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Graphene-based electrocatalysts for the oxygen evolution reaction

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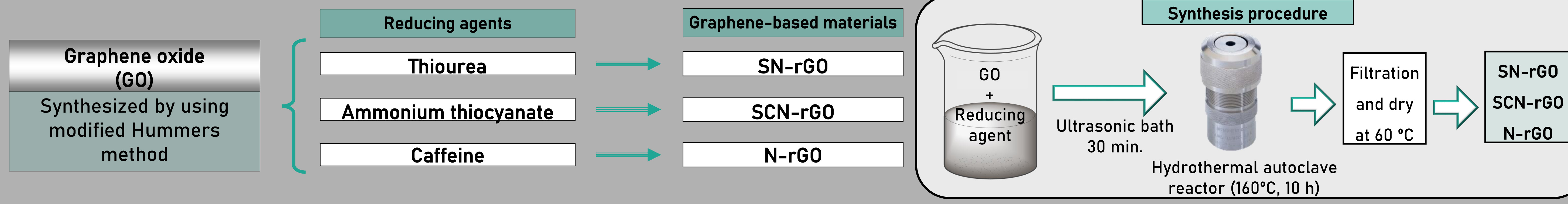
Summary

The increasing global warming caused by the combustion of fossil fuels is leading to a search for alternatives environmentally friendly, accessible, and economically attractive. Hydrogen is considered a clean fuel for the future because it acts as a green energy carrier and provides a method for the storage and transport of energy. A variety of processes are available for H₂ production, based on conventional or renewable technologies. Water electrolysis offers a practical route for sustainable hydrogen production by utilizing a renewable electrical energy source for water splitting. The oxygen electrode in electrolyzers plays a central role as its catalytic activity and stability are conditioned by its slow kinetics under operating conditions [1,2].

Graphene-based electrocatalysts emerged as promising materials to improve efficiency in numerous electrochemical reactions since they are low-cost, abundant, and electrical conductors with tunable catalytic activity. Insertion of heteroatoms into graphene network may produce electronic and geometric distortions of the carbonaceous grid, and consequently, the activity toward several electrochemical reactions may be altered. Basically, two types of doping may occur in the graphene network depending on the interatomic distance between carbon-heteroatom compared to C-C. Thus, B-C, N-C and C-C have similar interatomic distance, and therefore, it is expected that after the heteroatom-modification the system will follow a similar modus operandi; on the other hand, P-C, Si-C and S-C show higher interatomic distance than C-C and their modification will display an exohedral doping, i.e., the heteroatom will be located above and/or below the graphene sheet. Another factor to take into account in the catalyst activity is the surface local acidity, which may be altered by the introduction of functional groups in the graphene network [3].

With the aim to solve the principal catalytic problems at the oxygen electrocatalysts in electrolyzers, S- and N-doped graphene-based materials were synthesized, characterized and tested toward the oxygen evolution reaction (OER) in alkaline medium. In-situ Raman spectroelectrochemistry, rotating ring-disk electrode (RRDE), cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques were used to determine the catalytic activity of heteroatom-doped graphene catalysts toward the OER. Main results indicate that the OER is strongly influenced by the nature and amount of the doping agent in addition to the interaction with the electrolyte media, which also conditioned Raman signals such as the position of the D- and G-bands and the Area_D/Area_G (A_D/A_G) ratio. Additionally, the percentage of molecular oxygen production is estimated by a novel procedure [1,2].

