07 ± 0.14

Table SI.1 RMS roughness values for bare and modified carbon substrates measured using AFM.

XPS Characterization of 4NND and 5NND adlayers

Previous work from our group had shown that the surface coverage determined via in situ methods (ATR-FTIR and quartz crystal microbalance) contains contributions from both physisorbed and chemisorbed molecules (see Ref. 21 in the main text). Therefore only a certain portion of molecules at the surface in spontaneously adsorbed layers have actually undergone dediazonation. In order to investigate whether 4NND and 5NND also led to mixed physi/chemisorbed layers we carried out XPS characterization of 4NND and 5NND modified surfaces at early reaction times. Samples were characterized after a gentle water rinse; this method has been shown to leave most of the adsorbed layer intact, thus allowing for the determination of chemical composition of adsorbed aryldiazonium layers.

Figure SI.4a and SI.4b show the N 1s region of 4NND and 5NND adlayers, respectively, deposited from 100 μ M solutions on a-C samples for 5 min, after a gentle aqueous rinse. XP spectra display two peaks

with maxima centered around 406 and 400 eV; the peak at 406 eV is assigned to -NO_2 groups, whereas the broader peak at 400 eV can be attributed to the presence of -N=N- moieties. The expected $A_{400} : A_{406}$ peak area ratio for molecules that adsorb with a diazo-group intact is 2 : 1; therefore, the ratio $(A_{400}/2) : A_{406}$ provides an estimate of the proportion of molecules that have not undergone nitrogen elimination (dediazonation) upon adsorption. A fit of the peaks at 406 and 400 eV in Figure SI.4 yielded estimates of 33% and 71% for the proportion of 4NND and 5NND molecules, respectively, that had undergone dediazonation upon adsorption. This indicates that in the case of 4NND the vast majority of molecules eliminate nitrogen and therefore are expected to be chemisorbed at the surface at early times. In the case of 5NND, on the contrary, the vast majority of the molecules have not undergone dediazonation and are therefore expected to remain weakly physisorbed at the carbon surface.

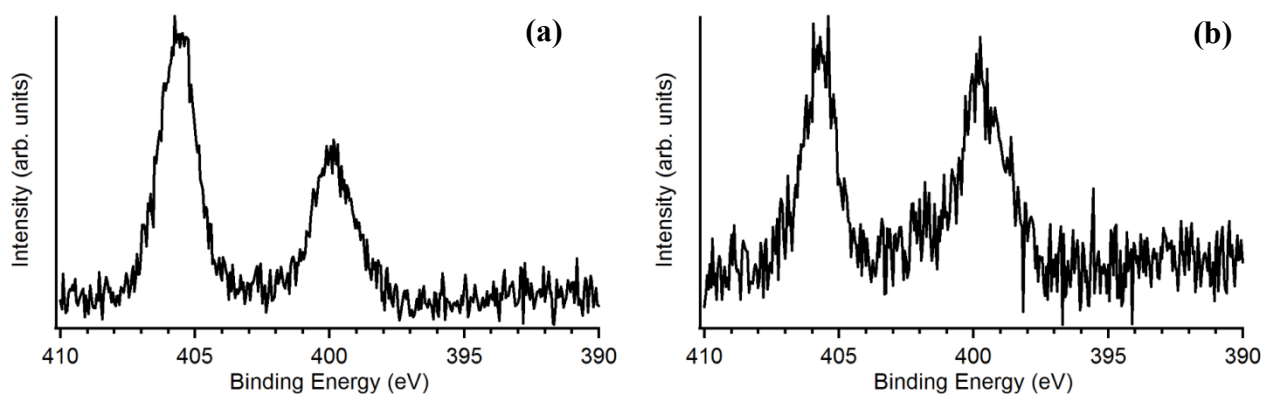


Figure SI.4: XP spectra in the N 1s region of 4NND (a) and 5NND (b) adlayers at a-C samples. Layers were prepared via immersion of the surfaces in 0.10 mM solutions of the aryldiazonium salt for 5 min, followed by gentle rinsing in water.

