Electronic Supplementary Material (ESI) for ChemComm.

SUPPLEMENTARY INFORMATION

Controlled Diazonium Electrografting Driven by Overpotential Reduction: A General Strategy to Prepare Ultrathin Layers

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Calculation of the nitrophenyl surface coverage

Surface concentrations of nitrophenyl tethered surfaces were estimated from CVs recorded in KOH 0.1 M by summing the charges for the irreversible reduction of Ar-NO_2 and the charge for Ar-NHOH reoxidation and assuming a 6-electron transfer for each nitro group, as proposed by S. S. C. Yu *et al.* in *Langmuir* **2007**, 23, 11074-11082.

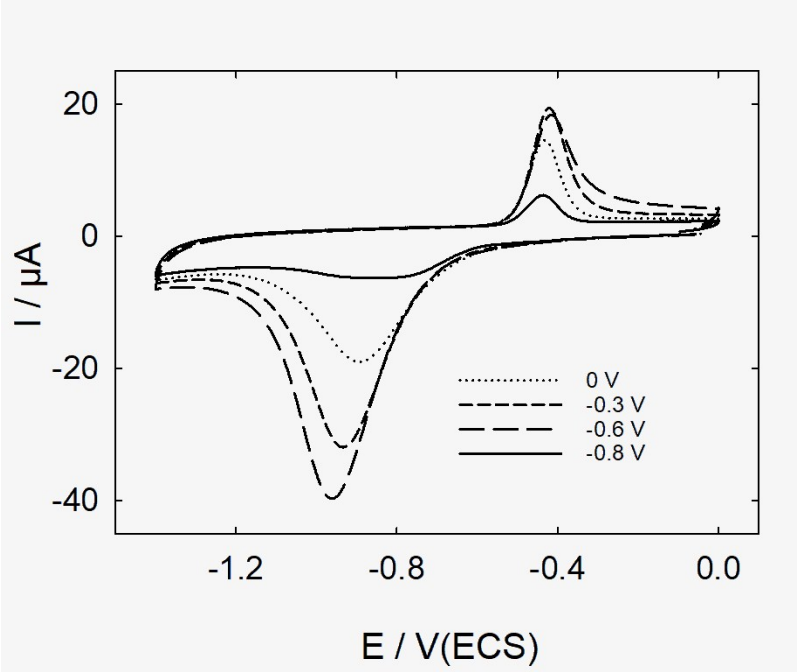

Figure S1. First CV recorded in aqueous deaerated 0.1M KOH on a modified glassy carbon electrode at 100 mV/s. Grafting was achieved at fixed potential for 2 min in the presence of 1 mM of 4-nitrobenzenediazonium in CH_3CN 0.1 M nBu_4NPF_6.

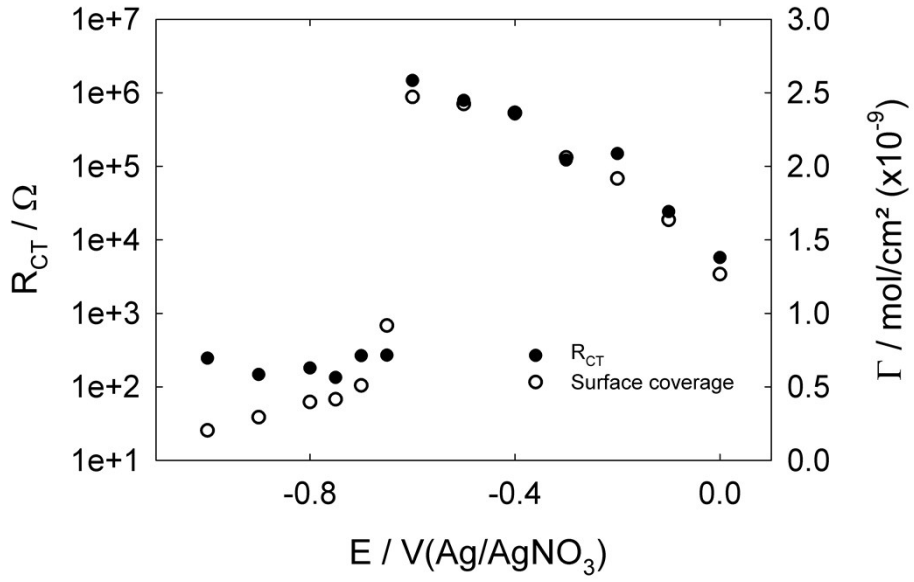

Figure S2. Charge transfer resistance measured on nitrophenyl modified glassy carbon electrode (●) in the presence of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ and corresponding nitrophenyl surface coverage (**O**) as a function of the potential applied for the chronoamperometric electrografting under atmospheric conditions. Grafting was achieved at fixed potential for 2 min in the presence of 1 mM of 4-nitrobenzenediazonium.