Experimental

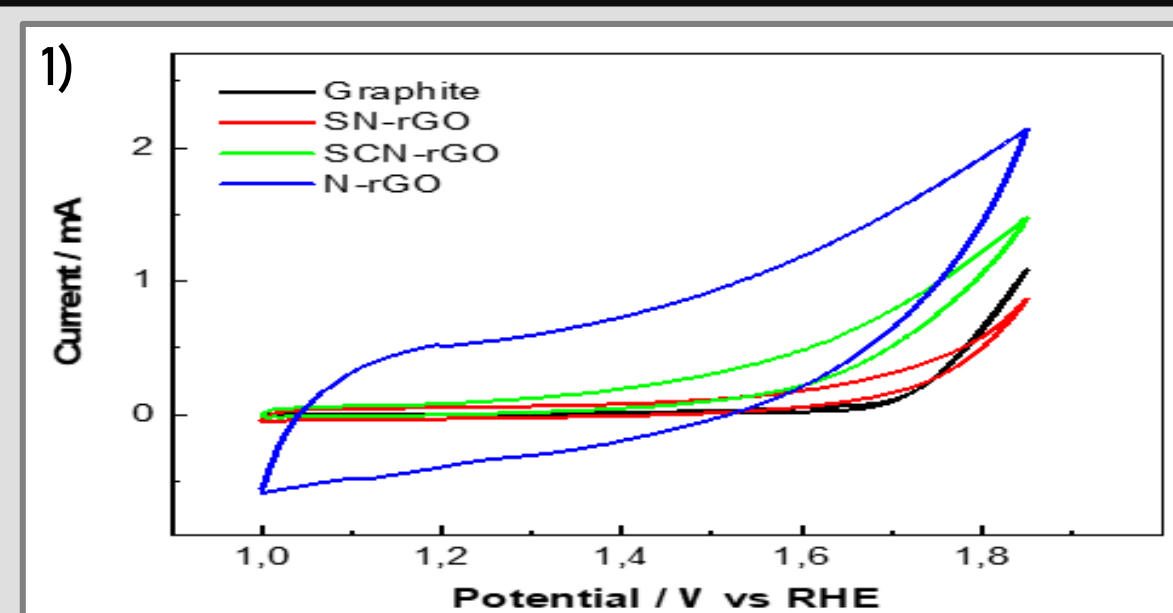


Physicochemical characterization

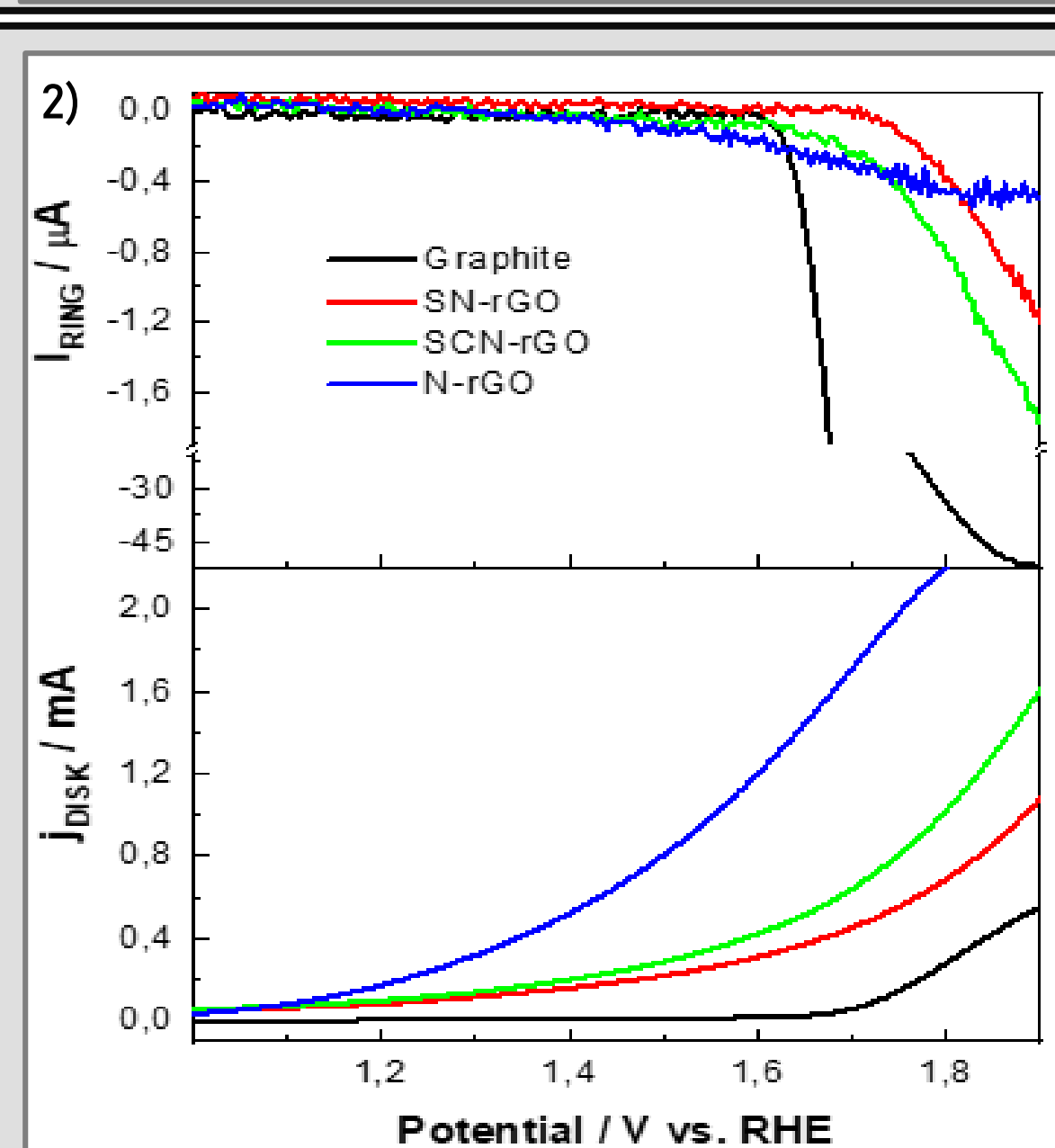
X-ray diffraction^a, Raman^b parameters and elemental analysis^c (wt%) for all studied materials

