Supporting information

Covalent Functionalization of Carbon Surfaces: Diaryliodonium versus Aryldiazonium Chemistry

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1. Cyclic voltammetry (CV)

To obtain the peak current, which provides an estimate of the number of reduced molecules during electrolysis, the first CV cycle of each tested concentration was considered. Nova 2.14. software with its automatic peak search tool was used to find the peak and extract the peak current. The automatic search mode uses a linear tangent for the baseline.



Figure S1. Overview of the first CV cycles for all tested concentrations of Ar₂-I and Ar-D.



Figure S2. The first CV cycle for of **Ar**₂-**I** (3 mM, left) and **Ar**-**D** (3 mM, right). The arrows indicate graphically the determination of the peak current (I_p) after peak fitting.



Figure S3. Cyclic voltammograms showing passivation of the electrode surface at for **Ar-D** and **Ar₂-I**. The concentration of both precursors is 0.1 mM.



Figure S4. Representative AFM height images of the concentrations not shown in the main text.



Figure S5. Variation in the surface coverage (%) as a function of the concentration of **Ar**₂**-I** and **Ar-D** obtained from AFM measurements.

AFM scratching of the covalently grafted films for estimation of thickness

Contact-mode AFM was used to locally remove the film on HOPG at a constant vertical tip force. All cantilever spring constants (nN/nm) were calibrated before each experiment applying a thermal single harmonic oscillator model. Force curves allowed extraction of the deflection optical lever sensitivity (nm/V) from the slope of repulsive part in the force curve. Both parameters combined allow to determine the setpoint (V) required for a given force. For each sample, 4 scratches (Figure S5a) of 250×250 nm² were created at a constant vertical force (100 nN) at a scan rate of 1.5 Hz, 96 points/lines. Figure S5b, c displays a representative scratched square highlighting a clean, flat graphite pit surrounded by a rough, high edge that is formed as a result of the accumulation of the material removed from grafted film. The film thickness was then calculated by fitting gaussian curves through the peaks present in the height histogram of the topographic image and obtaining the difference between the two peaks.



Figure S6. Calculation of layer thickness from AFM de-grafting experiments. (a). Four 250×250 nm² scratches performed on the covalent film obtained from 1 mM **Ar-D**. (b). A magnified image showing the top left scratch. (c). A line-profile through the scratch presented in panel (b). (d). Histogram of topographic height for the AFM image presented in (a) with gaussian fittings on both peaks. The layer thickness is thus the difference the peak positions read from the X-axis.



Figure S7. A control experiment demonstrating the non-destructive nature of scratching protocol towards HOPG itself. In this experiment, the scratching was performed across a graphite stepedge. (a) A set of four 250×250 nm² scratches performed on the covalent film obtained from 1 mM **Ar**₂-**I.** Note that the top-right square is scratched across a graphite step edge. (b) A digital zoom of the square scratched across the step edge. If the vertical force applied during scratching was detrimental to the graphite films, one expects to observe a peeling of the graphene layer. (c). A line-profile showing a clean/flat graphite step edge after the scratch is performed.









Force required to remove the covalent films obtained from Ar2-I and Ar-D

Figure S9. Determination of the force required to remove the grafted layers. AFM topography images showing $250 \times 250 \text{ nm}_2$ scratches made for a range of constant forces for the two systems. **[Ar₂-I] = [Ar-D] =** 7mM. Image size = $400 \times 400 \text{ nm}_2$. It can be readily noticed that the force required to remove the covalently attached film is higher for **Ar₂-I** that that required for **Ar-D**. Given the similar chemical composition of the films in the two scenarios, we attribute this difference to the layer property namely, the compactness of the films.



Figure S10. XPS survey spectrum for grated films obtained from 2 and 10 mM **Ar**₂**-I** and **Ar-D** on HOPG substrates.

