Supplementary Information

One-step Preparation of Bifunctionalized Surfaces by Bipolar Electrografting

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Cell Design

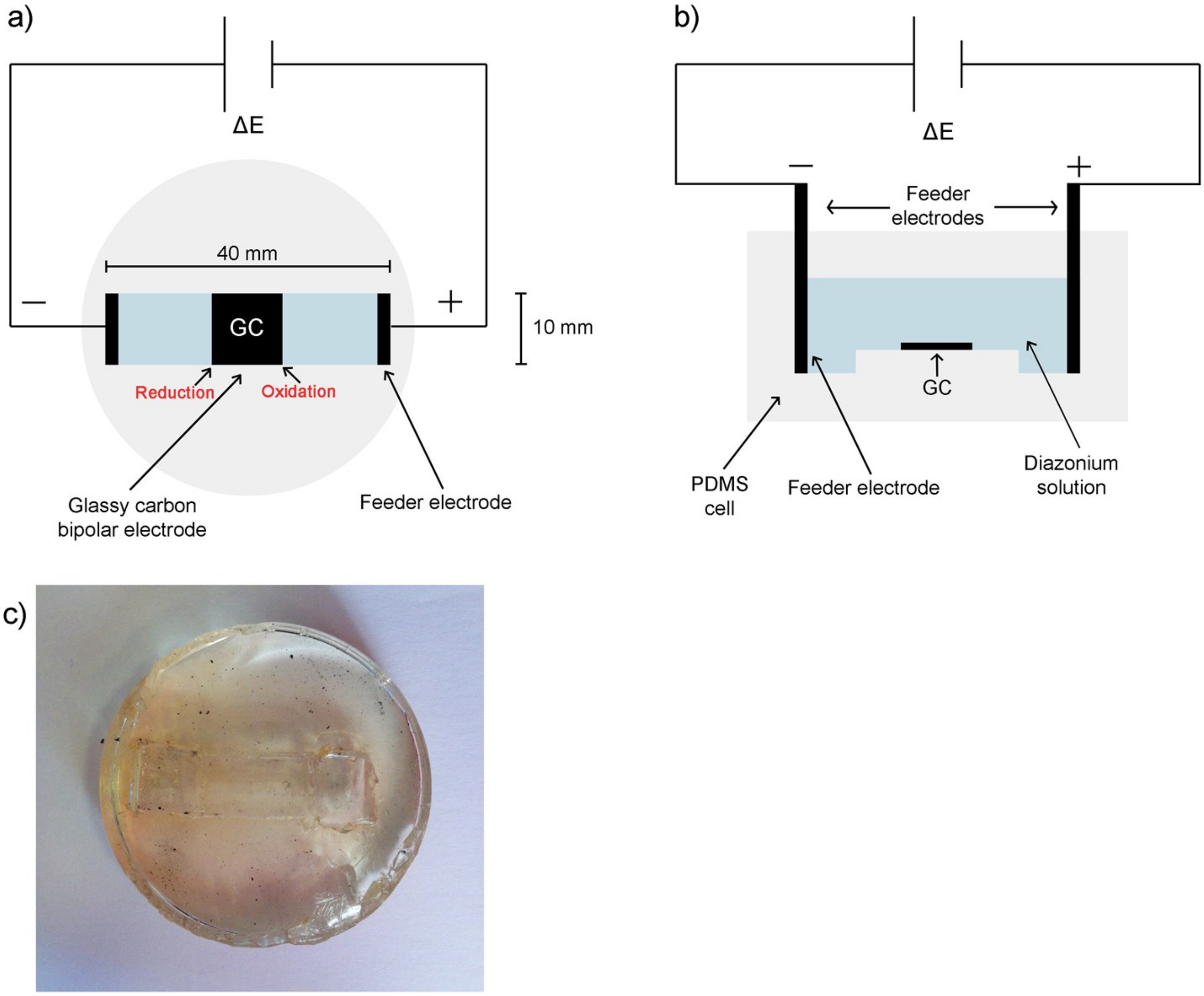


Figure S1. Illustration of the electrochemical cell used to perform bipolar grafting experiments: a) top view and b) side view. c) shows an optical image of the PDMS cell.

