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Nitro-graphene oxide in Iridium Oxide hybrids: Electrochemical modulation of N-graphene redox states and Charge capacities

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Carbon plays a significant role in the development of electrode materials that include catalysis, energy storage and sensing. Graphene-based coatings and carbon nanotubes on the other hand have expanded that role beyond through nanostructuring in hybrids or the formation of composites. In particular, the formation of hybrids of nanocarbons with iridium oxide yield nanostructured materials through direct anodic deposition, with substantially improved charge capacities vs pure IrOx. Modifying the possible redox sites, new structuring of hybrids and enlarged charge capacities are expected. This work shows that N-doped graphenes, as part of a IrOx hybrid, offer a new redox chemistry on graphene oxide through electrochemical modulation of the redox states of nitrogen in graphene and yielding stable nitro groups bound to carbon, so far the largest oxidation state reported in N-doped graphene. The hybrid materials are obtained in the form of coatings thanks to the spontaneous adhesion of iridium oxo species on N-doped graphenes and further anodic electrodeposition of the mixture. While the oxidizing synthesis process already involves a modification of the oxidation state of nitrogen, further electrochemical cycling evidence the electrochemical processes for both IrOx and N groups attached to graphene oxide. All hybrids obtained present a wide range of nitrogen –based groups that include the nitro group, and a significant charge capacity that remains large upon electrochemical cycling and that involves all the faradic processes from the iridium and graphene components. Among all cases, a particular hybrid, including the highest starting oxidation state, reaches a significantly larger charge capacity, also larger than the graphene oxide hybrid, with 70% retention upon cycling. Although Nitrogen doping of graphene is considered a reducing process, this case shows that the oxidized range of nitrogen doping is also possible. IrOx and the reversible redox processes that iridium offers, are thought to be essential in stabilizing an unusual nitro-carbon-oxide system and allowing a sustained high charge storage capacity that doubles that of pristine graphene or graphene oxide hybrids.

Introduction

Carbon has played a unique role in the design of electrochemical catalysis and energy storage systems or sensors. Its intrinsic capacitance has been explored in capacitors and batteries, alone and in combination with other components [1] while additional faradaic contributions from other components in nanostructured hybrid materials have been crucial to develop new nanostructures and also to improve supercapacitor electrodes as nicely reviewed in [2-4]. Furthermore, when in form of graphene or nanotubes (CNT), nanocarbons show added electrochemical features.[5] When hybrids are formed, with IrOx for example, a key component in O2 reduction and water oxidation, [6] or in biocompatible electrodes, [7,8] charge capacities are found to increase several orders of magnitude in the nanostructured material beyond the values expected from charge attributed to redox processes, and remain stable during electrochemical cycling, while maintaining the redox properties and biocompatibility of the original material. [9-12] The underlying nanostructure is significant from the basic point of view. In the case of carbon nanotubes, the carbon tubes sustain the oxide as in a reinforced concrete structure, [9] allowing thicker coatings and very stable electrodes as compared with pure IrOx. Nanocarbon hybrids are also remarkably different to graphite hybrids in terms of reversibility, since they retain most of the capacity beyond 1000 cycles while for the graphite hybrids charge capacity drops during the first 100 cycles to the original value for IrOx. The large size of graphite particles may favor carbon loss during cycling, probably through a smaller interaction with IrOx. [10] Within that frame, a further increase of charge capacities is also envisaged if nanocarbons include redox species that may contribute to the pseudocapacity in the potential window available in aqueous solutions, without becoming hydrophobic. In that sense, among the many types of possible graphene based materials, N-containing graphenes are good candidates for hybrid formation in terms of chemical interactions. Several strategies allow the introduction of heteroatoms into graphene, both during its synthesis and via post-treatment of the already synthesized material. Thin films and individual layers of nitrogen doped graphene can for instance be prepared by low-energy N2+ ion sputtering, [13] laser irradiation [14] and chemical vapor deposition (CVD) [15]. The introduction of nitrogen into previously synthesized samples can be achieved by a variety of protocols, being graphene oxide widely employed as starting
material. These include microwave treatment, [16] hydrothermal synthesis, [17] laser-assisted reaction [18], and ammonolysis of graphene oxide [19]. In general, the microstructure of hybrids with graphene derived phases has been observed highly correlated with the type of graphene [10-11], for the same deposition method.