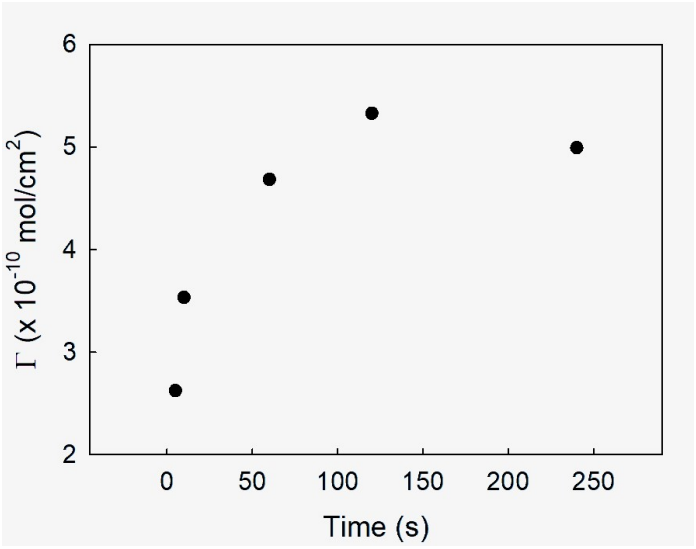

Figure S3. Calculated nitrophenyl surface coverage as a function of the grafting time at an applied potential of -0.8 V vs $Ag/AgNO_3$ under atmospheric conditions in the presence of 1 mM of 4-nitrobenzenediazonium.

Table 1. Atomic composition, determined by X-ray Photoelectron Spectroscopy, of modified surfaces at -0.6 V vs $Ag/AgNO_3$ under atmospheric and oxygen-free conditions.

	C 1s	O 1s	N 1s (406 eV)
Atmospheric conditions	83.0	13.2	3.8
Oxygen-free conditions	83.2	12.5	4.3

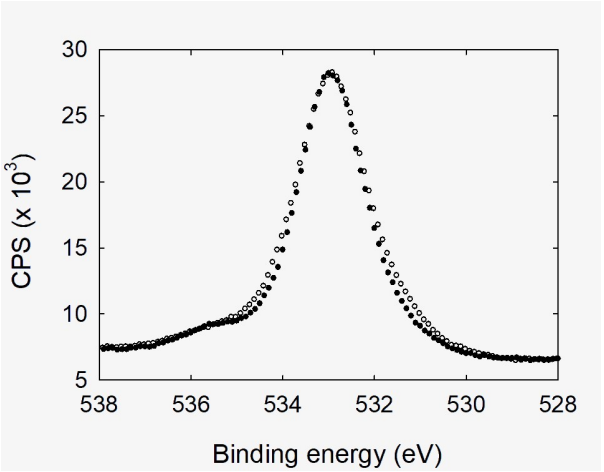

Figure S4. XPS O1s core level spectra of modified surfaces at -0.6 V vs $Ag/AgNO_3$ under atmospheric conditions (ꕥ) and under oxygen-free conditions (ꕥ).

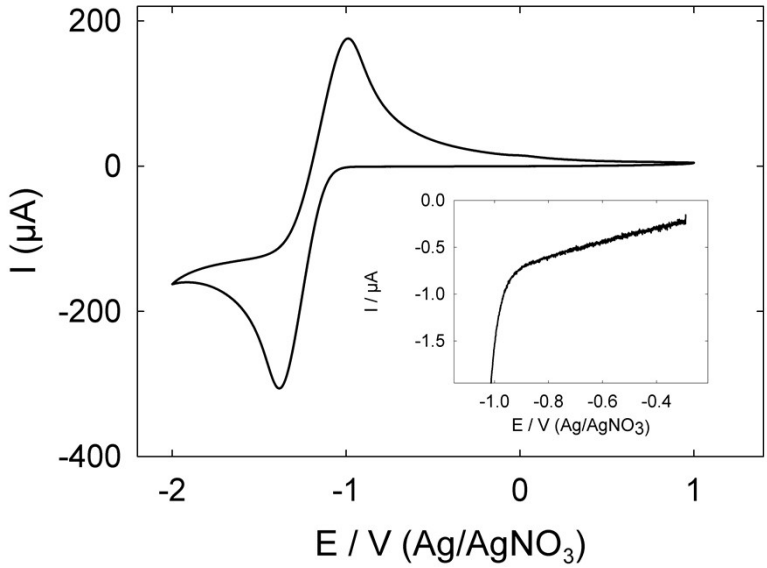

Figure S5. CV recorded at 50 mV/s in acetonitrile 0.1 M nBu_4NPF_6 on a bare glassy carbon electrode under atmospheric conditions. Inset: zoom on the starting reduction signal.

