



supplementary materials

Effect of Electrolytic Medium on the Electrochemical Reduction of Graphene Oxide on Si(111) as Probed by XPS

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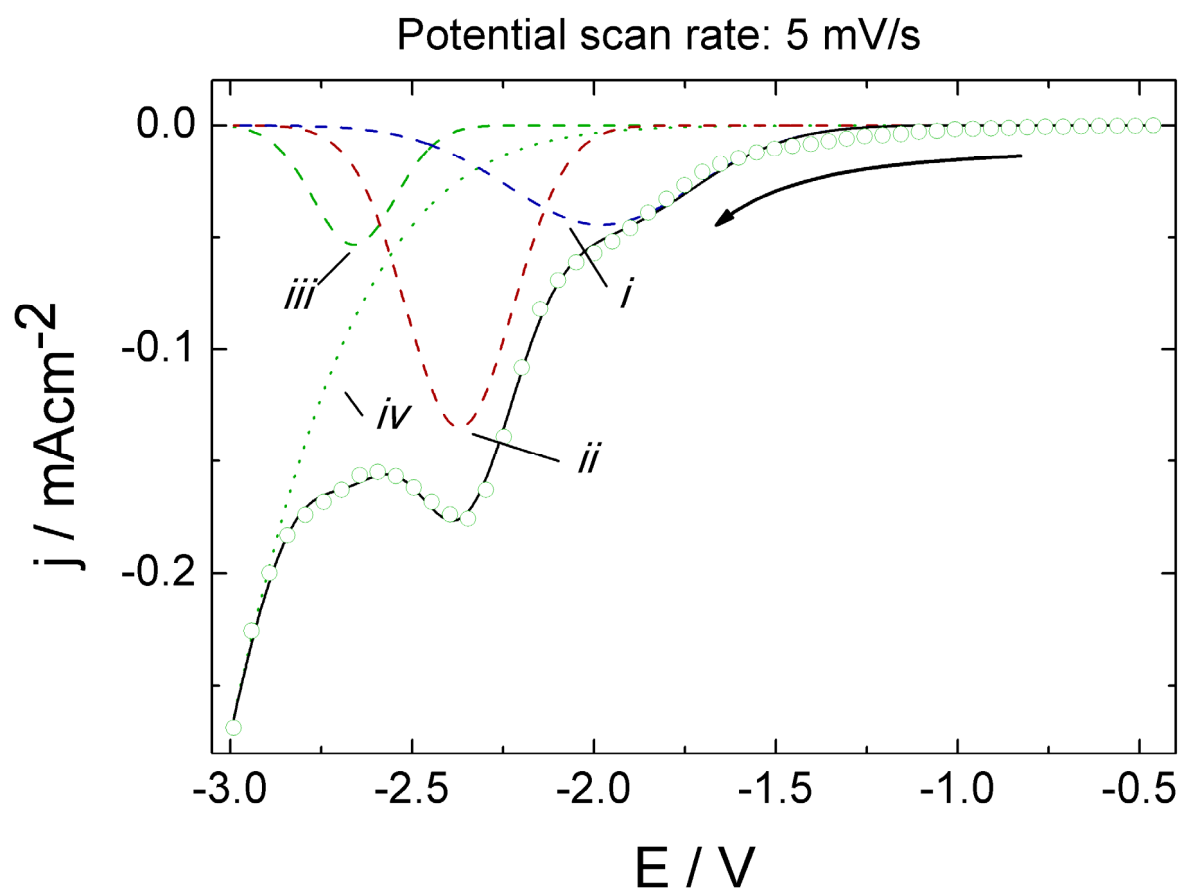


Figure S1. Deconvolution of cathodic wave related to the electrochemical reduction of a GO-coated silicon electrode in 0.1 M TBAPF₆/CH₃CN solution at 5 mVs⁻¹ potential scan rate. The graph shows: experimental current-potential data (olive open circles), deconvolution peaks (coloured dashed lines, from *i* to *iii* as indicated) and simulated envelope voltammogram (black solid line). The solvent contribution curve *iv* is also depicted. The reference electrode was a silver wire immersed in 0.01 M AgNO₃/0.1 M tetrabutylammonium perchlorate (TBAP, Sigma-Aldrich) in CH₃CN (+0.544 V vs. NHE, +0.345 V vs. Ag/AgCl).