N-doped graphene hybrids have been explored by using direct chemical processes with a variety of metals and metal oxides [20-23] including cobalt and manganese oxides. Their intrinsic electrochemical properties, however, have been mainly explored in terms of oxygen reduction catalysis in pure form N-graphenes. [24] Within the context of hybrid formation, and in particular with IrOx for ease of comparison with the hybrids mentioned above, studying the electrochemical modulation of N-doping species in graphitic oxide, could offer a new window in terms of fundamental modification of graphene in oxidizing conditions and also in the range of charge capacities.

In particular, a significant difficulty arises when developing materials as coatings on substrates with different shapes for electrode applications, if nanocarbons are desired as part of the coating. Although other metal oxides have been hybridized with graphenes, IrOx-CNT and IrOx-graphene (exfoliated graphene and graphene oxide, GO) hybrids represent the only case where electrodeposition driven by the oxide phase allows a final conducting coating. Anodically deposited IrOx is an amorphous conducting material with iridium in mixed valence form and empirical formula IrO$_x$(OH)$_{2.7-0.4}$ H$_2$O. This structure deintercalates K$^+$ ions when immersed in aqueous solutions poor in K$^+$, undergoes redox processes that activate water oxidation, and increases charge capacity (CSC) in bioelectrodes when used as coating, decreasing also the electrodes impedance. [8-12] That increased capacity yields a better biological response under electric field stimulation, but further increase is desired in electrostimulation if using low frequency electric fields. In IrO$_x$-C hybrids, the electrodeposition of the material coating is not self-limited as it occurs when IrO$_x$ is deposited alone from solution [9-11], possibly due to a better conductivity of the deposited hybrid material. Significantly, neither graphene, graphene oxide, nor carbon nanotubes get electrodeposited independently within the available aqueous solution potential ranges, but in presence of iridium oxo species in solution, both materials deposit together, as if iridium as precursor species would carry the carbon nano and microparticles attached. [9-11] This fact suggests a direct chemical interaction in solution between the carbon species and iridium ions, through chemical interaction in functionalized CNTs and graphene oxide, and has been observed in other cases (Ni-Co double hydroxides) [25]. Such interaction, however, also exists when using graphene obtained from electrochemical exfoliation of graphite without any added oxygen, possibly through labile adsorbed oxygen from the exfoliation process. [11]

On the basis of those previous observations, it would be of interest to explore further the possible chemistry related to the nitrogen doping groups in graphene and the subsequent increase in charge capacity of other graphene species through interaction with IrO$_x$, as well as the stability and reversibility of the hybrids as electrode coatings. Based on the large variety of possible graphenes, the variety of resulting hybrid materials is even larger in terms of nano and microstructures, and in turn their electrical and electrochemical properties. In particular, electrodeposition of nanostructured graphene hybrids is largely an unexplored region, with the exception of our previous work on millifeuille IrO$_x$-graphene and CNT hybrids. [10,11] Although different oxidation conditions or use of high energy physical methods result in different electrochemical and capacitive behavior [26-28] in graphenes, oxidizing hybrid formation is rather unusual. This work shows the first hybrid coatings of iodide oxide and N-containing graphene, in oxidative conditions, in which various types of nitrogen are observed, including the highest oxidation state of nitrogen-graphene. Oxidative conditions create a new type of N-graphene hybrid with oxidized nitrogen or nitro groups, which are significantly new in the field of graphene. N-containing-graphene precursors obtained at low temperatures, up to 300°C, have been chosen, to achieve hydrophilic phases, a key feature for the interaction with IrOx precursors in aqueous media, but also in their use in aqueous electrochemical cells and in electrostimulation electrodes. The redox contribution from iodide and nitrogen groups has been studied as well as the resulting changes in faradic and charge capacity properties, despite the difficulty of having a complex redox behavior including nitrogen groups and iodide mixed valence. This work shows that a remarkable increase in charge capacity related to the formation of the hybrids, much above the values achieved for the corresponding IrO$_x$-Graphene oxide, IrO$_x$-COOH or pristine graphene hybrids. Chemical transformation of the N-groups is observed during anodic deposition of the hybrids and also during further electrochemical cycling. The most stable N-graphene oxide-IrO$_x$ hybrid corresponds to the N-graphene prepared at higher temperatures, presumably because of a stronger N-C bond or through a stronger interaction N-Ir. Nitrogen redox processes are considered to add to the global charge capacity of the hybrid, reflecting the chemistry of the amine, amide and also the most significant, nitro groups in graphene, while the intrinsic mixed valence behavior of Ir interacts directly in the formation of the hybrid and their final electrochemical processes.

