Supporting Information

Co_3O_4/rGO catalysts for oxygen electrocatalysis: on the role of the oxide/carbon interaction

I. Abidat [1], E. Cazayus [2], L. Loupias [1], C. Morais [1], C. Comminges [1], T. W. Napporn [1], D. Portehault [2], O. Durupthy [2], A-S. Mamede [3], C. Chanéac [2], J-F. Lamonier [3], A. Habrioux [z,1], K. B. Kokoh [1].

[1] *Université de Poitiers, IC2MP CNRS UMR 7285, 4 rue Michel Brunet, TSA 51106, 86073 Poitiers, Cedex 9, France.*

[2] *Sorbonne Université, CNRS, Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris, 4 place Jussieu, F-75005 Paris, France*

[3] *Univ. Lille, CNRS, ENSCL, Centrale Lille, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France.*

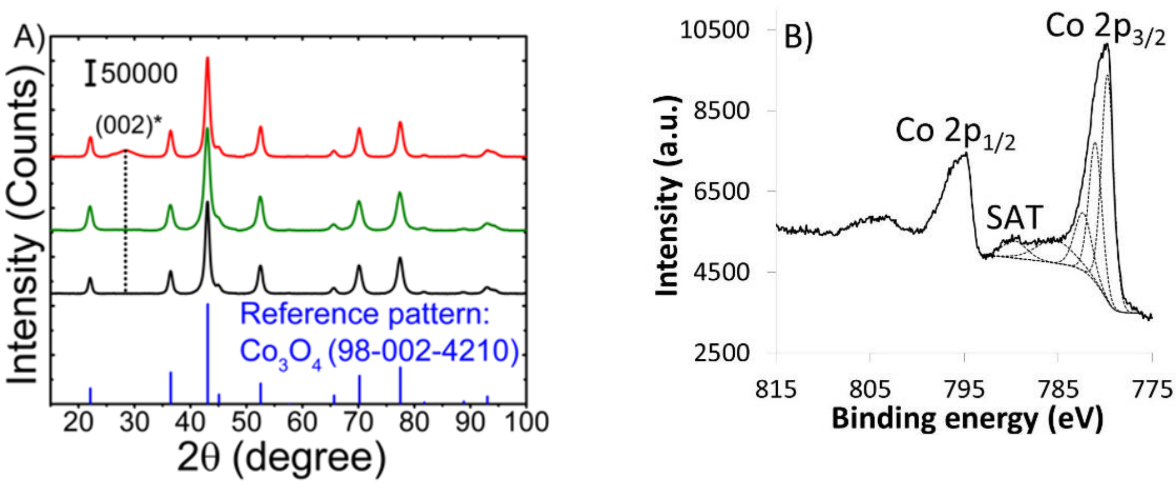

Figure S1: A) Powder X-ray diffraction patterns of as-prepared Co-based nanocomposites: Co_3O_4/GO (black line), Co_3O_4/rGO-PR (green line) and Co_3O_4/rGO-SR (red line) B) High resolution XPS spectrum of Co 2p region registered with Co_3O_4/GO sample.