Material	Interplanar spacing (nm) ^a	Edge plane size (L _c , nm) ^a	Basal plane size (L _a , nm) ^b	Number of layers ^a	C/O ^c	S ^c	N ^c
Graphite	0.34	47.18	90	140	4.0	-	-
SN-rGO	0.36	1.88	16	6	5.6	7.3	2.7
SCN-rGO	0.36	1.76	19	6	4.4	13.6	9.2
N-rGO	0.35	2.90	20	9	3.5	-	6

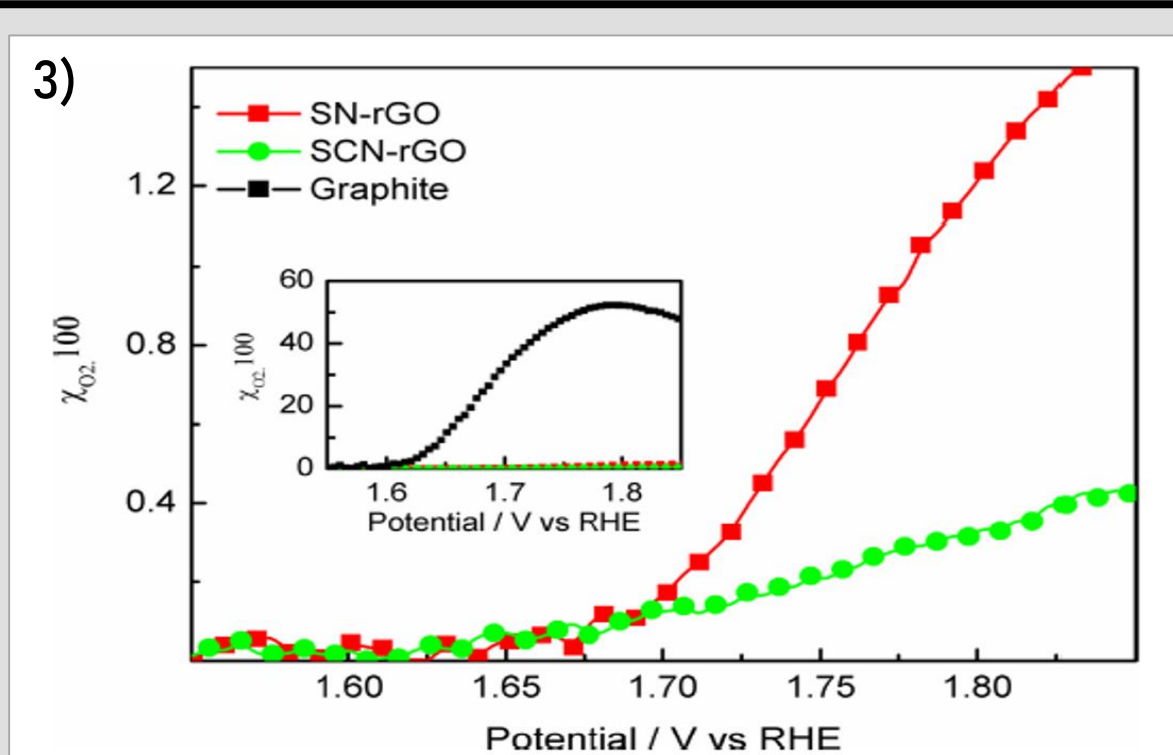
Electrochemical characterization



Cyclic voltammetry (CV) is an electrochemical technique which consists in applying to the working electrode a linear variation of the potential between two limited potentials at a constant speed while registering the current. Figure 1 displays the CVs recorded in deaerated alkaline solution at 10 mV s⁻¹ of the synthesized graphenic materials compared with graphite. An increase in the capacitive current is observed with the insertion of nitrogen into the graphenic structure.