Experimental

Synthesis of graphene oxide (GO): GO was prepared using a modified Hummers method. [29] Briefly, 5 g of graphite powder (<20 μm, Sigma-Aldrich), 115 mL of H$_2$SO$_4$ (Panreac, 98 %) and 2.5 g of NaNO$_3$ (Sigma-Aldrich, < 99 %) were mixed together keeping the temperature down to 0 °C during 30 minutes. Afterwards, 15 g of KMnO$_4$ (Panreac 99 %) were added slowly and the mixture was continuously stirred for 30 min. Then, 230 mL of distilled water were slowly added maintaining the reaction temperature at 98 °C for 2 h. Finally, 1 L of distilled water and 5 mL of H$_2$O$_2$ (Acros Organic, 30 %) were added and the reaction mixture was cooled down. The resulting graphene oxide was purified by subsequent centrifugation and washing with distilled water until the pH of the solution was neutral.

Ammonolysis treatment of GO: In order to obtain N-containing reduced graphene oxide (NRGO) samples, 100 mg of GO were spread in a sintered alumina boat and subsequently annealed during 1h at temperatures ranged between 100 °C and 300 °C under ammonia flow rate of 300 mL·min$^{-1}$ (Carburos Metálicos 99.99 %).[30] The Nitrogen doped graphene oxides were named respectively GN100, GN220 and GN300 according to the temperature used in their preparation.
Anodic electrodoposition of IrOx hybrid films containing N-containing graphene oxides was carried out by dynamic potential electrodoposition methods, using a three-electrode electrochemical cell. The pre-deposition iridium solution for hybrid formation is a modification of the one used by for pure irOx [8], and was prepared from 5.5 mg·mL⁻¹ of N-containing GO precursors dispersed by sonication during 30 minutes in 10 mL of milliQ water, and further addition of 2·10⁻⁴ mol IrCl₃·H₂O (Aldrich 99.9%) and 5·10⁻⁴ mol of K₂CO₃ (Aldrich 99%), with a final pH of 10. The solution was aged at 37 °C for 7 days and stored at 4 °C until use to allow for iridium hydrolysis. The working electrode, where the sample is deposited, is a transparent soda-lime glass slide (38x12 mm²), AFORA which has been previously coated with 5 nm of titanium (as adhesion layer) and 12 nm of platinum by thermal evaporation [8]. A Platinum sheet (Goodfellow 99.9%) of the same geometric shape and frontal area was used as counter electrode, placed in a parallel arrangement and with a separation of 1 cm from the working electrode. A platinum wire, 0.5 mm in diameter (Goodfellow 99.9%) was used as pseudo-reference electrode, its potential versus Ag/AgCl being 0.02 V [8]. Thin films were obtained at room temperature by a potentiodynamic sweep involving 50 potential cycles, and observations were made also at 25 cycles. Cyclic potential sweep rate was 5 mV·s⁻¹, and the potential limits were from equilibrium potential (near 0.0 V) to 0.85 V vs Pt for all graphene hybrids. The maximum potential in cycling was optimized empirically since the potential used for bare IrOx did not yield any deposit. A VMP potentiostat (Biologic) was used for electrodeposition control. Bare IrOx coatings used for comparison, also deposit. Transversal cut of the hybrids GN-IrOx also deposit. Transversal cut of the coatings shows a layered millieuille structure, but large grains related to the graphene precursors are apparent. SEM images show cracks clearly related to dehydration under vacuum and are more visible for the thickest coatings, that of GNIr220 and GNIr300, which also contain more highly hydrated IrOx. Coatings adhesion is greatly improved by the chosen dynamic potential sweeping for electrodeposition, using potential values from rest potential (near 0 V vs Pt (equal to vs Ag/AgCl)) to 0.8 V vs Ag/AgCl. Profiles of cut samples show that for the same electrodeposition time GNIr100 systematically yields a thinner coating, while GNIr220 and GNIr300 result in thicker coatings than the reported GO-IrOx [8-12].

