Supporting information for

In situ and real time characterization of spontaneous grafting of aryldiazonium salts at carbon surfaces

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AFM characterisation of pNBD adlayer homogeneity

Figure SI-1 shows Atomic Force Microscopy (AFM) height images in tapping mode of pNBD-coated a-C:H after (a) 2 min and (b) 60 min of immersion in a 100 µM pNBD aqueous solution. Roughness analysis indicates that samples obtained after pNBD adsorption for 2 and 60 min display rms roughness values of (1.7±0.1) nm and (1.81±0.1) nm, respectively. These values are slightly lower than that of a bare a-C:H carbon substrate; these results therefore indicate that there is no evidence for the presence of inhomogeneities in pNBD adlayers deposited via spontaneous adsorption at a-C:H over the timescale of our experiments.

![Figure SI-1: Tapping mode AFM images of (a) 2 min and (c) 60 min pNBD coated a-C:H; z-deflection range in both images is 0-20 nm.](image)

Figure SI-2 shows Atomic Force Microscopy (AFM) height images in tapping mode of of pNBD-coated a-C after (a) 2 min and (b) 60 min of immersion in a 100 µM pNBD aqueous solution. Roughness analysis indicates that, after pNBD adsorption, coated samples display average rms roughness values of (0.9±0.1) nm and (0.7±0.1) nm, respectively. These roughness values are lower than that of a bare a-C carbon substrate. These results indicate that there is no evidence of inhomogeneities present in pNBD adlayers deposited at a-C over the timescale of our experiments.

![Figure SI-2: Tapping mode AFM images of pNBD coated a-C substrates after (a) 2 min and (b) 60 min of deposition from 100 µM pNBD solutions; z-deflection range is 0-20 nm.](image)
XP spectra of pNBD adlayers obtained after sonication in organic solvents

XP spectra of pNBD adlayers deposited for 2 min and 60 min after sonication in organic solvents (acetonitrile and methanol). Results are shown in figure SI1 along with XP spectra obtained after gentle water rinsing for comparison.

Figure SI-3: XP spectra in the N 1s region of adlayers deposited from 100 µM pNBD solutions after (a) 2 min and (b) 60 min before and after sonication in ACN and methanol.
Cyclic voltammetry (CV) of pNBD adlayers deposited on a-C substrates

Figure SI-4 shows a typical cyclic voltammogram obtained in 0.1 M H$_2$SO$_4$ at 0.2 V s$^{-1}$, using a-C electrodes after immersion in 100 µM pNBD solutions for 2 min followed by sonication in acetonitrile and methanol. The CV displays an irreversible reduction peak at -0.5 V vs. Ag/AgCl that is characteristic of the 6e electroreduction of Ar-NO$_2$ groups.$^1$ The absence of a reduction peak after a second sweep indicates that the majority of nitrophenyl groups are reduced during the first cycle.

![Cyclic voltammogram](image)

**Figure SI-4:** Cyclic voltammogram in 0.1 M H$_2$SO$_4$ at 0.2 V s$^{-1}$ of a-C electrodes modified via pNBD adsorption for 2 min from 100 µM solutions. First (—) and second (- - -) sweeps are reported.
Comparison of pNBD adsorption curves at a-C, a-C:H and Au surfaces

Adsorption curves showing surface coverage vs. deposition time, obtained in 100 µM pNBD solutions at a-C, a-C:H and Au surfaces.

Figure SI-5: QCM adsorption curves for 100 µM pNBD at a-C, a-C:H and Au surfaces.

References