SUPPORTING INFORMATION

Self-Limiting Covalent Modification of Carbon Surfaces: Diazonium Chemistry with A Twist

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Experimental section

<u>Materials</u>

4-Nitrobenzene diazonium (NBD) tetrafluoroborate (Sigma Aldrich, 97%), 4-bromobenzene diazonium (BBD) tetrafluoroborate (Sigma Aldrich, 96%) and L-ascorbic acid (Sigma Aldrich, 99%) were used as received. 4-Carboxybenzene diazonium (CBD) chloride and 4-Methoxybenzene diazonium (MBD) chloride were synthetized as reported in the literature.1 Briefly, a 0.8 mL aniline solution, containing the amount of aniline to obtain a final diazonium solution volume of 1 mL of the desired concentration (20 mM in our case) in 50 mM HCl, was mixed with an excess of 0.1M NaNO₂ (0.2 mL) to induce the formation of the diazonium salt. The resulting solution of 1 mL was shaken for 10 seconds before its incorporation to the surface. High purity water (Milli-Q, Millipore, 18.2 M Ω ·cm) was used for all the experiments. The highly ordered pyrolytic graphite (HOPG, grade ZYB, Advanced Ceramics Inc., Cleveland, USA) substrates were mechanically cleaved before use.

Preparation of the samples

For NBD and BBD, appropriate amounts for obtaining a 20 mM solution were dissolved in 50 mM HCl. For CBD and MBD the solution used consisted on the synthesis solution. Ascorbic acid was dissolved in Milli-Q water and the pH was adjusted to 3.8 with 0.1 M KOH. For the sequential protocol 100 μ L of the ascorbic acid solution was added to the freshly cleaved HOPG surface and after that 100 μ L of the diazonium salt solution was incorporated. After 10 min, the reaction was stopped by rinsing with acetonitrile. Then the samples were rinsed with acetonitrile and water three times. Finally, the samples were dried under a stream of argon for further characterization.

Scanning Probe Microscopy

AFM imaging was performed with a Cypher ES (Asylum Research) system at 32 °C in tapping mode in air and a Multimode 8 (Bruker) with a Nanoscope V controller. OMCL-AC240TS-R3 probes (spring constant \sim 2 N/ m) with a resonance frequency around 70 kHz were used. All STM experiments were performed at room temperature using a PicoLE (Keysight) machine operating in constant-current mode. STM tips were prepared by mechanical cutting of Pt/Ir wire (80%/20%, diameter 0.25 mm). Gwyddion software was used for AFM and STM image processing.2

Raman Spectroscopy

Raman spectra were collected with a confocal Raman microscope (Monovista CRS+, S&I GmbH) using a 632.8 nm He–Ne laser directed on the surface through an objective (OLYMPUS, BX43 100x, N.A. 0.7) with an optical density at the sample surface of about 590 kW/cm₂. The Raman scattering was collected using the same objective and guided to a Raman spectrograph (S&I GmbH) equipped with a cooled-charge coupled device (CCD) camera operated at -100 °C (Andor Technology, DU920P-BX2DD). Raman spectra were taken in at least 10 different positions on the sample. All measurements were carried out under ambient conditions at room temperature. Accumulation time for all spectra was 6 s.

Electrochemical experiments

A three electrodes homemade Teflon electrochemical cell was used. As reference electrode a Ag/AgCl (KCl saturated) was employed. The counter electrode consists of a platinum wire and as working electrode our modified HOPG surface was used. For the electron transfer experiments a 2.5 mM solution of ferrocene in acetonitrile/TBAPF₆ was employed. Cyclic voltammetry experiments were performed using an Autolab PGSTAT101 potentiostat (Metrohm-Autolab BV, The Netherlands)

X-Ray Photoelectron Spectroscopy

Spectra were recorded on a Kratos Axis Supra X-ray Photoelectron Spectrometer employing a monochromated Al K α (h ν = 1486.7 eV, 150 W) X-ray source, hybrid (magnetic/electrostatic) optics with a slot aperture, hemi-spherical analyser, multichannel plate and delay line detector (DLD) with an emission angle of 0° relative to the sample surface normal. Survey spectra were acquired with a pass energy of 160 eV and high-resolution spectra with 20 eV. The resulting spectra were processed using CasaXPS software. Binding energy was referenced to Ag 3d5/2 at 368.21 eV measured on sputter cleaned silver under the same analysis conditions, on the same day as the samples. Components in high resolution spectra were fitted using the "LA(α ,m)" lineshape for symmetric peaks. Details of this lineshape function are available in the CasaXPS documentation online.³ The asymmetric carbon 1s component due to graphite was fitted using a component derived from the spectrum for pure HOPG (empirical lineshape).