Results and discussion

Using aged oxo-iridium solutions with suspended N-containing reduced graphene oxide (N-graphene) it was possible to deposit coatings of N-graphene-IrOx hybrid materials. N-graphenes were obtained by treatment of graphene oxide at 100ºC (GN100), 220ºC (GN220) and 300ºC (GN300) with ammonia gas. Taking into account that pure suspensions of N-graphenes do not deposit, it seems that the driving force for such deposition is the IrOx formation. For ease of nomenclature, the hybrid coatings will be named GNIr100, GNIr220 and GNIr300 (depending on the precursor used). Visual inspection reveals the presence of uniform coatings (see Figure 1 optical and SEM low resolution images), and shows that the first stages of deposition involve blue IrOx. Only after the electrode is coated with IrOx, the hybrids GN-IrOx also deposit. Transversal cut of the coatings shows a layered millieuille microstructure, but large grains related to the graphene precursors are apparent. SEM images show cracks clearly related to dehydration under vacuum and are more visible for the thickest coatings, that of GNIr220 and GNIr300, which also contain more highly hydrated IrOx. Coatings adhesion is greatly improved by the chosen dynamic potential sweeping for electrodeposition, using potential values from rest potential (near 0 V vs Pt (equal to vs Ag/AgCl)) to 0.8 V vs Ag/AgCl. Profiles of cut samples show that for the same electrodeposition time GNIr100 systematically yields a thinner coating, while GNIr220 and GNIr300 result in thicker coatings than the reported GO-IrOx [8-12].

It is worth noting that the large particles observed in the SEM images from powder GN precursors (Figure 1d) do not represent the final dispersed particles in the iridium containing solutions from which electrodeposition is performed, as clearly seen when comparing Figure 1d and 1e. The morphology of the resulting deposits is globular and resemble those obtained when GO is used, although individual particles follow the millieuille layered nanostructure observed for IrOx-exfoliated graphene hybrids [see details in high resolution SEM images in Figure 1, Supplementary Figure S1 and [11]]. On the other hand, the size and morphology of the dispersed graphene particle seems to define the morphology of the hybrid material which results a very uniform coating at all scales tested (as shown in Backscattering SEM images Figure S1 in Supplementary Material). Previously characterized suspensions [8, 10] evidence Ir-O species, of 10 nm size according to DLS, adhered to graphene platelets, that develop into 2 nm Ir metal particles under conditions of TEM measurements. The size of the graphene platelets, reported before as about 10 microns in the xy plane, is much larger than the size of IrOx agglomerates, explaining the final microstructure and roughness of the coating (see Table 1). Dehydration in SEM conditions creates additionally the cracks observed in Figure 1e, and
thus the roughness derived from SEM images is overestimated, while no AFM has been possible in these rough coatings (Table 1).

Table 1. Thickness and roughness parameters for GNIr coatings as compared with Go hybrids and IrOx

| Sample      | Thickness (nm) | Roughness RMS (μm) |
|-------------|----------------|--------------------|
| GNIr100     | 700            | 2.22               |
| GNIr220     | 2000           | 5.3                |
| GNIr300     | 3700           | 4.1                |
| G0Ir [10]   | 1500           | 2.4                |
| IrOx [8]    | 140            | 0.002              |

Surface XPS characterization

The general XPS spectra of the hybrid coatings obtained by anodic electrodeposition show in all the cases the elements expected in graphene precursors and in IrOx (Figure 2-4; see Figure S1-S3 for general spectra). K, Ir, and O are always present for the mixed-valence phase K₁.₅IrO₅(OH)₂.₀.₄H₂O electrodeposited (named “IrOₓ” usually) [8] and C, N and O for the N-graphene oxides studied previously [29] (See Supplementary Material Figure S2-S4 for General Spectra). For ease of comparison, the XPS C1s, N1s and O1s data of the N-graphene precursors are also included the figures. Table 2 shows the atomic quantifications observed for each coating and relevant atomic ratios, in comparison with the precursors used, that facilitate identifying significant data. The resulting K/Ir ratio equals to that of electrodeposited IrOₓ in all cases, evidencing the existence of the iridium oxohydroxide phase described as “IrOₓ”, as reported in [8], without change. Also, a freshly prepared GO-IrOₓ (GOIr) hybrid shows reproducible values with respect to those previously reported [10]. The C/Ir ratio, as compared with the endemic carbon seen in IrOₓ, evidences a large proportion of graphene per Ir atom. Thus iridium oxide anodic deposition is able to carry a substantial amount of carbon-graphene in the process. As reported before for GO −IrOₓ hybrid, (GOIr) adhesion of iridium phases to the graphene oxide already exists in solution, and explain the resulting global deposition [10, 11]. As expected the Oxygen contribution from IrOₓ raises the O/C ratio for all hybrids with respect to graphene precursors, while the oxygen from graphene also adds in the hybrid materials. The notable increase of O/C ratios in the hybrids, however, goes beyond the contribution from IrOₓ, about 4 O/Ir, reaching up to O/Ir = 10, much beyond the O content from graphene precursors, suggesting extended hydration.