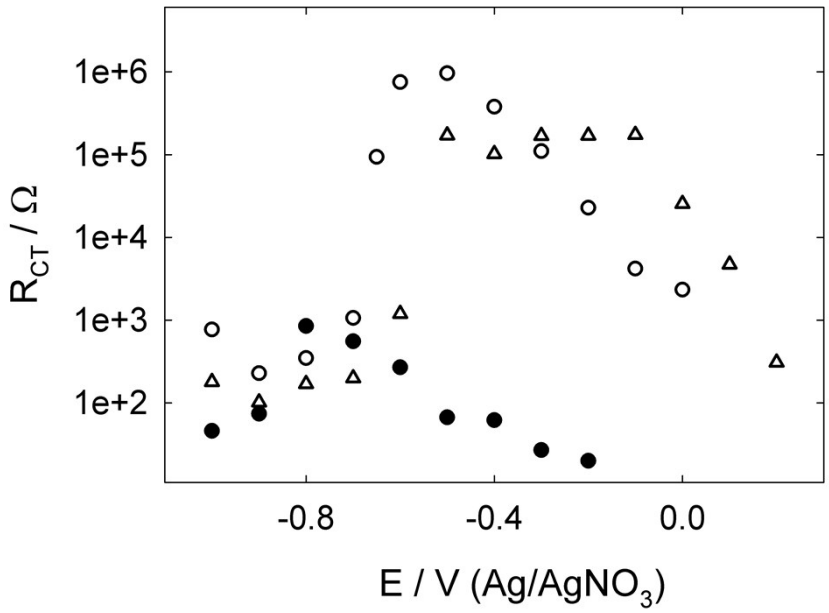

Figure S6. Charge transfer resistance measured on bromophenyl (○), 4-(2-aminoethyl)phenyl (●) and 1-anthraquinone (❐) modified glassy carbon electrode in the presence of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ as a function of the potential applied for the chronoamperometric electrografting under atmospheric conditions. Grafting was achieved at fixed potential for 2 min in the presence of 1 mM of the corresponding diazonium derivative.

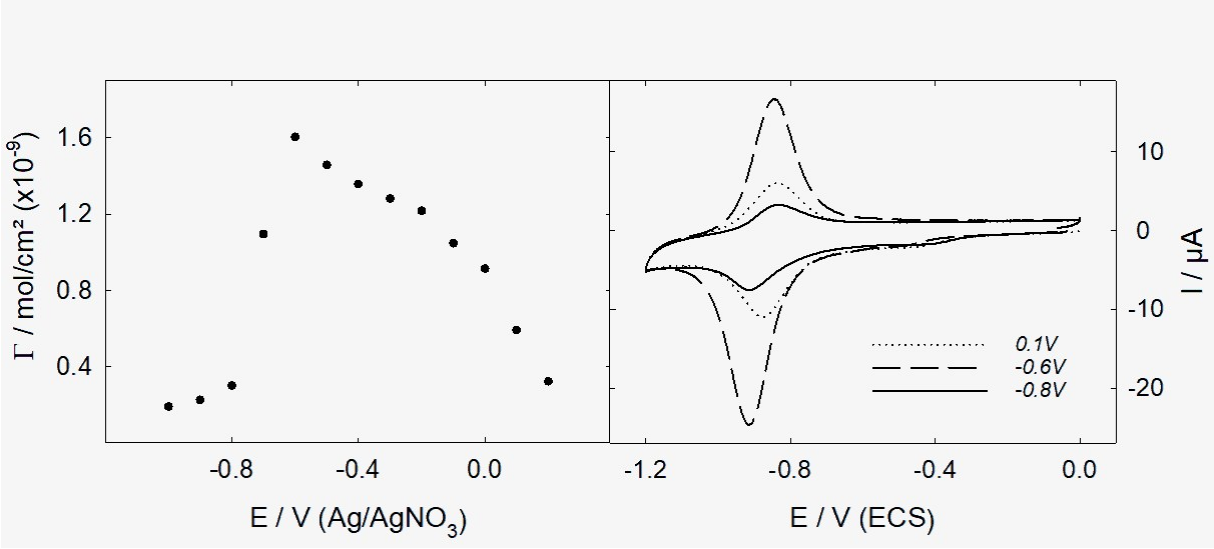

Figure S7. Left: anthraquinone surface coverage, determined from voltammetric data recorded in KOH 0.1 M, on a modified glassy carbon electrode as a function of the potential applied for the chronoamperometric electrografting under atmospheric conditions. Right: corresponding CVs for modification carried out at 0.1 V, -0.6 V and -0.8 V vs $Ag/AgNO_3$.