Current developed during a potential excursion in the positive-going direction at 1 mV/s (polarization curve) is associated to both oxidation of the carbon material producing CO₂ and the evolution of oxygen (OER). A rotating ring disk electrode (RRDE) allows distinguishing between both processes and consists of two working electrodes: a platinum ring and a glassy carbon disk with the catalysts ink. Potentials applied at these electrodes can be selected independently. During the measurement, both electrodes are rotating and the products generated at the disk can be detected at the ring. Figure 2 shows the OER polarization curves for all catalysts (bottom panel) and the signal acquired simultaneously at the ring electrode (upper panel) corresponding to the detection of O₂. N-rGO presents the earliest onset potential for the disk current (≈ 1.1 V) followed by SCN-rGO, SN-rGO and graphite. Besides N-rGO has the earliest potential, it develops less current detected by the ring and therefore, its OER activity is the lowest one.



$$I_{Disk} = I_{O_2} + I_{CO_2} \quad (1) \quad \chi_{O_2} = \frac{I_{O_2}}{I_{O_2} + I_{CO_2}} \quad (3)$$

$$I_{O_2} = I_{Ring} / N \quad (2) \quad \chi_{O_2} = \frac{I_{Ring}}{I_{Disk} N} \quad (4)$$

From the data in Figure 2 and the equations above (where the current is denoted as I and N is the collection efficiency of the RRDE), the molar fraction of O₂ (χ_{O₂}) generated at the catalyst can be obtained as it is shown in Figure 3. By setting the ring potential to 0.4 V, O₂ produced at the working electrode arrives at the ring and it is reduced to water but at this potential, the CO₂ cannot be reduced, i.e. current at the disk is only related to the OER. Graphite exhibits the highest OER activity (~55% O₂ generation) but a very low percentage of molecular oxygen production and high degradation rate were observed for all graphene-based catalyst, being confirmed that N-rGO presents the poorest OER activity of the studied materials. It is shown that this novel method to estimate the O₂ production offers high sensibility even at very low efficiencies.

