

SUPPLEMENTARY INFORMATION

Effect of confined space reduction of graphite oxide followed by sulfur doping on oxygen reduction reaction in neutral electrolyte

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Supplementary Results:

Table S1. Changes in oxygen content for the experiments in 0.5 Na₂SO₄.

Sample	O ₂ Concentration (mg L ⁻¹)
RGO-O ₂	before/after CV 7.83/9.29
RGO-N ₂ above	before/after CV 7.83/2.76
RGO-N ₂ In and above	before/after CV 2.01/3.30
RGOS-O ₂	before/after CV 7.83/8.08
RGOS-N ₂ above	before/after CV 7.83/2.56
RGOS-N ₂ In and above	before/after CV 1.92/2.40

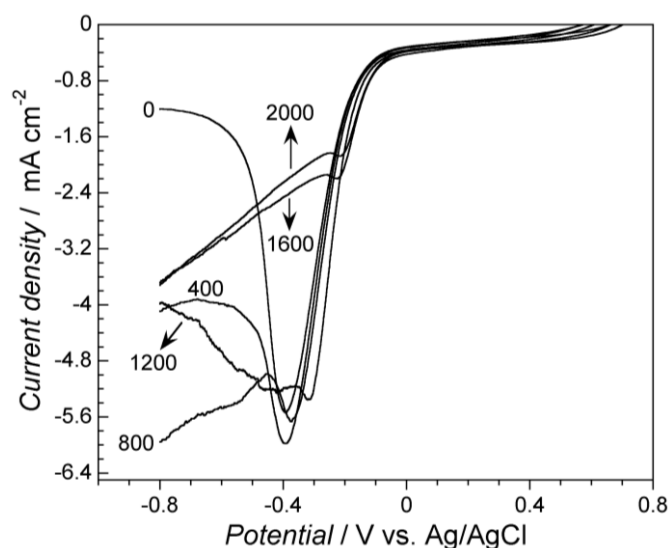


Fig. S1. Linear sweep voltammograms on modified glassy carbon RDE in air-saturated 0.5 M Na_2SO_4 at different rotation speeds at scan rate of 5 mV s^{-1} for GO-800.

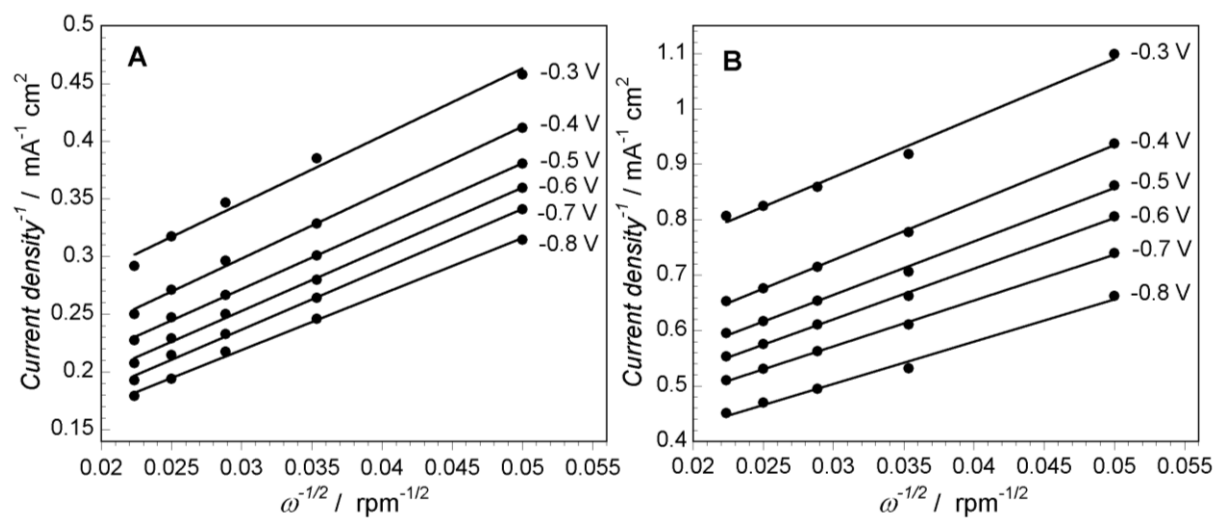


Fig. S2. Koutecky–Levich plots for: A) RGO and B) RGOS.