	Concentration /% at.					
Sample	F 1s	I 3d	0 1s	N 1s	C 1s	Cl 2p
Ar-D (2 mM)	0.42 ± 0.06	-	8.94 ± 0.12	4.32 ± 0.15	86.26 ± 0.18	0.06 ± 0.02
Ar-D (10 mM)	0.34 ± 0.06	-	10.11 ± 0.13	4.68 ± 0.14	84.83 ± 0.18	0.05 ± 0.01
Ar₂-I (2 mM)	0.34 ± 0.06	0.03 ± 0.01	8.69 ± 0.14	3.27 ± 0.15	87.66 ± 0.19	-
Ar 2- I (10 mM)	0.30 ± 0.07	0.08 ± 0.01	10.57 ± 0.14	4.17 ± 0.15	84.84 ± 0.19	0.04 ± 0.02

Table S1. Elemental composition of covalently modified HOPG samples.



Figure S11. High resolution I 3d XPS spectra 2 mM (left) and 10 mM (right) Ar₂-I modified HOPG.

Sample	Component	Binding energy /eV	FWHM /eV	Conc. /% at.
Ar₂-I (2 mM)	I- j=5/2	620.7	1.11	0.02
	I- j=3/2	632.2	1.11	0.01
Ar₂-I (10 mM)	I- j=5/2	620.5	1.15	0.04
	I- j=3/2	632.0	1.15	0.03

622.5

634.0

1.32

1.32

0.01

0.01

Table S2. Data obtained from the high resolution XPS spectra in the iodine 3d region for Ar₂-I.

Table S3. High resolution XPS spectra in the nitrogen 1s region for Ar₂-I and Ar-D.

C-I j=5/2

C-I j=3/2

Sample	Component	Binding energy /eV	FWHM /eV	Conc. /% at.
Ar-D (2 mM)	-NH2, -N=N-	400.1	1.41	1.02 ± 0.12
	-NH3+, -N2+	402.2	1.41	0.20 ± 0.13
	-NO2	405.9	1.41	3.09 ± 0.23
Ar-D (10 mM)	-NH2, -N=N-	399.8	1.37	1.06 ± 0.15
	-NH3+, -N2+	401.3	1.37	0.33 ± 0.12
	-NO2	405.8	1.37	3.29 ± 0.23
Ar₂-I (2 mM)	-NH2	399.6	1.24	0.29 ± 0.10
	-NH3+, -N2+	402.3	1.24	0.17 ± 0.12
	-NO2	405.9	1.24	2.81 ± 0.23
Ar₂-I (10 mM)	-NH2	399.6	1.31	0.36 ± 0.10
	-NH3+, -N2+	401.5	1.31	0.23 ± 0.09
	-NO2	405.7	1.31	3.57 ± 0.22



Figure S12. High resolution XPS analysis of the covalently grafted films obtained using 10 mM **Ar-D** and **Ar₂-I**. (a, b) Nitrogen 1s and carbon 1s spectra for **Ar-D**. (c, d) Nitrogen 1s and carbon 1s spectra for **Ar₂-I**.

Sample	Component	Binding energy /eV	FWHM /eV	Conc. /% at.
Ar-D (2 mM)	Graphitic	284.4	1.00	53.19 ± 1.21
	C-C/C=C	285.1	1.43	21.87 ± 0.65
	C-N	286.4	1.43	5.90 ± 0.31
	C=0	288.1	1.43	1.01 ± 0.18
	π* ←π	291.1	4.78	4.29 ± 0.70
Ar-D (10 mM)	Graphitic	284.4	1.00	49.23 ± 1.01
	C-C/C=C	285.0	1.36	22.45 ± 0.70
	C-N	286.3	1.36	6.69 ± 0.32
	C=0	288.0	1.36	1.26 ± 0.15
	π* ←π	291.0	5.05	5.21 ± 0.66
Ar 2-I (2 mM)	Graphitic	284.3	1.00	54.85 ± 0.88
	C-C/C=C	285.1	1.42	23.22 ± 0.69
	C-N	286.4	1.42	5.21 ± 0.24
	C=0	288.1	1.42	0.98 ± 0.14
	π* ←π	291.3	4.26	3.39 ± 0.55
Ar 2-I (10 mM)	Graphitic	284.4	1.00	46.49 ± 0.97
	C-C/C=C	284.9	1.39	26.32 ± 0.59
	C-N	286.3	1.39	6.63 ± 0.38
	C=0	288.0	1.39	1.03 ± 0.16
	π* ←π	291.2	4.45	4.37 ± 0.67