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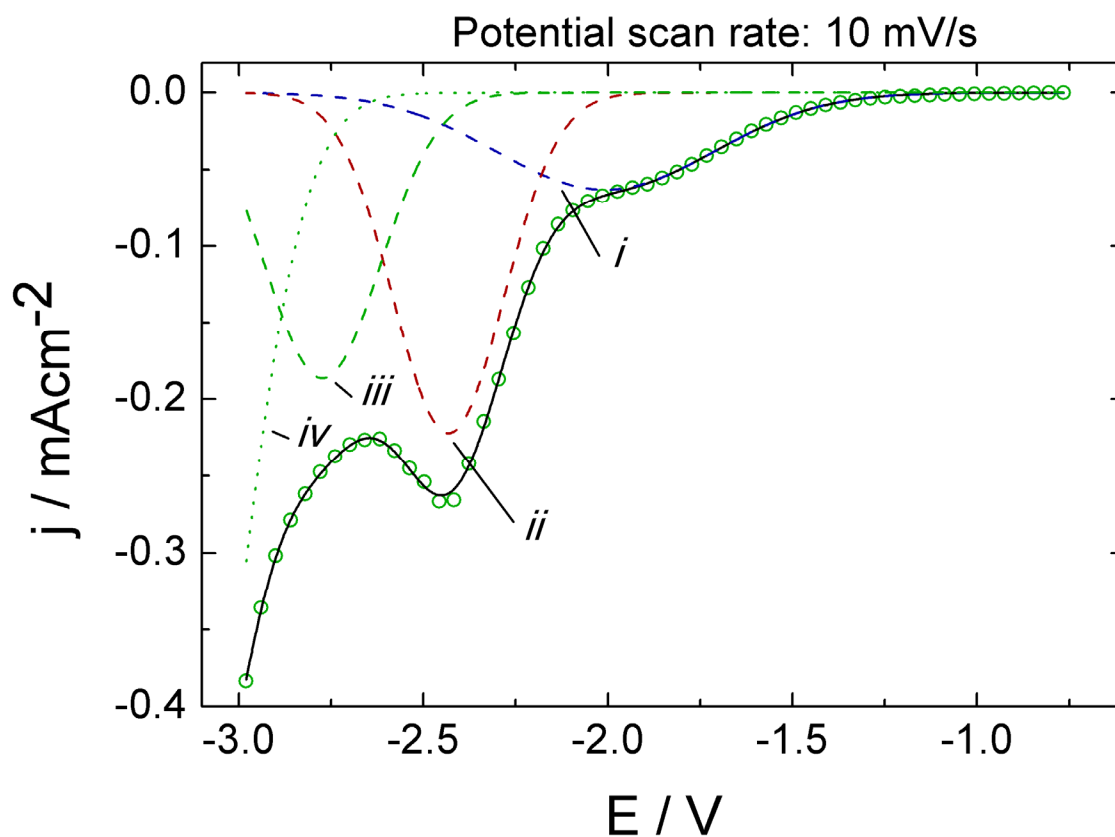


Figure S2. Deconvolution of cathodic wave related to the electrochemical reduction of a GO-coated silicon electrode in 0.1 M TBAPF₆/CH₃CN solution at 10 mVs⁻¹ potential scan rate. The graph shows: experimental current-potential data (olive open circles), deconvolution peaks (coloured dashed lines, from *i* to *iii* as indicated) and simulated envelope voltammogram (black solid line). The solvent contribution curve *iv* is also depicted. The reference electrode was a silver wire immersed in 0.01 M AgNO₃/0.1 M tetrabutylammonium perchlorate (TBAP, Sigma-Aldrich) in CH₃CN (+0.544 V vs. NHE, +0.345 V vs. Ag/AgCl).