Spectroelectrochemical characterization

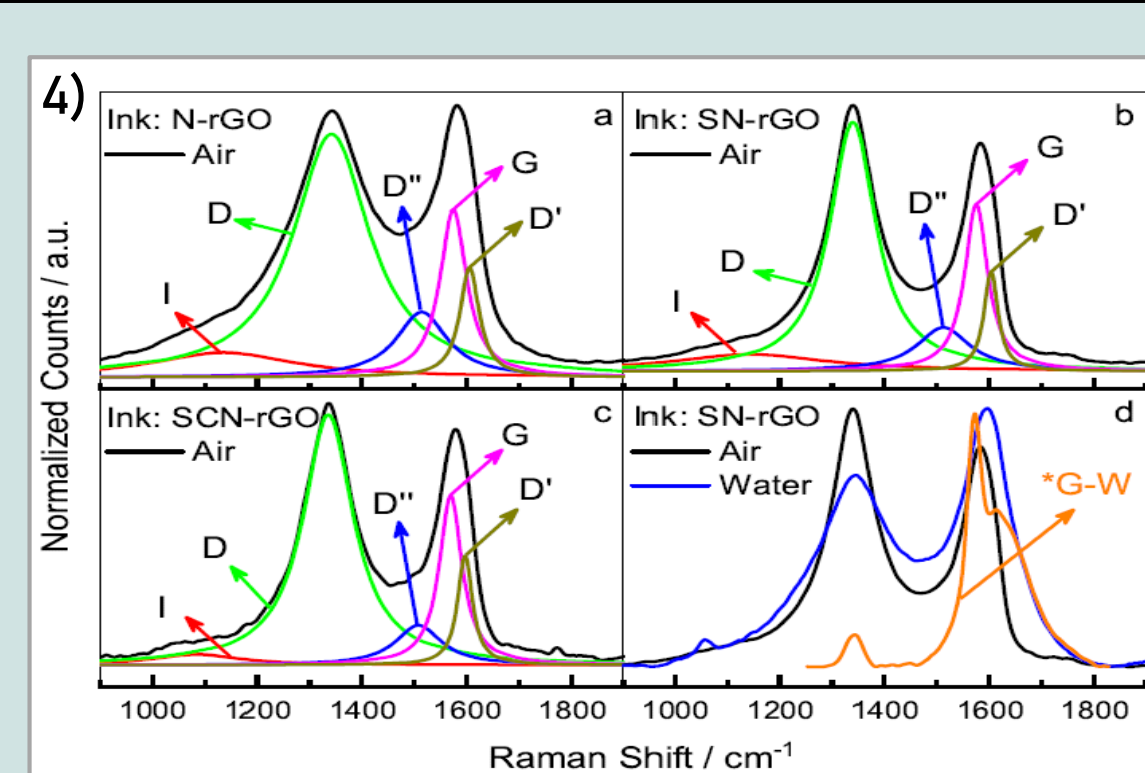


Figure 4 shows the Raman spectra of graphene-based materials in air. Two main bands are observed: the peak at ca. 1340 cm⁻¹ (D-band) and at ca. 1570 cm⁻¹ (G-band). D-band is associated with the presence of sp³ carbon domains and is strongly influenced by the presence of defects in the structure whereas G-band is related to the presence of sp² bonds into the graphitic network [4]. Additional vibrational modes are apparent: i) I mode is associated to defects of non-homogeneous nature; ii) D' band can be attributed to disorder in graphite; and iii) D'' contribution is related to interstitial defects from amorphous sp²-bonded forms of carbon. The materials show a similar profile, but the relation of intensity of these bands is affected in the presence of water (Figure 4d).