Poly(dimethylsiloxane) (PDMS) cell fabrication.

We used the RTC615-kit from Momentive Performance Materials. The two components of the kit were mixed in a ratio 10:1 in mass then centrifuged for 5 min at 5000 rpm to remove air bubbles. Then the liquid was spread around a mold and rest overnight at 60°C. To finish the mold was removed and the desire shape had been obtained.

Cyclic Voltammetry

For the cyclic voltammetric measurements a standard three-electrode setup (CH Instruments 601C) consisting of a GC disc electrode (diameter = 1 mm) as working electrode, a platinum wire as counter electrode and a Ag/AgI pseudo-reference electrode (i.e., a silver wire immersed in a CH_3CN solution of 0.1 M Bu_4NBF_4 and 0.01 M Bu_4NI) in 10 mL degassed 0.1 M Bu_4NBF_4/CH_3CN solution was employed. 4-(2-Aminoethyl)benzenediazonium tetrafluoroborate (11.8 mg, 0.05 mmol) or 4-(carboxymethyl)benzenediazonium tetrafluoroborate (0.025 g, 0.1 mmol) was added to the solution. A cyclic voltammogram was recorded at a sweep rate of 0.1 V s^{-1} to determine the peak potential (E_p) of the reduction and oxidation wave, respectively. The E_p values were referenced against SCE using a previous determination of $E^{0}_{Fc^{+}}$ = 0.41 V vs. SCE in CH_3CN.[S1]

Reduction of 4-(2-aminoethyl)benzenediazonium tetrafluoroborate. The first sweep shows a broad irreversible reduction wave with a peak potential at –0.56 V vs. SCE corresponding to the reduction of the aryldiazonium moiety (see Figure S2a). Two additional cyclic voltammograms were recorded showing the passivation of the electrode due to grafting.

Oxidation of 4-(2-aminoethyl)benzenediazonium tetrafluoroborate. The first sweep shows a small irreversible oxidation wave with a peak potential at 1.51 V vs. SCE corresponding to the oxidation of the amine functionality (see Figure S2b). Two additional cyclic voltammograms were recorded showing the passivation of the electrode due to grafting.

