

Supporting Information

Influence of sp^3 - sp^2 Carbon Nano-Domains on Metal/Support Interaction, Catalyst Durability and Catalytic Activity for the Oxygen Reduction Reaction

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Section S1: FTIR of carbon supports

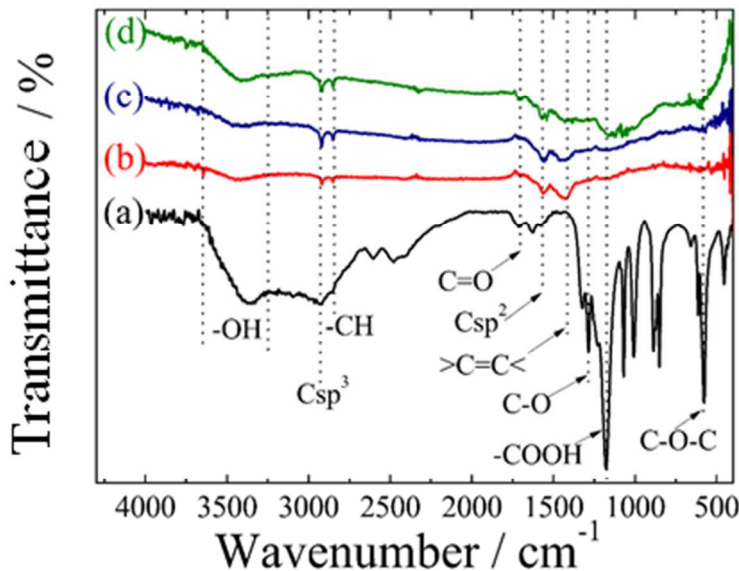


Figure S1. FTIR spectra of (a) Vulcan, (b) CNT, (c) *f*-CNT, and (d) *e*-CNT, from 4000-400 cm^{-1} , at RT.

To put in evidence the evolution of functional groups grafted onto carbon supports, FTIR measurements were carried out, using KBr pellets, in the spectral region from 4000 to 400 cm^{-1} . KBr pellets were done with 0.1 mg of carbon support and mixed with 150 mg of KBr

(Aldrich, >99%). Measurements were carried out in a Perkin-Elmer Spectrum 100, at room temperature.

All materials showed a signal between 3600 and 3300 cm^{-1} due to the O-H stretching. At 2900 and 2850 cm^{-1} the vibrations are associated with the symmetrical and asymmetrical stretching of Csp^3 hybridization, and C-H, respectively. At 1720 cm^{-1} , it is possible to appreciate the C=O band, on Carbon (Vulcan) and the exfoliated CNT (*e*-CNT). The weak signal intensity at 1720 cm^{-1} can be thus attributed to C=O groups. sp^2 ($=\text{C}-\text{H}_2$) hybridized carbon signal vibration is observed at 1560 cm^{-1} . The $>\text{C}=\text{C}<$ conjugated alkene system is centered at 1428 cm^{-1} . The carbon (Vulcan) however, shows bands related to C-O and COOH at 1280 and 1200 cm^{-1} . On *e*-CNT these signals are, nevertheless, weaker. Finally, it is possible to observe the signal associated to the oxygenated aromatic ring systems vibration at 600 cm^{-1} . FTIR spectroscopy strongly puts in evidence that carbon (Vulcan) and *e*-CNT surface possess the highest density of oxygenated functional groups, being small on the latter.

Section S2: ORR electrochemistry

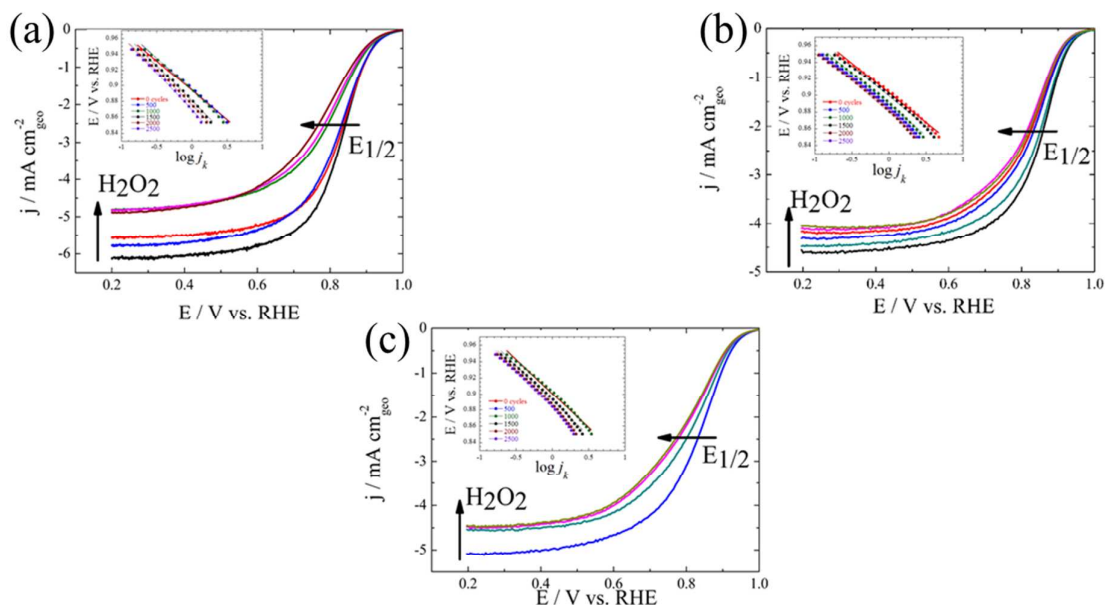


Figure S2. ORR polarization curves and Tafel plots (inserts) through the AST of a)Pt/C, b) Pt/CNT and c)Pt/f-CNT, all prepared by photodeposition. Measurements were done in 0.1M HClO₄, at 25 °C, 1.02 to 0.2V, 5 mV/s, every 500 cycles.

We can observe the shift to negative electrode potentials of the reduction-wave shape as number of cycles increases, as well as the half-wave potential ($E_{1/2}$) and the limited current value. Pt/f-CNT is the material that shows the highest stability.

The Tafel slopes of all materials suggest that the oxygen reduction process is carried out by the same mechanism. The kinetic current is more stable on Pt/f-CNT.