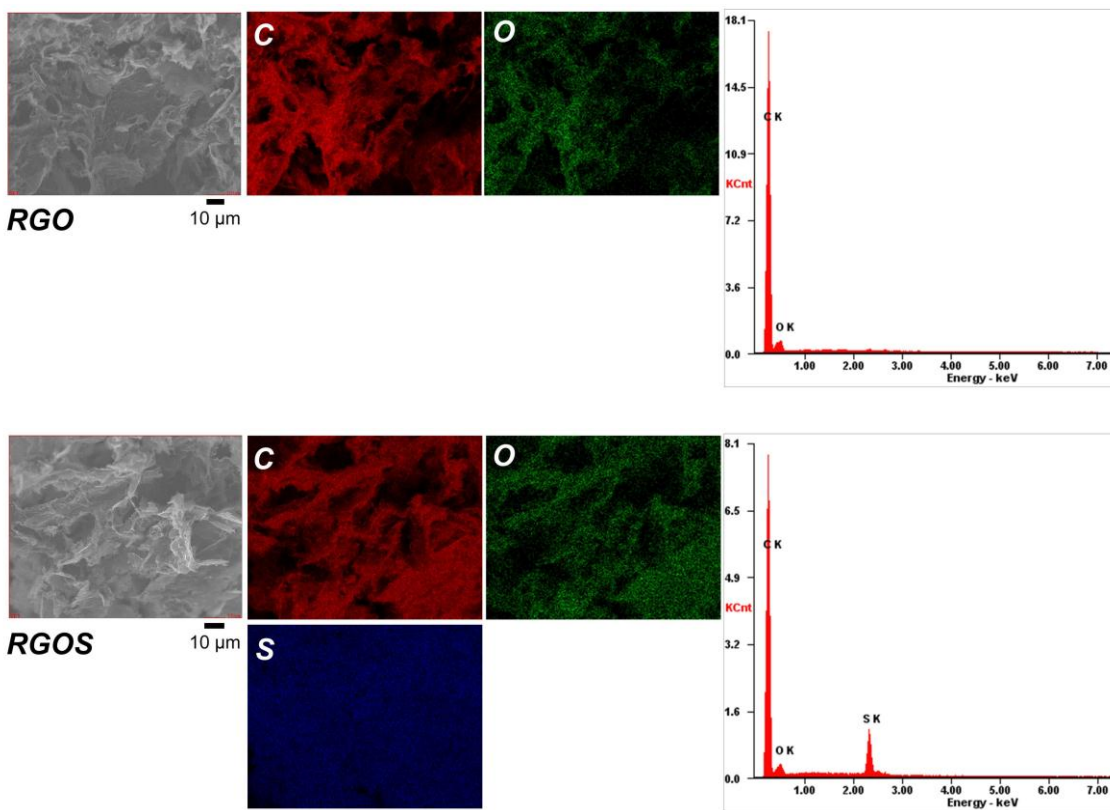


Fig. S3. EDX maps for RGO and RGOS.

Table S2. The contents of elements on the surface.

Sample	C	O	S	C	O	S
	EDX (in at. %)			XPS (in at. %)		
RGO	90.7	9.3	---	91.1	8.7	0.2
RGOS	91.3	5.7	3.0	94.4	2.8	2.8

Table S3. Chemical states of C, O and S atoms on RGO and RGOS with a surface concentration (in atomic %) and their binding energy (in parenthesis; [eV]).

Sample	C-(C,S)	C-O	C=O	C(O)O	O-IV	O-I	O-II	O-III	S ⁰ /S ₈	R-SH	C-S-C/ R-S ₂ -OR	R ₂ -S=O
					(O/OH ⁻)	(O=C)	(-O-C)	(O)				
RGO	83.4	4.3	2.0	1.4	0.5	1.2	6.7	0.3	---	0.16	0.02	0.02
	(284.4)	(286.6)	(287.6)	(289.0)	(530.3)	(531.5)	(533.1)	(535.2)		(163.8)	(164.4)	(167.2)
RGOS	94.3	---	0.1	---	0.4	0.6	1.6	0.2	0.18	2.28	0.21	0.13
	(284.5)		(287.3)		(530.5)	(531.9)	(533.6)	(535.3)	(162.0)	(163.8)	(164.8)	(166.8)