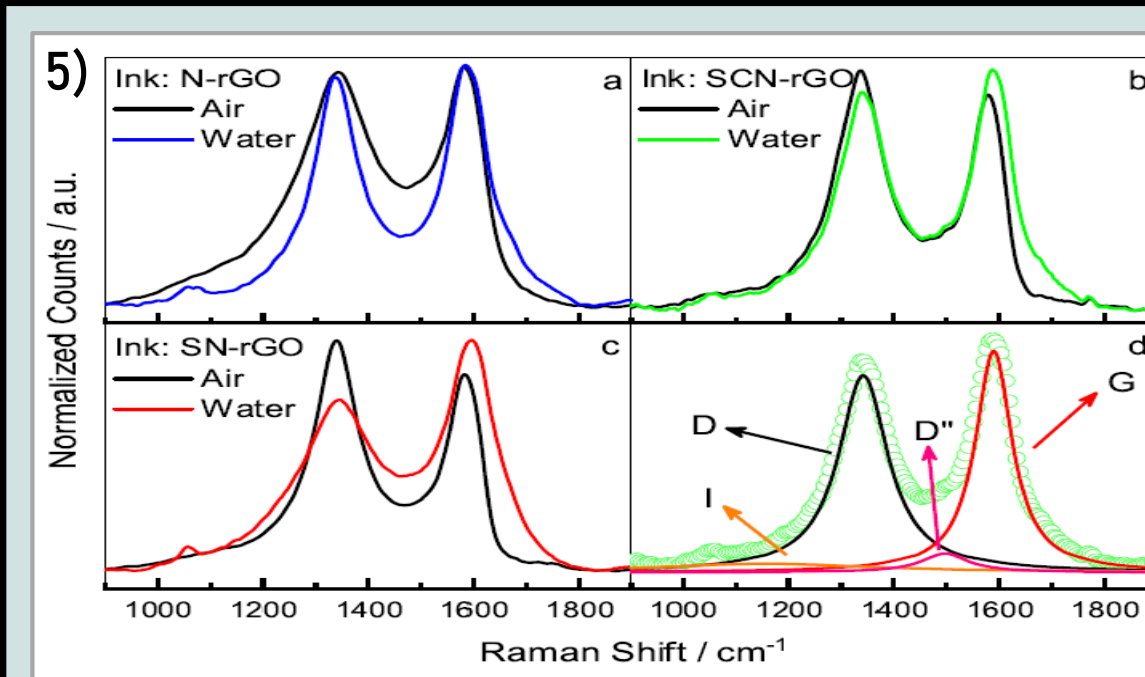
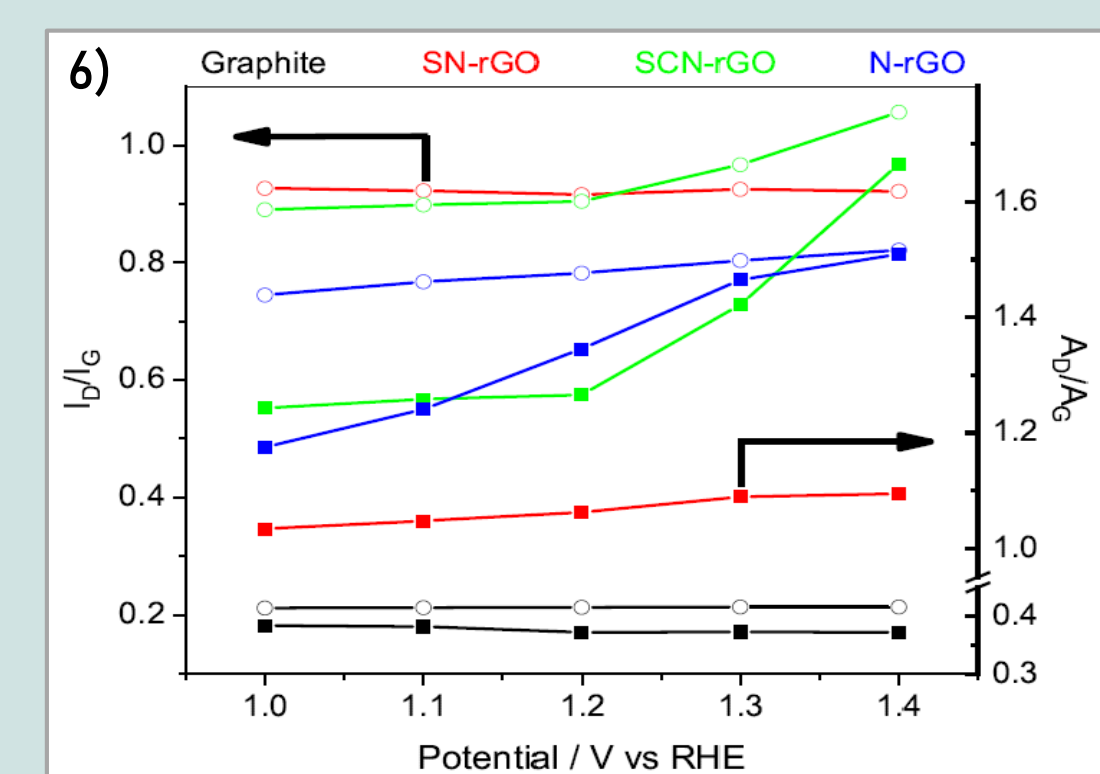


Figure 5 compares Raman spectra in presence of air and water for all graphene-based materials. These all Raman bands (I, D, D', G, D'') are strongly affected in presence of water, and consequently, it induces to an alteration of the relationship between the intensities of these peaks (I_D/I_G). This ratio gives information about the disorder of the structure: low values are related to a higher order, mainly graphitic; and great values indicates a high structural disorder.

In-situ Raman spectroelectrochemistry was carried out in alkaline solution to study the evolution of I_D/I_G and Area_D/Area_G with the variation of the potential (from 1.0 to 1.4 V) (Figure 6), in order to get information about the changes in the disorder structure. I_D/I_G is expected to be inversely proportional to the size of the basal plane (L_a in the table of physicochemical characterization), that is graphite << N-rGO < SCN-rGO ≈ SN-rGO. This sequence agrees better with *in situ* I_D/I_G electrochemical data than Area_D/Area_G ratio values (which increase in the following way: graphite << SN-rGO < SCN-rGO ≈ N-rGO).



Conclusions

The properties of N-rGO, SN-rGO and SCN-rGO materials as catalysts for the OER were studied and compared with graphite by using a novel method to estimate the amount of O₂ production. Besides, *in-situ* Raman spectroscopy appears as a suitable technique to monitor the structural and morphological changes of the catalysts during the OER.

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