Ultraviolet photoelectron spectroscopy (UPS) of carbon surfaces

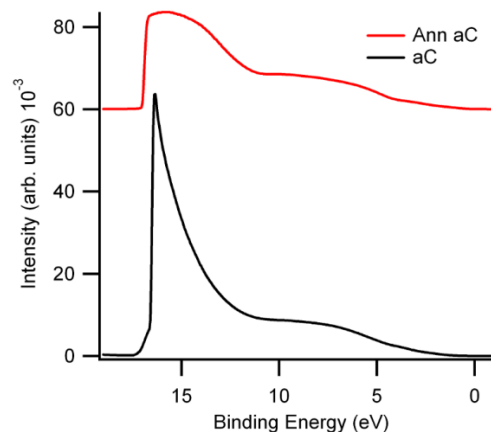


Figure SI.5: Normalized UPS spectra of annealed a-C700 and as deposited a-C surfaces.

Impedance spectra of a-C and a-C700 electrodes

The high frequency region of the complex plane impedance (Nyquist) plots for a-C and a-C700 carbon electrodes are shown in Figure SI.6. A modified Randles circuit was found to give the best fit with an average χ^2 value of 0.05. In this equivalent circuit the resistance R_s represents the electrolyte resistance; the parallel combination of the constant phase element (CPE_p) and a resistance (R_{CT}) represent the double layer capacitance and the charge transfer resistance, respectively; finally, the Warburg element (W) models the diffusional impedance. Best-fit parameters are reported in Table SI.2.

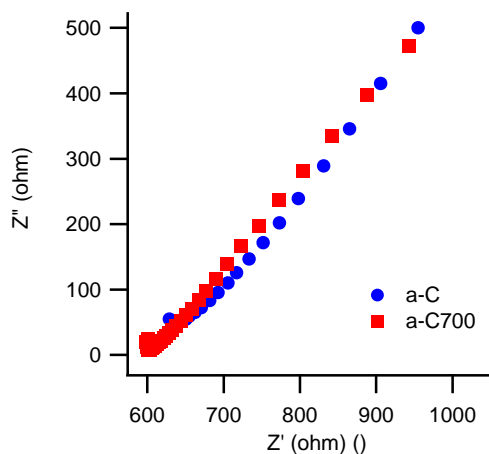


Figure SI.6: Comparison of EIS spectra of a-C and a-C700 substrates at high frequency.

	a-C	a-C700
R_{CT}	7.35 k Ω	39.7 Ω
R_s	654 Ω	603 Ω
W	264 γ_0	207 γ_0
CPE_p	4.3 μ Mho	111 μ Mho

Table SI.2: Summary of best-fit parameters obtained from EIS data for a-C and a-C700 electrodes in 0.0010 M $Ru(NH_3)_6^{+3/+2}$ aqueous solutions in 0.1 M KCl as supporting electrolyte.

Impedance spectrum of annealed amorphous carbon (a-C700) and glassy carbon (GC)

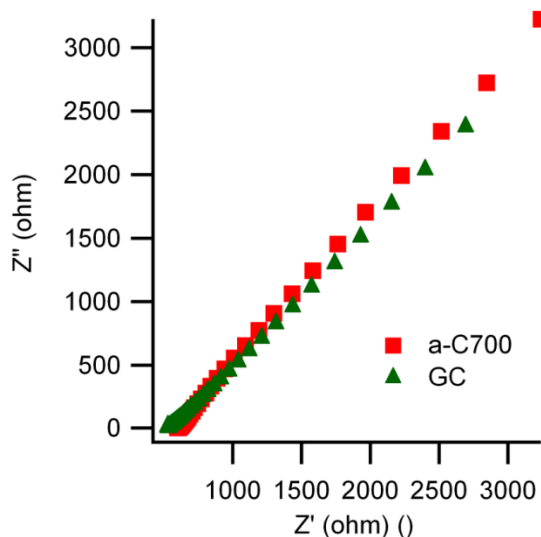


Figure SI.7: EIS spectrum of a-C700 and commercially available glassy carbon (GC) substrates.

Formal potentials of redox species vs. Standard Hydrogen Electrode (SHE) and vs. vacuum

	4NND	5NND	$Ru(NH_3)_6^{3+/2+}$
E_{redox} (V) vs. SHE	0.29 ± 0.01	0.04 ± 0.02	0.03 ± 0.002
E_{redox} (V) vs. vacuum	-4.72 ± 0.01	-4.47 ± 0.02	-4.46 ± 0.002

Table SI.3: Summary of electrochemical potentials of redox species used in our experiments referenced to SHE and to the vacuum level.