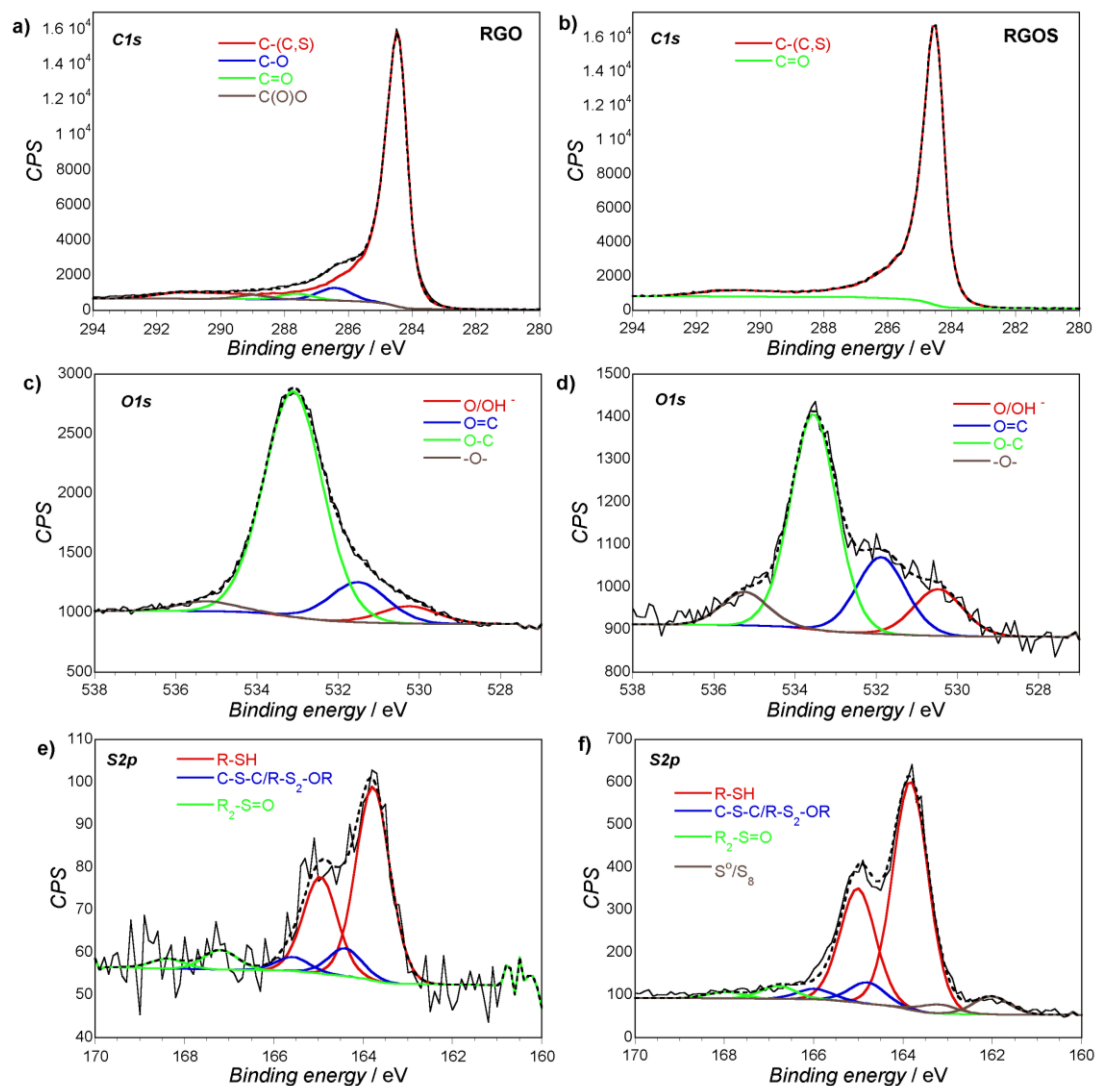


Fig. S4. The results of XPS spectra for C1s, O1s and S2p.

FTIR analysis

The FTIR spectra before and after all CV cycles are presented in Fig. S7. To clearly show the changes in the chemistry of modified GO, the spectrum for the initial GO is also included.^{S1} The bands at 1050 cm⁻¹ and 1380 cm⁻¹ represent the vibrations of C-O and O-H bonds, respectively.