Figure 1. a) Representative I (mA) vs E (V) vs Ag/AgCl (E(Pt) = E(Ag/AgCl) for the dynamic anodic deposition process. b) Naked view image of initial deposition stages (25 cycles) and final (50 cycles) coatings from GNIr220 electrodeposition, c) Detail of layered structure in the coatings, and SEM surface and profile images for d) GN powder precursors SEM images at various magnifications, e) SEM images for GNIr hybrid coatings, f) Transversal images of GNIr coatings.
The existence of endemic carbon even in IrO$_x$ precludes some conclusions, but the relative comparisons between phases taken in a semiquantitative way and in particular the N/Ir ratios, show clear features.

A direct interaction between IrO$_x$ and N-graphenes even if the identity of each component remains, may explain the type of changes observed in some fractions like N/C. Thus, if we were to assume the invariability of IrO$_x$, changes in the O content in the hybrid would be attributed to the modification of the N-graphenes, but the results show more complex data. This is evidenced by the fact that N/C increases up to 5 times with hybrid formation according to XPS quantifications. Furthermore, the N/C relative quantifications are inverted with respect to the corresponding N-graphene precursors, and the GN1r100 hybrid is the one with the significantly large N/C and N/Ir values, and however smallest O/C. In particular, O is easily exchanged in IrO$_x$, in the form of OH$^-$ and mixed valence properties that allow further ionic intercalations/deintercalations. [8] Thus, part of the oxygen in IrO$_x$ fraction of the hybrid may come from the N-graphene derivative, but is also highly probable that during anodic deposition, functional oxygenated C groups such as COO$, 

Table 2. Atomic quantification and significant atomic ratios for the coatings of the hybrid materials compared with the precursors and with the GO hybrid. “c” samples are the hybrids coatings after being cycled electrochemically. (* coating detaches systematically after cycling)

|                  | C1s  | N1s  | O1s  | K2p  | Ir4f | C/Ir | O/Ir | K/Ir | N/Ir | N/C  | O/C  |
|------------------|------|------|------|------|------|------|------|------|------|------|------|
| GNir100          | 25.4 | 11.4 | 50.4 | 7.9  | 4.9  | 5.1  | 10.2 | 1.6  | 2.3  | 0.45 | 1.98 |
| GNir220          | 21.6 | 7.7  | 55.1 | 9.8  | 5.9  | 3.7  | 9.4  | 1.7  | 1.3  | 0.36 | 2.55 |
| GNir300          | 24.1 | 4.4  | 55.4 | 10.0 | 6.0  | 4.0  | 9.2  | 1.7  | 0.7  | 0.18 | 2.29 |
| IrO$_x$ [8]      | 15.7 | -    | 47.6 | 23.5 | 13.2 | 1.2  | 3.6  | 1.8  | -    | -    | 3.03 |
| GOIr             | 27.3 | -    | 47.4 | 16.0 | 9.3  | 2.9  | 5.1  | 1.7  | -    | -    | 1.74 |
| GN100 precursor  | 73.0 | 7.6  | 19.4 | -    | -    | -    | -    | -    | -    | 0.10 | 0.27 |
| GN220 precursor  | 78.5 | 11.1 | 10.3 | -    | -    | -    | -    | -    | -    | 0.14 | 0.13 |
| GN300 precursor  | 82.0 | 11.0 | 7.0  | -    | -    | -    | -    | -    | -    | 0.13 | 0.09 |
| After electrochemical cycling: | | | | | | | | | | | |
| GNir100 c        | 21.3 | 2.0  | 67.2 | 5.3  | 4.1  | 5.2  | 16.3 | 1.3  | 0.5  | 0.1  | 3.2  |
| GNir220 c *      | 29.5 | 3.9  | 47.0 | 12.1 | 7.5  | 4.0  | 6.3  | 1.6  | 0.5  | 0.1  | 1.6  |
| GNir300 c        | 20.2 | 2.8  | 64.1 | 7.4  | 5.4  | 3.7  | 11.8 | 1.4  | 0.5  | 0.1  | 3.2  |