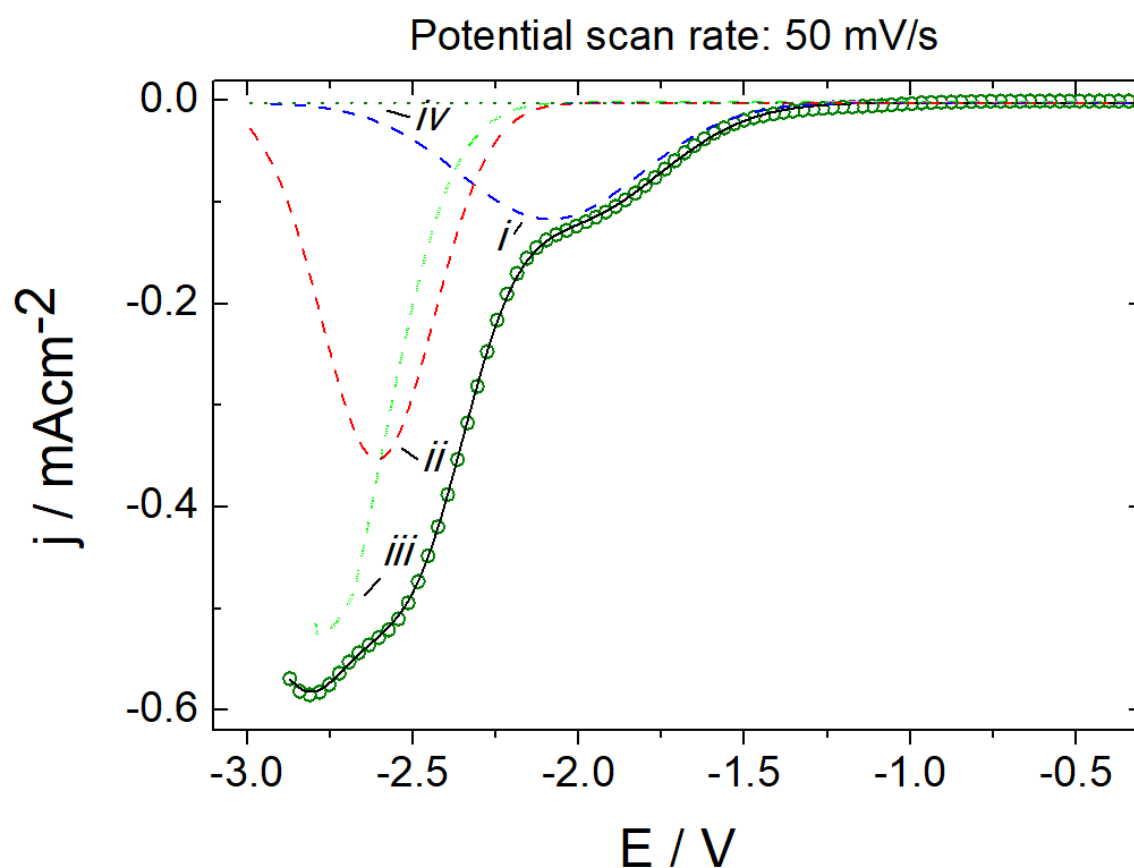


Figure S3. Deconvolution of cathodic wave related to the electrochemical reduction of a GO-coated silicon electrode in 0.1 M TBAPF₆/CH₃CN solution at 50 mVs⁻¹ potential scan rate. The graph shows: experimental current-potential data (olive open circles), deconvolution peaks (coloured dashed lines, from *i* to *iii* as indicated) and simulated envelope voltammogram (black solid line). The solvent contribution curve *iv* is also depicted. The reference electrode was a silver wire immersed in 0.01 M AgNO₃/0.1 M tetrabutylammonium perchlorate (TBAP, Sigma-Aldrich) in CH₃CN (+0.544 V vs. NHE, +0.345 V vs. Ag/AgCl).