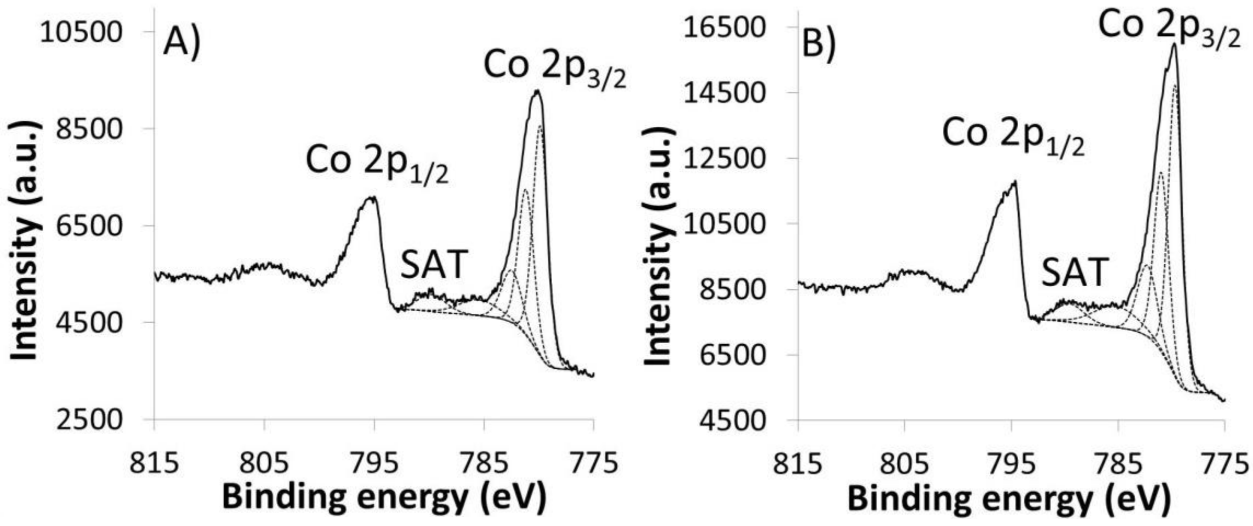

Figure S2. High resolution XPS spectra of Co 2p region registered with A) Co_3O_4/rGO-PR and B) Co_3O_4/rGO-SR samples

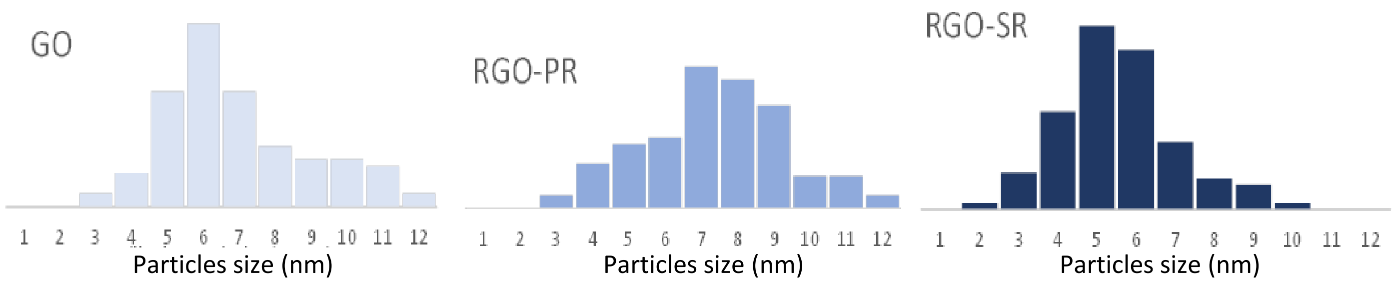

Figure S3. TEM size distributions

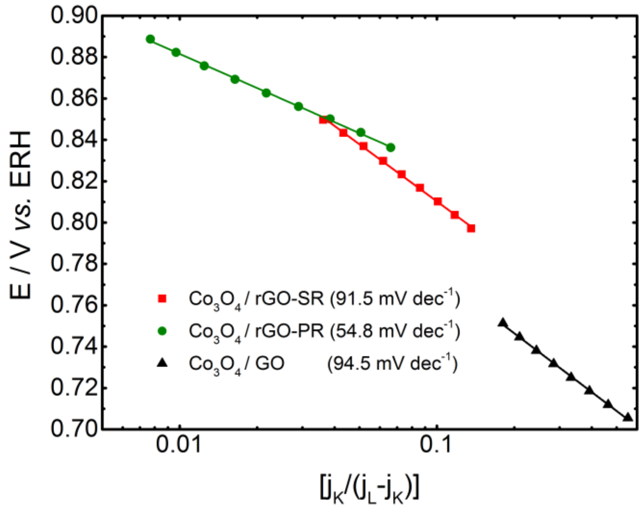

Figure S4. Tafel plots obtained from the kinetic (j_K) and limiting current densities (j_L).