Furthermore, oxygen exchange between graphenes and iridium ions has been observed before. While graphene from electrochemical exfoliation of graphite had not shown extra oxygen in the hybrid, [11] with O/Ir remaining near 4 as in IrO$_x$, the GO-Ir$_x$ hybrid shows an O/Ir near 5.0 (for a GO with O/C ratio of 0.4) [10]. That involves 2.5 GO per IrO$_x$. In this work a final O/Ir near 9-10 and C/Ir around 4 units in excess of the endemic carbon cannot come from O/C ratios in graphene precursors, 0.1-0.3 in value. Only the large degree of hydration shown by the cracks observed in SEM may explain this
value. Such increased hydration may come from aqueous pockets favored by the presence of oxoiridium and oxalic acid.

Using only quantitative information from XPS, the formation of Ir Ox hybrids also shows different chemical reactivity and possible change in the functional and doping N groups. On the other hand, high resolution XPS for each element yields significant information with respect to the chemical moieties present upon hybrid formation. See Figure 2 to S for Ir 4f, C1s, N1s and O1s spectra for each hybrid as compared with the graphene precursors, and after cycling electrochemically.

Ir 4f signal remains as previously reported for IrO x [8] and is constant in all cases, with an asymmetric doublet for 4f3/2 and 4f5/2 signal at 62.5 and 65.1 eV, that contains Ir satellite peaks (shown in Figure 2) Therefore, in all cases the signal corresponds to a similar oxidation state.

On the other hand, the formation of the hybrids modifies the deconvolutions of C 1s, O 1s and N 1s peaks (See Figures 3-5), and the relative amount of components. In the case of C 1s, the main peak for all samples corresponds to so called aliphatic carbon, and is used to normalize all spectra and that also coincides with graphitic signals. The GN100 phase C 1s deconvolution renders other 3 peaks related to carbons C-O, (and C-N), C=O and COO- at 286, 288 and 290 eV respectively. Upon anodic hybrid formation with IrO x, in GN100, the signal intensity increases at larger binding energies, 288 eV, corresponding to higher oxidation species like carboxylates, involving oxidation of functionalized carbons, and a substantial decrease of the 286 eV peak (C-N) occurs. The case is similar for GNIr100 and GNIr300 hybrids vs precursors GN220 and GN300, although in these cases the peak at 286 eV was originally smaller.

Especially significant is the case of N1s signals. The low relative sensitivity of this element in XPS renders a noisy signal for the hybrids with lower N content (see Table 2), although significant features may still be observed. All precursors have the two main signals between 399 and 400 eV, assigned to amide, pyridinic-N (~398.6 eV) and amine and pyrrolic N (400 eV) respectively. [30] Pyridinic and pyrrolic peaks are usually correlated to N atoms at the edge of graphene planes, each of them bonded to two C atoms and donating electrons to the aromatic π system. However, their binding energy overlap with that of N-based aliphatic groups, proven to exist in these samples. A peak at 401.3 eV, corresponding to quaternary-N or graphitic-N in which N atoms are incorporated into the graphene layer and replace directly C atoms, [29,31,32] is also observed. However, upon anodic deposition of the hybrid two new peaks appear a very high binding energy, 403 and 406 eV, that are only ascribable to oxidized nitrogen, or nitrogen-oxide groups such as the pyridine-N-oxide and nitro groups [33] respectively, and/or to nitrogen bound to Ir, although Ir 4f signal is insensitive to such interaction. The only reference found for chemical adhesion of Ir species to graphene does not show such high energy peaks [34], evidencing that no oxidation occurs by direct chemical reaction with iridium in the precursor solutions. Therefore, it is by the oxidative synthesis of the hybrid that oxidation of the nitrogen in graphene occurs. This fact results relevant since it may allow modulation of the N electronic states in graphene, and use it as a redox reservoir.