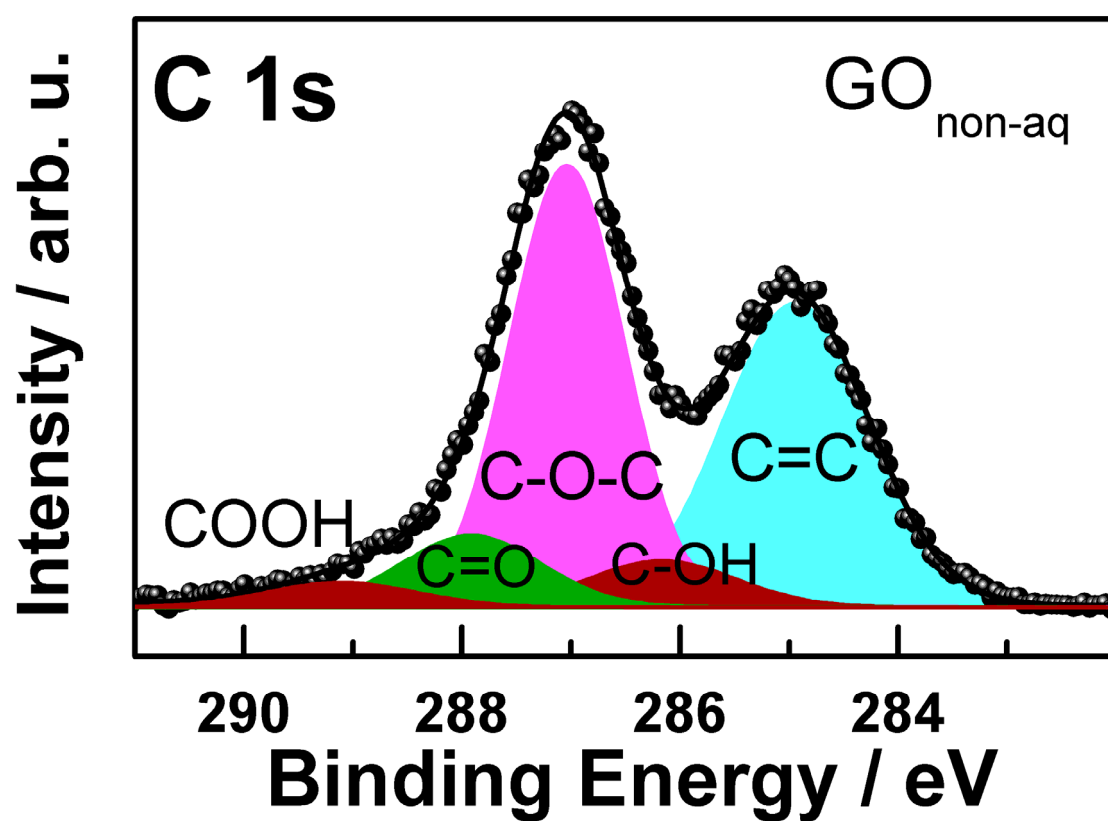


Figure S4. C 1s XP spectrum of pristine GO_{non-aq} sample. Raw data are displayed with dots, while fitting reconstruction with a continuous line and color filled curves.

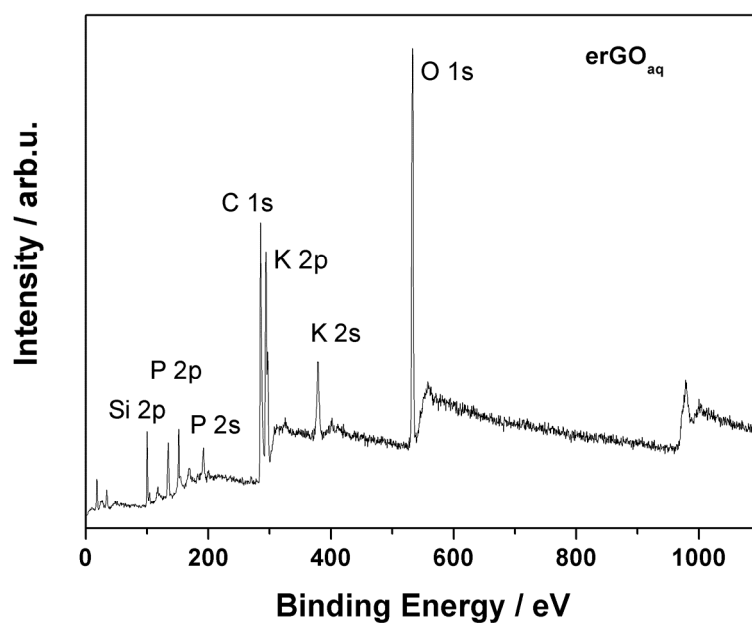


Figure S5. Wide XP spectrum of erGO_{aq} sample.

