

## SUPPORTING INFORMATION

### EXPERIMENTAL SECTION

#### Reagents.

Carbon powder (Norit-S50) was purchased from Norit, 4-aminobenzene sulfonic acid (99%), lithium perchlorate (99%), potassium ferricyanide (99%) and potassium ferrocyanide (98.5%) were received from Acros. Sodium nitrite (97%) was purchased from Aldrich. All solutions were prepared from nanopure water (18.2 MΩ cm).

#### Synthesis of 4-diazobenzene sulfonic acid (4-DBSA)

4-DBSA was synthesized by diazotization of 4-aminobenzene sulfonic acid. 4-aminobenzene sulfonic acid (1 g) was dispersed in 1M HCl (25 mL) under sonication during 30 min at room temperature. Having cooled the solution with an ice-water bath, sodium nitrite (0.478 g, 1.2 eq.) was added. The mixture was stirred for 1 h and the obtained precipitate was filtered and washed with cold water (50 mL). It must be noted that the white solid obtained is very explosive.

#### Glassy carbon (GC) electrode modification.

Prior to the electrografting or grafting, the GC electrode surface was polished with 0.05 μm alumina powder and sonicated in ethanol for 5 min just after polishing. The electrografting was carried out under potentiostatic conditions at an applied potential 100 mV less than the peak potential for 10 min. For the self-diazotization procedure, the electrografting was performed in deaerated nanopure water containing 5 mM 4-ABSA + 0.1 M LiClO<sub>4</sub> in presence of 3 equivalents of sodium nitrite. For the conventional diazotization procedure, the electrografting was performed in 0.5 M HCl. Spontaneous derivatization was carried out by immersing the GC during 1 h at room temperature in the diazotization bath, all conditions being equal. In all cases, mixtures react 30 min prior to the derivatization step. After modification, the GC was sonicated in nanopure water for 5 min, washed in benzene under stirring for 10 min and sonicated again in nanopure water for 5 min.

The blocking properties of modified GC electrodes against redox reaction was investigated in deaerated nanopure water + 0.1 M LiClO<sub>4</sub> containing 5 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]/K<sub>4</sub>[Fe(CN)<sub>6</sub>] 1:1 mixture. The pH of the ferri-ferrocyanide solution was equal to 7.53.

#### Carbon powder modification. Preparation of NS1, NS2, NS3 and NS4.

In all cases, the carbon powder was first sonicated for 30 min. in 30 mL of nanopure water before the reagents were added. The reaction mixtures were stirred for 24 hours at room temperature and then vacuum filtered on a Teflon filtration membrane (from Sartorius Stedim) having a pore size diameter of 0.2 μm. The modified carbon powders were washed successively with water (100 mL), DMF (100 mL), methanol

(100 mL) and acetone (100 mL). Finally, the modified carbons were dried over night at 80 °C.

**Preparation of NS1 and NS2.** 4-aminobenzene sulfonic acid (577 mg; 0.2 eq. vs. carbon) and sodium nitrite (690 mg; 0.6 eq. vs. carbon) were added to an aqueous suspension of Norit-S50 carbon (200 mg in 30 ml of deionized water) after 30 min. sonication. For the preparation of NS2, 2 ml of concentrated HCl (37 %) was added in ultrapure water 5 min. before the end of the sonication step.

**Preparation of NS3 and NS4.** 4-diazobenzene sulfonic acid (600 mg; 0.16 eq. vs. carbon) was added to an aqueous suspension of Norit-S50 carbon (200 mg in 30 ml of deionized water) after 30 min. sonication. For the preparation of NS4, 2 ml of concentrated (37 %) HCl was added in ultrapure water 5 min. before the end of the sonication step.

