

Supplementary Materials: Electrografting of 4-carboxybenzenediazonium: the effect of concentration on the formation of mono and multilayers

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XPS of electrografted GCE surface

The XPS measurements were performed on bare GCE and grafted GCE (CP/GCE). The grafting was made using CV at two concentrations of 4-CBD: 0.15 mmol.L⁻¹ (1 and 22 cycles) and 2.50 mmol.L⁻¹ (1 and 3 cycles). XPS survey spectra, Fig. S1, displays two main C 1s and O 1s photoelectron peaks and additional N 1s line of low intensity. The corresponding atomic concentrations are presented in Table S1. Comparison of survey spectra obtained for bare GCE and CP/GCE grafted with 2.50 mmol.L⁻¹ 4-CBD (1 cycle) reveals that for the CP/GCE, the peak of C 1s decreased while the peak for O 1s increased compared to bare GCE. This leads to higher ratio of O 1s/C 1s for CP/GCE (0.182) compared to GCE (0.077). However, when GCE was grafted using 0.15 mmol.L⁻¹ 4-CBD (1 cycle), the spectra did not show significant difference in the atomic concentrations of C 1s and O 1s, for which the ratio of O 1s/C 1s was 0.086 compared to 0.077 for the bare. When the grafting was performed using 0.15 mmol.L⁻¹ 4-CBD (22 cycles) the ratio O1s/C1s increased to 0.199 which is close to the ratio obtained for grafting with 2.50 mmol.L⁻¹ 4-CBD, 1 cycle (0.182). For grafting with 3 cycles using 2.50 mmol.L⁻¹ 4-CBD the ratio of O 1s/C 1s was 0.206, which is not different from the values obtained for 1 cycle. These results indicate that grafting for 1 cycle using 0.15 mmol.L⁻¹ is not enough to form a detectable amount of CP moieties at the surface. A multilayer is probably formed when the grafting is made using higher concentration of 4-CBD (1 cycle) or multiple scans (22 cycles) using the lower concentration.

The high-resolution spectra of C 1s and O 1s for bare GCE, CP/GCE grafted using 0.15 mmol.L⁻¹ 4-CBD (22 cycles), and 2.50 mmol.L⁻¹ 4-CBD (1 cycle) are presented in Fig. S2. The C 1s high-resolution spectrum was fitted with four components at 284.2 eV (sp² C in GCE), 285.4 eV (C-OH, C-O-C), 287.0 eV (C=O) and 288.6 eV (O-C=O). In Fig. S2, the two components at 284.2 and 288.6 eV are indicated for comparison. The main component at 284.2 eV (sp² C) decreased from 100% on bare GCE to 93% on CP/GCE for the lower concentration, 0.15 mmol.L⁻¹ (22 cycles) and to 94% for the higher concentration, 2.50 mmol.L⁻¹ (1 cycle). The decrease in the peak intensity for CP/GCE may be due to the formation of a thick layer that shields the carbon sp² from the GCE. For CP/GCE, another component that appeared at 288.6 eV corresponds to carboxylic group, HO-C=O [1]. This component accounted for 7 atomic % when the grafting was made with 0.15 mmol.L⁻¹ (22 cycles) and 6 atomic %

42 for 2.50 mmol.L⁻¹ (1 cycle). This peak, which was absent for the bare GCE, confirms that the GCE
43 surface was successfully grafted with carboxyphenyl to almost the same extent.

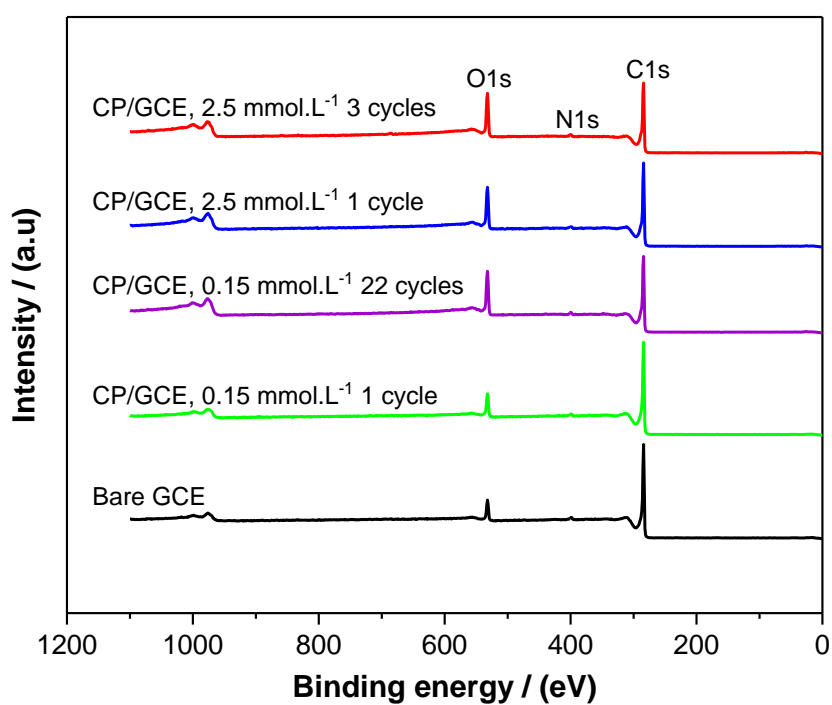
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45 The high-resolution spectra of O 1s for the grafted GCE also displayed two components,
46 corresponding to the carboxylic functional group in the grafted layers. For CP/GCE grafted with 0.15
47 mmol.L⁻¹ (22 cycles) the components appeared at 533.1 eV for O=C-O-H (50%) and 531.6 eV for O=C-
48 O-H (48%) [1, 2]. The corresponding components for CP/GCE grafted with 2.50 mmol.L⁻¹ (1 cycle)
49 appeared at 533.0 eV for O=C-O-H (56%) and 531.5 eV for O=C-O-H (39%) [1, 2]. The intensity ratio
50 of these two components is close to 1.1. This is another confirmation that the carboxyphenyl layer
51 obtained from 4-CBD is grafted on the GCE.