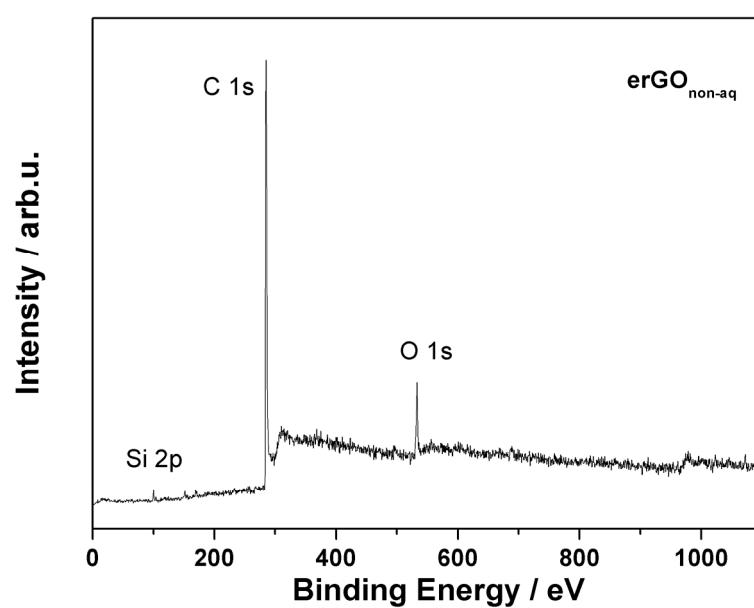


Figure S6. Wide XP spectrum of $\text{erGO}_{\text{non-aq}}$ sample.

Table S1. Relative removal degree percentage of four different OFGs (as indicated) after the electrochemical reduction process of typical GO-coated Si electrodes in and aqueous medium (1.0 M pH=7.2 PBS buffer solution) and in a non-aqueous one (0.1 M TBAPF₆/CH₃CN solution). The potential scan rate was 20 mV s⁻¹ and for a whole electrochemical process of five cycles. In all cases these OFG content values were calculated from the C 1s XPS spectra.

Sample	C-OH	C-O-C	C=O	COOH
erGO_{aq}	-193.0	84.2	63.7	-71.0
$\text{erGO}_{\text{non-aq}}$	-27.0	83.7	80.6	74.1

Oxygen/carbon atomic ratio ($R_{O/C}$) calculation from XPS spectra

The oxygen-to-carbon ratio ($R_{O/C}$) was calculated from the XPS data. Due to the inevitable absorption of water molecules and oxidation of H-Si, the O 1s peak includes these components besides the oxygen in GO, and hence it is not appropriate to directly use O 1s peak area to calculate $R_{O/C}$. Then, as proposed by Yudi Tu et al. [1,2], a semiquantitative approach has been followed. The percentages of different oxygenated groups (P_X , X refers to the different surface-bound oxygenated groups of GO) in C 1s spectra are used to calculate $R_{O/C}$ through the following equation S1:

$$R_{O/C} = \frac{P_{C-OH} + 1/2 P_{Epoxide} + P_{C=O} + 2 P_{COOH}}{P_{C=C} + P_{C-OH} + P_{Epoxide} + P_{C=O} + P_{COOH}} \quad (S1)$$

References

1. Tu, Y.; Utsunomiya, T.; Kokufu, S.; Soga, M.; Ichii, T.; Sugimura, H. Immobilization of Reduced Graphene Oxide on Hydrogen-Terminated Silicon Substrate as a Transparent Conductive Protector, *Langmuir* **2017**, *33*, 10765–10771.
2. Tu, Y.; Nakamoto, H.; Ichii, T.; Utsunomiya, T.; Khatri, O.P.; Sugimura, H. Fabrication of reduced graphene oxide micro patterns by vacuum-ultraviolet irradiation: From chemical and structural evolution to improving patterning precision by light collimation, *Carbon* **2017**, *119*, 82–90.