## Instrumentation and Procedure

**Electrochemical measurements.** All electrochemical experiments were performed under nitrogen atmosphere, in a three-electrode cell. The working and counter electrodes consisted in a glassy carbon disk (Bioanalytical Systems, 3 mm diameter; model MF-2012) and a platinum wire, respectively. Potential values referred to SCE system. A potentiostat/galvanostat model VSP (from Bio-Logic) monitored by ECLab software was used. The pH was measured with a standard pH-meter from Radiometer (model PHM210).

**Elemental analysis.** Chemical compositions of modified carbon powders were determined with an organic elemental analyzer from Thermo (model FLASH 2000).

**X-ray photoelectron spectroscopy (XPS).** XPS data have been collected at different cycles of the electrode using a Kratos Ultra Axis spectrometer. The X-ray source is Mg K working at 1253.6 eV and the spot size  $0.7 \times 0.3 \text{ mm}^2$ . Semi quantitative XPS analysis has been performed using pseudo-voight function constrained by full width at half maximum (FWMH) ranges typical of each element.

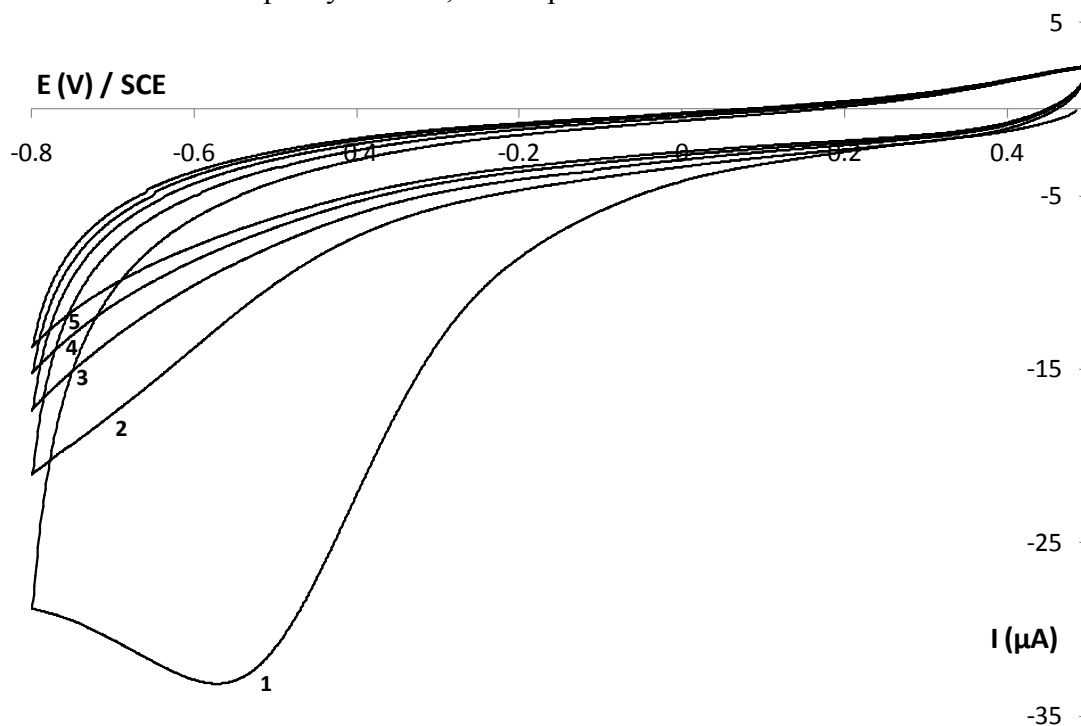
**UV-Vis measurements.** Absorbance and spectral experiments were performed with a PerkinElmer UV-Visible Spectrometer (model Lambda 950) monitored by UV WinLab software (version 3.00), using 1 cm optical cells. After addition of 3 eq. of  $\text{NaNO}_2$  in 10 mL of nanopure water or 0.5 M HCl containing 5 mM 4-ABSA, an aliquot (30  $\mu\text{L}$ ) is diluted with 3 mL of nanopure water and after homogenization, the absorbance was measured against the corresponding blank. The diazotization reaction was monitored by UV-visible spectroscopy from the time evolution of UV-visible spectra.