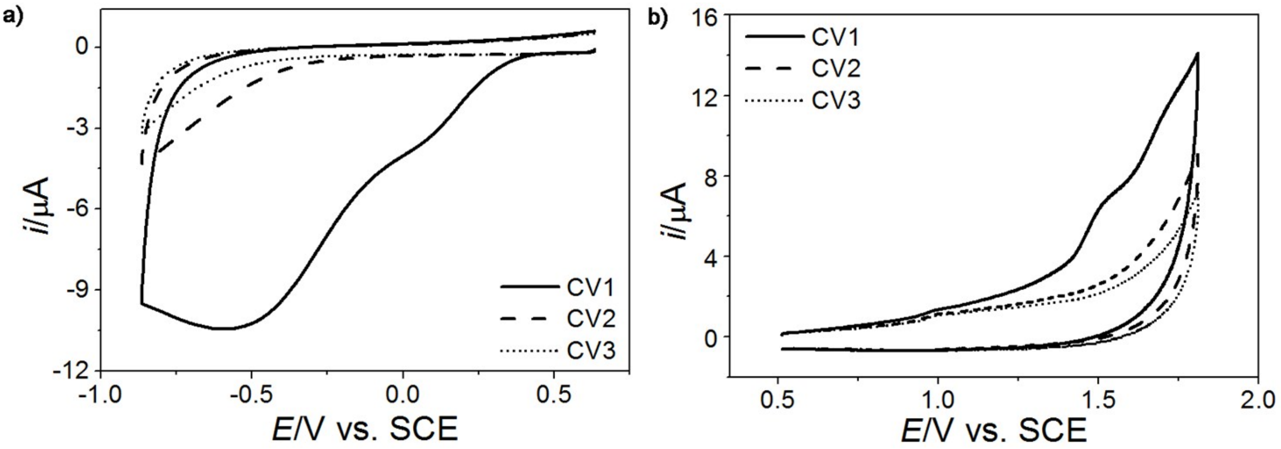


Figure S2. First, second, and third cyclic voltammograms recorded of 5 mM 4-(2-aminoethyl)benzenediazonium at a sweep rate of 0.1 V s^{-1} in 0.1 M Bu_4NBF_4/CH_3CN for the (a) reduction of the diazonium moiety and (b) oxidation of the amine functionality.

Reduction of 4-(carboxymethyl)benzenediazonium tetrafluoroborate. The first sweep shows a broad irreversible reduction wave with a peak potential at −0.29 V vs. SCE corresponding to the reduction of the diazonium moiety (see Figure S3a). Two additional cyclic voltammograms were recorded showing the passivation of the electrode due to grafting.

Oxidation of 4-(carboxymethyl)benzenediazonium tetrafluoroborate. The first sweep shows a small irreversible oxidation wave with a peak potential at 1.11 V vs. SCE corresponding to the oxidation of the carboxymethyl functionality (see Figure S3b). Two additional cyclic voltammograms were recorded showing the passivation of the electrode due to grafting.

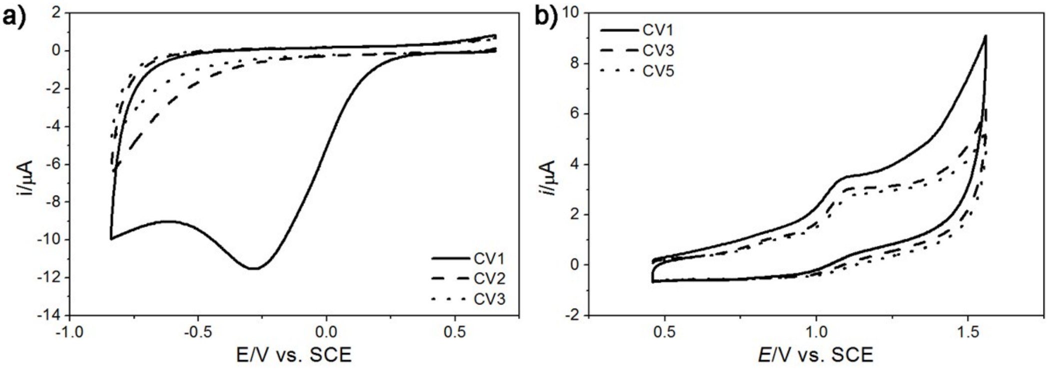
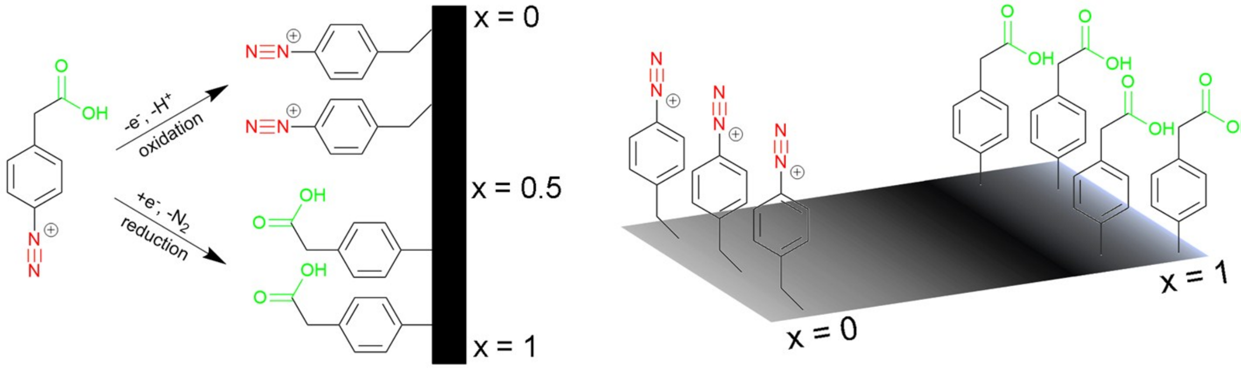