Table S4. Data from the high resolution XPS spectra in the carbon 1s region for Ar₂-I and Ar-D.



Figure S13. Overview of STM current images of the concentrations not shown in the main text. Imaging parameters: Tunneling current (I_t) = 0.05 nA, Sample bias (V_s) = -0.8 V.

Protocol for STM imaging and analysis Imaging:

As discussed in the main text, STM imaging of thick grafted samples results in tip instability and/or removal of grafted molecules (also see Figure S16 below). Therefore, on every new area probed, an overview scan ($200 \times 200 \text{ nm}_2$, Figures S12a) was performed. The next scan was performed by zooming in to a $100 \times 100 \text{ nm}_2$ area (Figure S12b) in the center of the previous scan. In this way the imaging instability is reduced to a minimum. Each of such $100 \times 100 \text{ nm}_2$ image was used to calculate the number density of the grafted molecules. Although this protocol cannot completely exclude removal and gives an underestimation of the grafting density, it allows a systematic approach to qualitatively determine the grafting density at the nanometer scale. The protocol applied on 10 macroscopic different area's by manually moving the sample stage.



Figure S14. Protocol for recording STM images on grafted HOPG substrates. [**Ar**₂-**I**] = 10 mM. (a). A 200 × 200 nm₂ overview scan. (b). The second STM scan at zoomed in approximately at the center of the overview scan measuring 100 × 100 nm₂. Imaging parameters: Tunneling current (I_t) = 0.05 nA, Sample bias (V_s) = -0.8 V.

Analysis:

STM current images were used to analyze the number density due to their higher contrast compared to the topography images. The number density was calculated using the particle and pore analysis tool of the Scanning Probe Imaging Processor (SPIP 6.3.5) software from Image Metrology Aps. A particle diameter of 0.3 nm was used as a threshold to exclude spikes from the analysis.



Figure S15. Estimation of the grafting density at the nanometer scale using STM data. The figure displays an STM current image obtained from an HOPG substrate modified using 10 mM **Ar**₂-**I**. The colored particles are generated from the SPIP particle and pore analysis software after employing a diameter threshold of 0.3 nm. Imaging parameters: $I_t = 0.05$ nA, $V_s = -0.8$ V.



Figure S16. A sequence of STM images showing the gradual removal of grafted nitrophenyl groups upon successive scanning of the same area. In going from panel (a) to (b) to (c), the number of particles present on the HOPG surface is reduced from $276\rightarrow 273\rightarrow 203$, respectively. **[Ar₂-I]** = 3 mM.

5. Raman spectroscopy analysis



Figure S17. Intensity ratio (*I*_{D/G}) Raman map of 3 mM **Ar**₂-**I** modified HOPG.

6. Control measurements

As a control experiment, one HOPG sample was subjected to CV with a acetonitrile solution containing only the supporting electrolyte. The cyclic voltammogram of this 'blank' sample exhibited no reductive peak and the Raman spectrum showed no D-peak.



Figure S18. (a) CV performed using acetonitrile containing the supporting electrolyte without the grafting precursors on HOPG. (b) Raman spectrum of the control sample showing absence of the D-peak. The spectrum of HOPG modified using 3 mM **Ar**₂-**I** is overlaid for the sake of comparison.



Figure S19. The stability of covalently modified HOPG substrate over time. Raman spectrum 2 days after modification (black) and 6 months after modification (red) showing negligible changes.