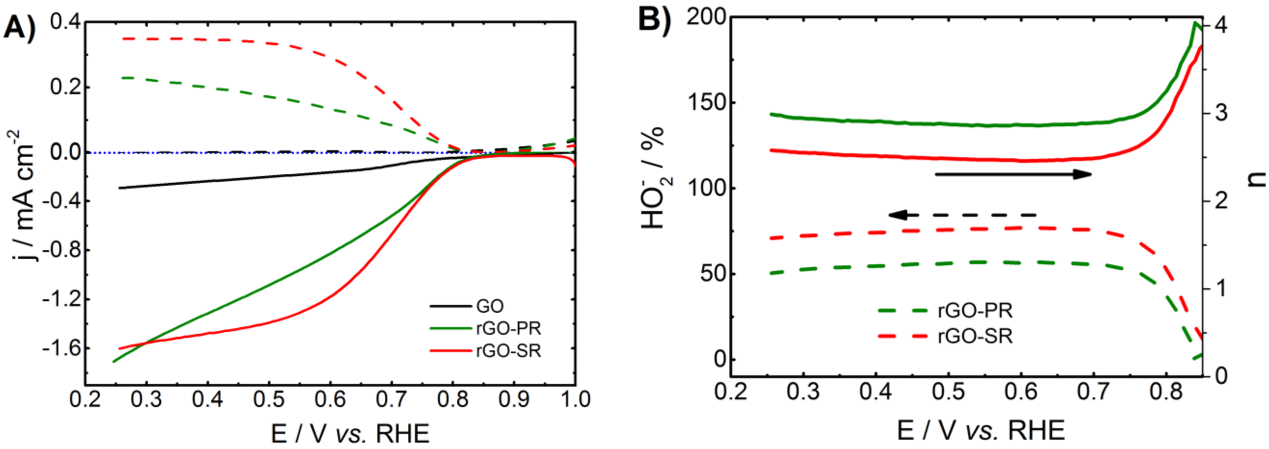

Figure S5. A) ORR polarization curves recorded with the different carbon based substrates using a RRDE. These curves were recorded in an O_2-saturated 1 mol L^{-1} KOH electrolyte at a scan rate of 5 mV s^{-1}, at 25 °C and at a rotation rate of 1600 rpm. The ring is polarized at 1.2 V vs. RHE during the experiment. B) Calculated peroxide yield and electron transfer number (n_{exp}) exchanged per oxygen molecule on the basis of RRDE electrochemical data.

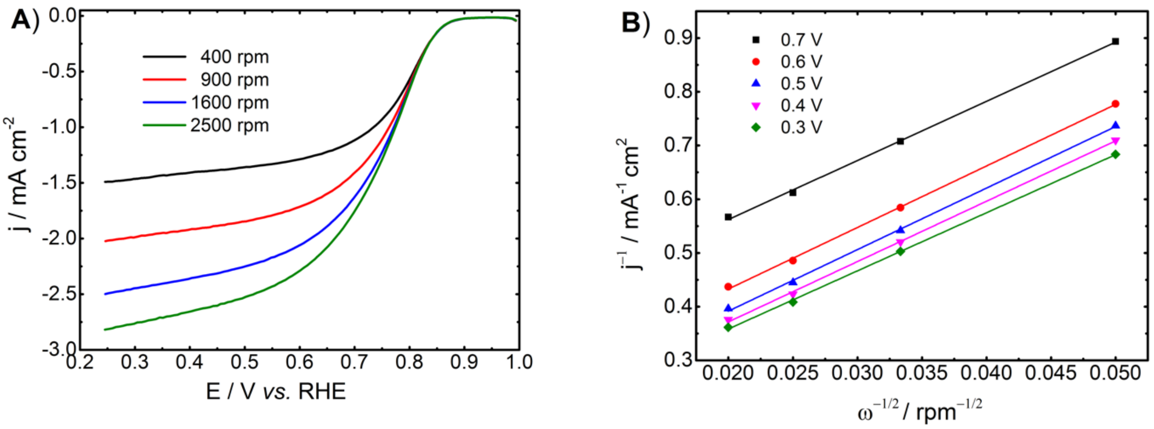

Figure S6. (A) ORR polarization curves recorded with Co_3O_4/rGO-PR catalyst in an O_2-saturated 1 mol L^{-1} KOH electrolyte at a scan rate of 5 mV s^{-1} and at different rotating rates for the RDE electrode. (B) Koutecky-Levich plots at different electrode potential values.

Table S1: Electrical performances of bifunctional catalysts from literature. E_{j10} is the potential required to drive a current density of 10 mA cm^{-2} during OER and $E_{1/2}$ is the ORR half-wave potential.

Catalysts	Catalyst loading (mg cm^{-2})	Electrolyte	E_{j10} (V/RHE)	$E_{1/2}$ (V/RHE)	E_{j10}-$E_{1/2}$ (V)	Ref.
Co_3O_4/rGO-PR	0.20	1 M KOH	1.62	0.77	0.85	This study
Co_3O_4/rGO	0.24 OER 0.17 ORR	0.1 M KOH	1.55	0.80	0.75	(1)
Co_3O_4/rGO	0.21	1 M KOH	1.67	0.78	0.89	(2)
Co_3O_4/N-rGO	0.24 OER 0.1 ORR	1 M KOH	1.58	0.85	0.78	(3)
Commercial IrO_2 powder	0.20	1 M KOH	1.62	N/A	N/A	This study
Commercial Pt/C (10 wt. %) powder	0.20	1 M KOH	N/A	0.90	N/A	This study