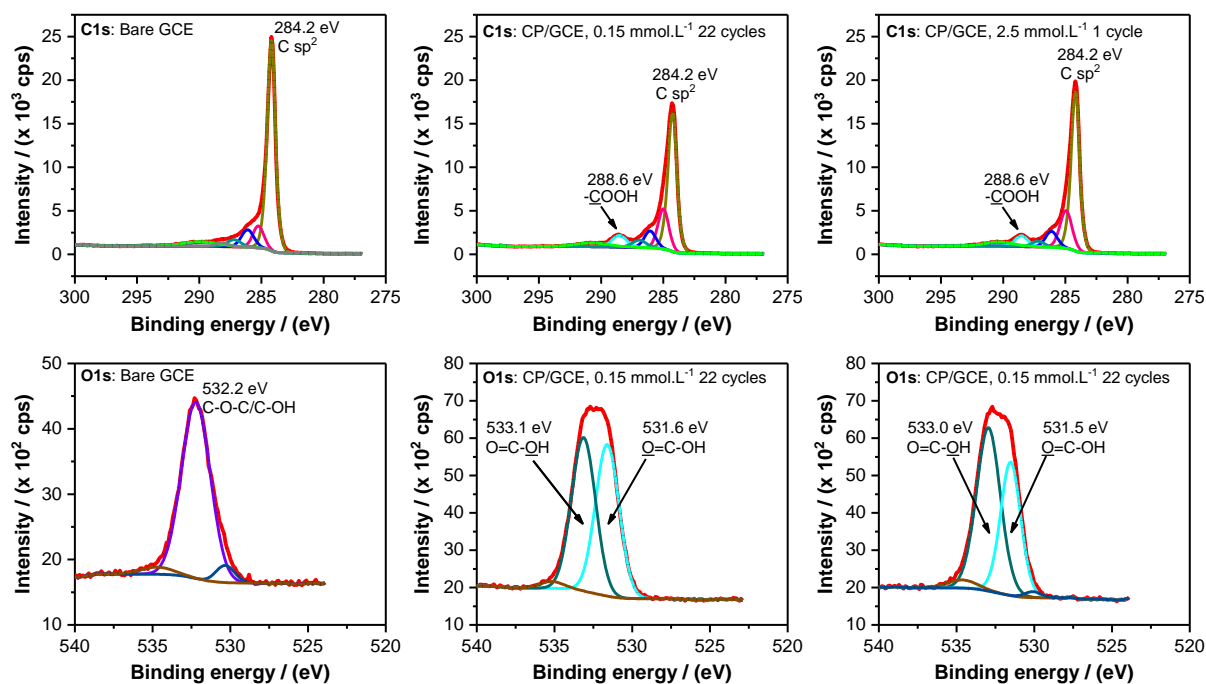
52 **Table S1.** Atomic compositions on bare GCE and grafted GCE (CP/GCE) using 0.15 mmol.L⁻¹ and 2.50 mmol.L⁻¹
 53 4-CBD at different grafting cycles.
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Electrode	Atomic concentration / (at.%)		
	C1s	O1s	N1s
Bare GCE	91.4	7.0	1.6
CP/GCE, 0.15 mmol.L ⁻¹ 1 cycle	92.1	7.9	-
CP/GCE, 0.15 mmol.L ⁻¹ 22 cycles	83.4	16.6	-
CP/GCE, 2.5 mmol.L ⁻¹ 1 cycle	83.5	15.2	1.4
CP/GCE, 2.5 mmol.L ⁻¹ 3 cycles	81.5	16.8	1.7

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 58 **Fig. S1.** Survey spectra of bare GCE (black), grafted GCE (CP/GCE) using 0.15 mmol.L⁻¹ 4-CBD: for 1 cycle (green)
 59 and 22 cycles (violet), and grafted GC (CP/GCE) using 2.50 mmol.L⁻¹ 4-CBD: for 1 cycle (blue) and 3 cycles (red).



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61 **Fig. S2.** High-resolution spectra of C 1s and O 1s for bare GCE and CP/GCE grafted using 4-CBD:
 62 0.15 mmol.L⁻¹ (22 cycles) and 2.50 mmol.L⁻¹ (1 cycle).

63 **References**

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