The band at 1630 cm^{-1} is attributed to either O-H vibration in water and/or to the presence of oxygen surface compounds such as cyclic ethers and the one at 1735 cm^{-1} corresponds to the vibrations of C=O in carboxylic groups.^{S2,S3} The band at about 990 cm^{-1} represents epoxy groups.^{S3} The vibration at 1225 cm^{-1} are visible and they may be related to S=O asymmetric stretching vibration in sulfones or sulfates and/or vibration of C-O in epoxides.^{S1,S3} In the range of higher wavenumbers three separate -OH modes can be identified with absorptions at 3610, 3420, and 3170 cm^{-1} . They represent the vibration of O-H in as isolated hydroxyl groups, intercalated H₂O, and -COH, respectively.

The spectra for both RGO and RGOS are rather flat owing to the black nature of carbon, high level of aromatization and small amount of functional groups. Nevertheless, after ORR in neutral electrolyte Na₂SO₄ some changes can be distinguished in the increase in the intensity of the band at 1500 cm^{-1} and 1380 cm^{-1} which represent stable forms of chemisorbed oxygen and deformation vibrations of O-H groups,^{S4} respectively. The absorption band at 1150 cm^{-1} and broad band with a center at 1020 cm^{-1} is attributed to C-O stretching vibrations and O-H bending modes and might be attributed to phenol, ether, lactones, carboxyl and phenolic structures. These changes indicate the oxidation of electrode surfaces.

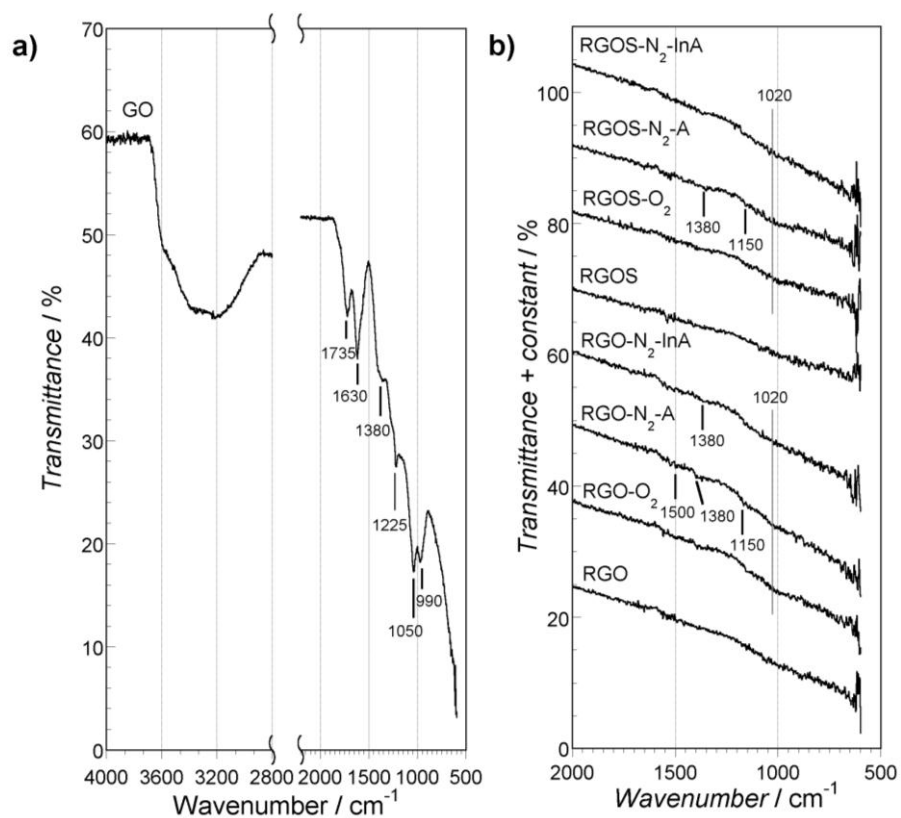


Fig. S5. FTIR spectra for the materials studied.

[S1] C. Petit, M. Seredych, T.J. Bandoz, *J. Mater. Chem.* **2009**, *19*, 9176.

[S2] T. Szabo, O. Berkesi, I. Dekany, *Carbon* **2005**, *43*, 3181.

[S3] C. Hontoria-Lucas, A.J. Lopez-Peinado, J. de D. Lopez-Gonzalez, M.L. Rojas-Cervantes, R.M. Martin-Aranda, *Carbon* **1995**, *33*, 1585.

[S4] J. Zawadzki, in *Chemistry and Physics of Carbon*, Vol. 21 (Ed: P.A. Thrower), Marcel Dekker, New York, USA **1989**, Ch. 2.