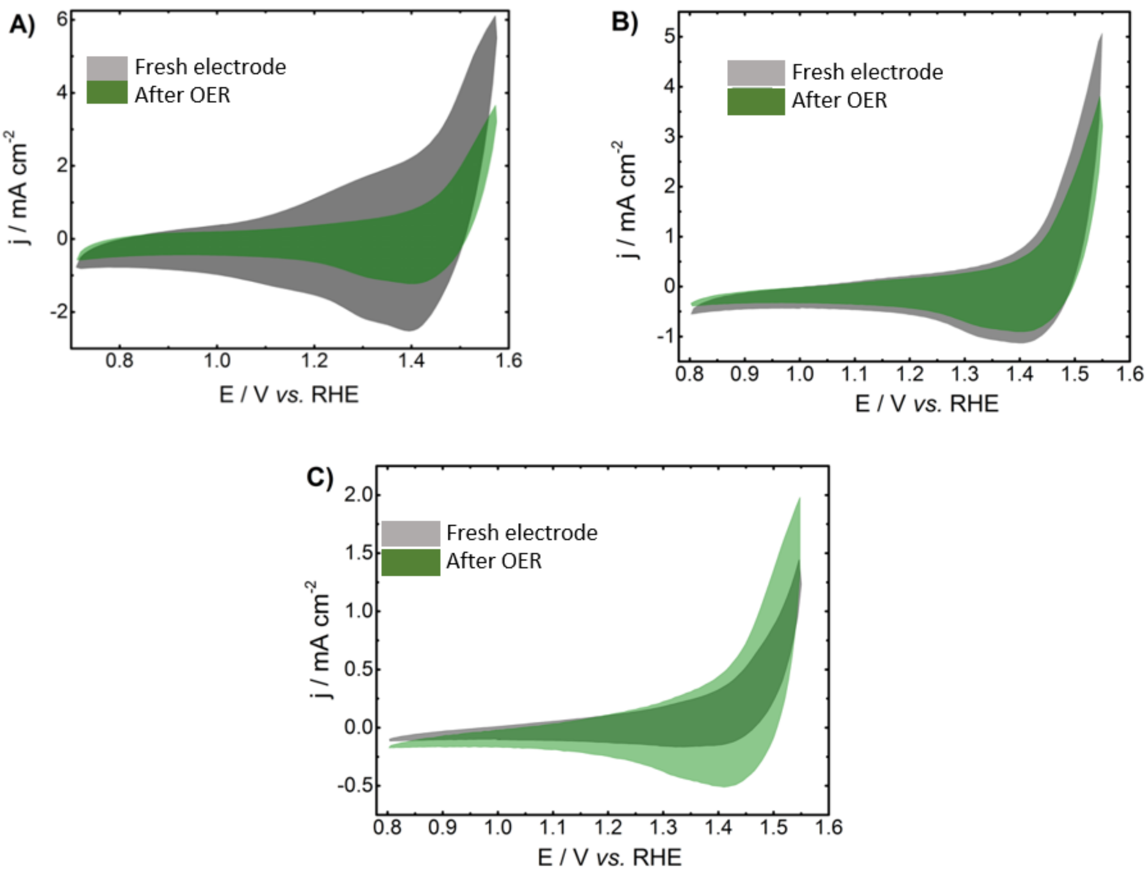

Figure S7. Voltammograms recorded in supporting electrolyte (1 mol L^{-1} KOH) under N_2 atmosphere at a scan rate of 50 mV s^{-1}, before and after 1000 voltammetric cycles at 200 mV s^{-1}. With A) Co_3O_4/rGO-SR, B) Co_3O_4/rGO-PR and C) Co_3O_4/GO.

References :

(1) Liang, Y.; Li, Y.; Wang, H.; Zhou, J.; Wang, J.; Regier, T.; Dai, H. Co_3O_4 nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction. *Nat Mater* **2011,** *10* (10), 780-786
(2) Kumar, K.; Canaff, C.; Rousseau, J.; Arrii-Clacens, S.; Napporn, T. W.; Habrioux, A.; Kokoh, K. B. Effect of the Oxide–Carbon Heterointerface on the Activity of Co_3O_4/NRGO Nanocomposites toward ORR and OER. *J. Phys. Chem. C* **2016,** *120* (15), 7949-7958
(3) Liang, Y.; Wang, H.; Zhou, J.; Li, Y.; Wang, J.; Regier, T.; Dai, H. Covalent Hybrid of Spinel Manganese–Cobalt Oxide and Graphene as Advanced Oxygen Reduction Electrocatalysts. *J. Am. Chem. Soc.* **2012,** *134* (7), 3517-3523