**NMR spectroscopy.** NMR measurements were performed with a Bruker 300 MHz spectrometer (model AVANCE III) in deuterated water. The diazotization reaction was

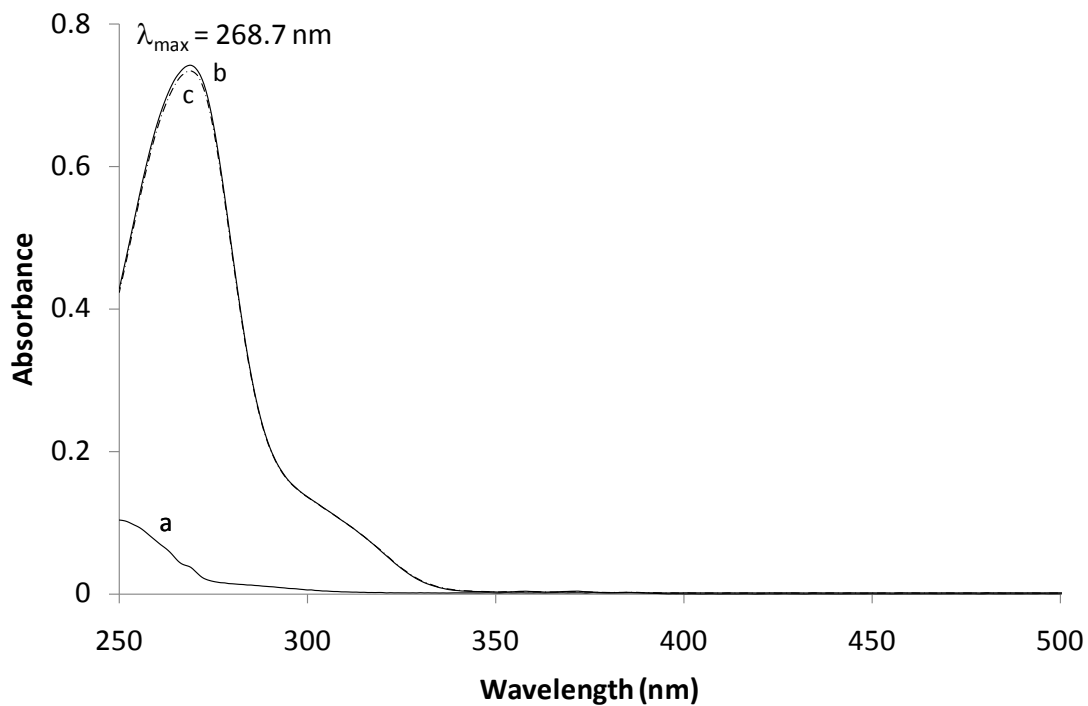
monitored by NMR spectroscopy from the time evolution of NMR spectra of a deuterated water solution containing 1 mg of 4-ABSA and 3 equivalents of  $\text{NaNO}_2$ .