Figure S3. Cyclic voltammograms recorded of 10 mM 4-(carboxymethyl)benzenediazonium at a sweep rate of 0.1 V s^{-1} in 0.1 M Bu_4NBF_4/CH_3CN for the (a) reduction of the diazonium moiety (first, second, and third CV) and (b) oxidation of the carboxymethyl functionality (first, third, and fifth CV).



Scheme S1. Simultaneous grafting of two different organic films on glassy carbon using bipolar electrochemistry with 4-(carboxymethyl)benzenediazonium.

XPS Spectra after Bipolar Grafting of 4-(Carboxymethyl)benzenediazonium

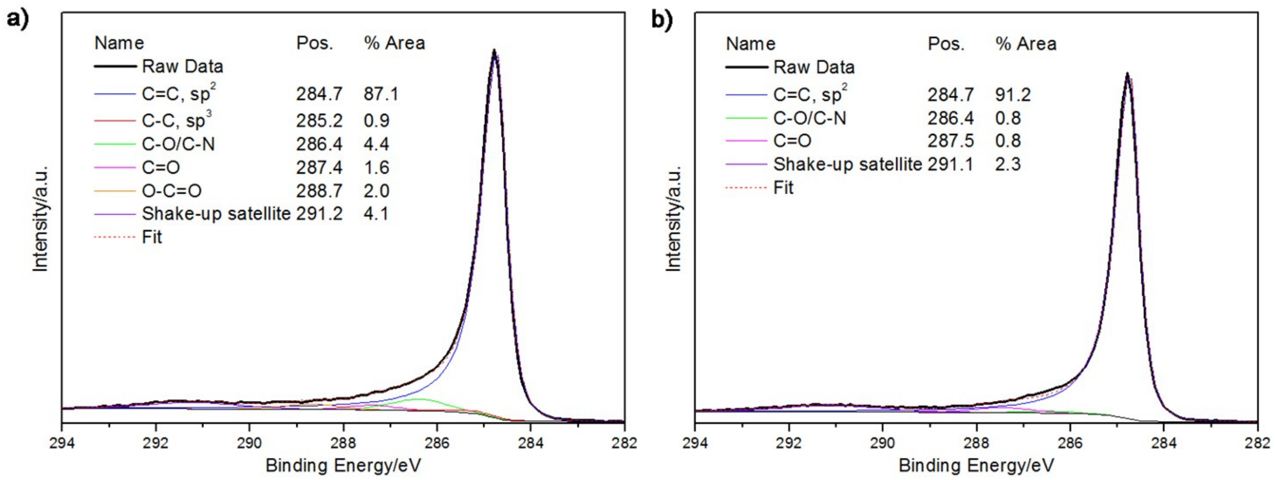


Figure S4. C 1s core level XPS spectra after bipolar grafting of 4-(carboxymethyl)benzenediazonium; a) x = 0, and b) x = 0.5. The spectra are fitted using an asymmetric peak shape for sp^2-hybridized C and symmetric peak shapes for the remaining of the contributions.

References

(S1) K. Daasbjerg, S. U. Pedersen and H. Lund, in *General Aspects of the Chemistry of Radicals*, ed. Z. B. Alfassi, Wiley, Chichester, U.K., 1999, 385-427.