Empirical relative sensitivity factors supplied by Kratos Analytical (Manchester, UK) were used for quantification. Use of these relative sensitivity factors does not account for any attenuation

due to overlayers or other surface contamination and assumes a uniform depth distribution of elements within the information depth of the sample. Matrix effects are also discounted._{4,5}



Figure S1. *XPS survey spectrum for HOPG (black) and grafted films obtained from NBD (blue), BBD (pink), CBD (orange) and MBD (green).*



Figure S2. *High resolution XPS spectra for the C 1s region of (a) NBD, (b) BBD, (c) CBD and (d) MBD.*

The NBD sample (Figure S2a) shows a component at 285.5 eV which can be assigned to the C-NO₂. The carbon 1s spectrum of BBD sample (Figure S2 b) shows components due to oxygen containing carbon species at 286.6 eV (C-O) and 288.4 eV (C=O), but no sign of C-Br, probably due to the high FWHM of the component peaks and resulting strong overlap between C-O and C-C environments between which the C-Br environment is expected to fall. In the case of CBD (Figure S2 c) the analysis of the high-resolution carbon 1s spectrum shows a clear high binding energy peak at 288.8 eV which can be assigned to the carboxyl carbon. An additional environment assigned to C-O is also present at 286.6 eV, presumably due to contamination. For MBD (Figure S2 d) the analysis of the carbon 1s spectrum shows C-O (286.3 eV) and C=O (288.0 eV) regions.



Figure S3. AFM images (2 μ m \times 2 μ m) showing the scratching on the surface to measure the thickness of the layers for (a) NBD, (b) BBD, (c) CBD and (d) MBD. (loading force applied was fixed at 100 nN)



Figure S4. Dependence of the RMS roughness of the modified substrates with the scan size of the image.



Figure S5. Topographic images $(2 \ \mu m \times 2 \ \mu m)$ using NBD for different times and concentrations. Raman spectra for the grafted samples are included with the corresponding I(D)/I(G) ratio.



Figure S6. Cyclic voltammograms of a 2.5 mM ferrocene in 0.1 M TBAPF₆/ACN solution on the modified substrates ($v = 20 \text{ mV s}_{-1}$).



Figure S7. AFM images and Raman spectroscopy for (a) a nanostructured grafted sample prepared as reported previously₆ and the same sample after a second grafting process with CBD and ascorbic acid.



Figure S8. Protocols used for the preparation of the thin films on the substrate. For the sequential protocol, the reaction takes place (*in situ*) on the surface by mixing the components on it (*in situ* mixing and reaction on surface). For the premixing protocol, the reagents are mixed shortly before deposition, and a drop of that solution is placed on the surface.



Figure S9. Topographic images $(2 \ \mu m \ \times 2 \ \mu m)$ using the sequential protocol (a-d) and the premixing protocol (e-h) for NBD (a and e), BBD (b and f), CBD (c and g) and MBD (d and h) after 10 min of reaction on substrate surface.

For NBD and BBD (Figure S9e and S9f) some islands of organic material can be seen on the surface. These islands are around 0.5 - 1 nm in height and are randomly distributed, although a preference for borders and step edges of the terraces can be found when compared to the basal plane. This is explained by the inherent higher reactivity of these substrate defects. In the case of the CBD sample (Figure S9g) the surface is completely covered by material but the average height is only around 0.3 - 0.5 nm. These values, closer to the height of an aromatic ring parallel to the surface (~ 0.3 nm), indicate that we deal with physisorbed material. For MBD (Figure S9h), a polymeric network structure can be found. These fibers have a height of 1 – 3 nm. They might be formed already in the premixed solution and are deposited upon drying of the droplet.



Figure S10. Raman spectra for the grafted samples with a) NBD, b) BBD, c) CBD and d) MBD. For all the precursors the spectra with the sequential (color) and the premixing (gray) protocol are shown. An inset with the comparison of the D-band intensity is included in all the graphs.



Figure S11. Covalent functionalization of Au(111)/mica substrate using the ascorbic acid mediated decomposition of NBD. AFM data shows that the thickness of the layer is around 1 nm suggesting that the reaction may be self-limiting on substrates other that HOPG. ($C_{NBD} = C_{ascorbic}$ acid = 10 mM, reaction time = 10 minutes)

References:

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