## RESULTS

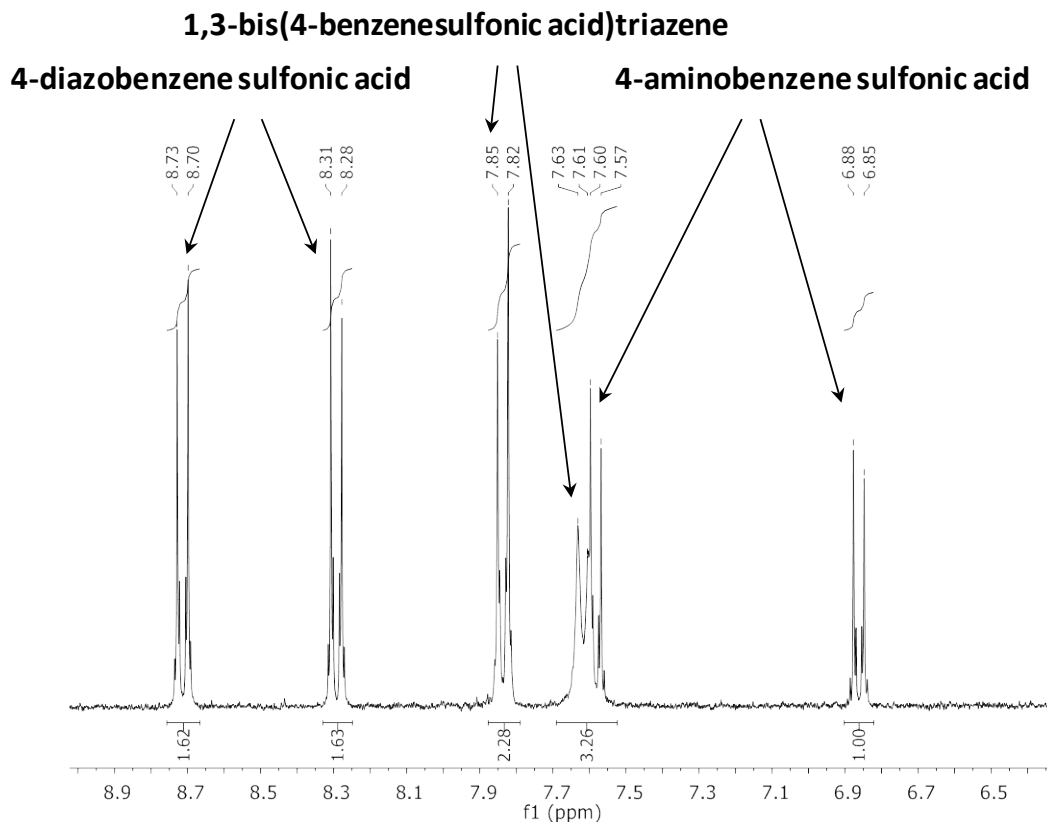
In 0.5M HCl, 4-ABSA was fully diazotized during the first ten minutes and no change in electrochemistry or in UV-visible absorption was observed after one day. The UV-visible spectrum shows a main absorption peak at 268 nm attributed to the diazonium ion and the first CV recorded at GC electrode shows an irreversible wave located at -0.57 V that corresponding to the reduction of the diazonium salt in situ produced to form the substituted phenyl radical, which passivates the carbon surface.



**Figure S1** : Five first CVs recorded at GC electrodes in deaerated 0.5 M HCl solution + 0.1 M  $\text{LiClO}_4$  containing 5 mM 4-ABSA and 3 eq.  $\text{NaNO}_2$ . The scan rate was  $50 \text{ mVs}^{-1}$ .



**Figure S2 :** UV-visible spectra of a 30  $\mu\text{L}$  volume of a 0.5 M HCl aqueous solution containing 5 mM 4-ABSA diluted with 3 mL of nanopure water in a 1 cm optical cell. UV-visible spectra were recorded before, curve a, and upon addition of  $\text{NaNO}_2$  after 10 min, curve b, and 60 min, curve c.



**Figure S3 :**  $^1\text{H}$  NMR spectra of a deuterated water solution containing 1 mg of 4-ABSA, 30 min after the addition of 3 equivalents of  $\text{NaNO}_2$ .

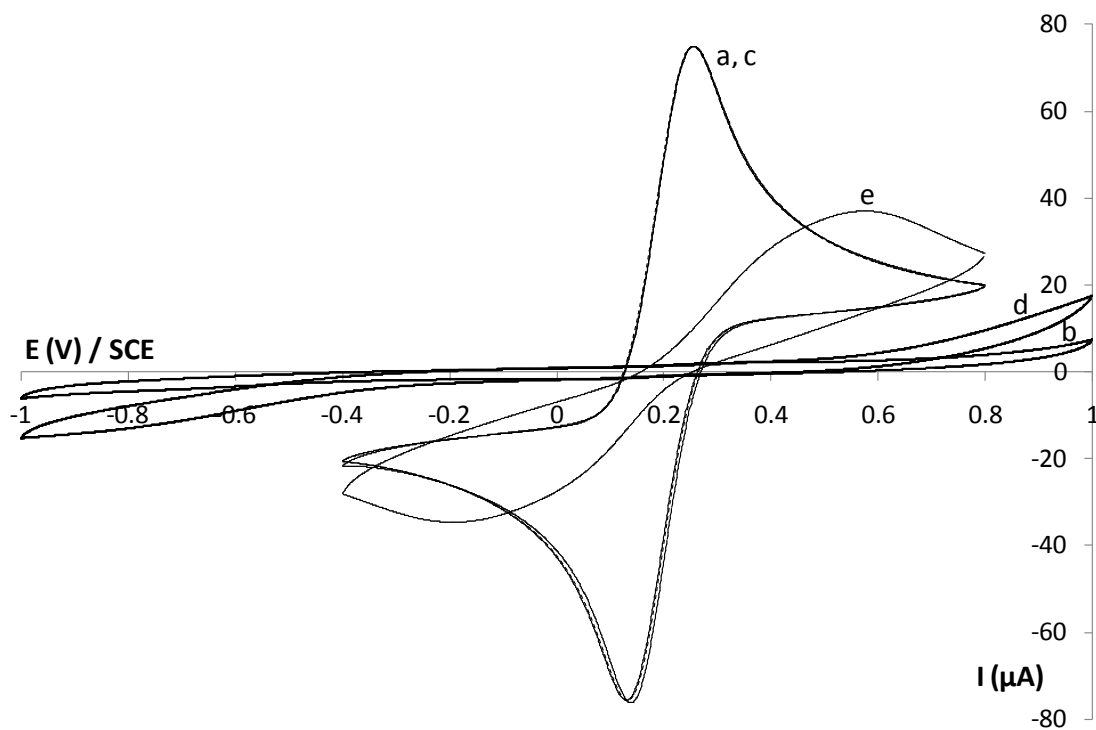
**4-diazobenzene sulfonic acid** (see ref 1) -  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ),  $\delta$  ppm, 8.72 (d,  $J = 9.1$  Hz, 2H), 8.29(d,  $J = 9.1$  Hz, 2H).

**1,3-bis(4-benzenesulfonic acid)triazene** (see ref 2) -  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ),  $\delta$  ppm, 7.84 (d,  $J = 8.8$  Hz, 4H), 7.62 (d,  $J = 8.8$  Hz, 4H).

**4-aminobenzene sulfonic acid** -  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ),  $\delta$  ppm, 7.58 (d,  $J = 8.8$  Hz, 2H), 6.86 (d,  $J = 8.8$  Hz, 2H).

[1] Gui, A.L.; Liu, G.; Chockalingam, M.; Le Saux, G.; Harpr, J.B.; Gooding, J.J. *Electroanalysis* **2010**, 22, 1283 – 1289

[2] Kažemėkaitė, M.; Talaikytė, Z.; Niaura, G.; Butkus, E. *Molecules* **2002**, 7, 706-711.



**Figure S4:** CVs recorded in 0.1 M LiClO<sub>4</sub> aqueous solution containing 5 mM Fe(CN)<sub>6</sub><sup>3-/4-</sup> at (a) bare GC electrode (solid line), (b) electrografted GC in HCl, (c) grafted GC in HCl (dotted line), (d) electrografted GC in pure water and (e) grafted GC in pure water. The scan rate was 50 mVs<sup>-1</sup>. Electrografting occurred at an applied potential 100 mV less than the peak potential for 10 min. Grafting occurred by dipping the GC electrode for 1 h. In all cases, the modification was accomplished in an aqueous solution + 0.1 M LiClO<sub>4</sub> containing 5 mM 4-ABSA and 3 eq. NaNO<sub>2</sub> with or without 0.5 M HCl.