The oxidation process and the interaction or coordination to iridium is not equal for all N-graphenes as hybrids are formed. GNIr100 and GNIr220 show a larger ratio of nitro N 1s signals at 403-406 eV while GNIr300 still contains larger relative amounts of the lower energy N 1s signals, as if hybrid formation has not involved such an extent of oxidation. GN300 has been described as containing more N dopant species within the carbon graphitic structure than GN100 and GN220, and indeed it should be more stable against oxidation, while GN100 and GN220 contain more reactive functionalization with N species attached to graphene but not part of the basal structure. As seen below, such added reactivity does not translate in additional electrochemical charge storage capacity as compared with GN300.

Although the conducting character of the coating introduces a significant modification of the Infrared spectroscopy base line and signal relaxation that usually, an attempt was made to identify functional groups (See Figure S4). However, no peaks corresponding to nitro groups neither to nitrite or nitrate (near 1500 and 1300 cm⁻¹), while bonds N-Ir would be hidden in the IrOx oxide low energy
frequencies (around 500 cm$^{-1}$). The only relevant peak at 2360 cm$^{-1}$ corresponds to CO$_2$.

Figure 3. C1s, N1s and O1s XPS signals for the (a) GN100 precursor, and the (b) hybrid GNlr100. For easiness of comparison, C1s, N1s and O1s for the electrochemically cycled coating (c) is also included.

O1s XPS signals in hybrids, have the usual three components related to O$^2-$, OH$^-$ and H$_2$O at 530, 531 and 532 eV respectively found for IrO$_x$ [8] that overlap with amide and carbonyl or carboxyl groups from N-graphenes usually found at binding energies 534, 532 and 531 eV respectively. Once the hybrid is formed, the relative amount of the signal near 532-531 eV increases with respect to IrO$_x$, evidencing such overlap of water and organic derived signals. The hybrids also reflect the high intensity of the 531 eV binding energy peak (ascribed to OH$^-$) usually found in IrO$_x$ and the large degree of hydration, 532 eV [8]. It is notable, however that the GN precursors had more intense high energy peaks, which are not present in the hybrid GN-IrO$_x$, very probably due to oxidation during anodic deposition.

Electrochemical behavior of hybrids.

Cyclic voltammetry (CV) of GNlr hybrid coatings in saline phosphate buffer show the previously reported IrO$_x$ wide waves, $E_{\text{max}}$ anodic near 0 and 0.55 V vs Pt, and corresponding $E_{\text{max}}$, cathodic near -0.5 and 0.0 V vs Pt related to intercalation/deintercalation processes in IrOx) [8] (Figure 6). On the other hand, each hybrid shows an intrinsically different change in the intensities of waves in CV depending on the graphene precursor used, suggesting additional contributions from graphene groups, not visible at first sight. In general, it is known that different electrochemical behaviors are observed for GO depending on the preparation method used [27]. Given the redox complexity of O and N graphene functionalities possible in GNlr hybrids, where pyrrolic, pyridinic, phenolic, amines and amides could show electrochemical oxidation waves [36, 37], in addition to the intrinsic behavior of IrO$_x$ mixed valence redox processes, [8, 36] an empirical approach to observed CV’s is the most suitable. Thus, it is remarkable that an increase in global current density is observed for all hybrid coatings as compared with pure IrO$_x$, although only in the second wave for GNlr100, and also a significant increase in currents and also lower potentials for oxygen evolution with respect to IrO$_x$. Within this general feature common to all hybrids, notable differences are also observed. GNlr100 shows an increase in intensity of the second oxidation wave for Ir (maximum at 0.5 V vs Ag/AgCl), but not in the first (near 0 V), while the rest of hybrids including non-nitrogenated G0Ir increase the
The intensity of both upon formation of the hybrid material. Pyrrolic, pyridinic and phenolic groups would contribute with redox waves near 0 V, 0.2 V and 0.6 vs Pt respectively, [36, 37] while O functionalities as COOH, C=O, C-O, may contribute at 0.2, 0.6 and -0.6 V vs Ag/AgCl [17]. Therefore, changes in these potential regions could be related to the O and N ring groups and to the modifications of the Ir redox activity in the hybrid. Significantly, only GNIr220 seems to have an extra anodic redox wave and larger intensity in the cathodic region, for which only actual electrolysis may help identify the responsible process.

The global current increase is largest for GNIr300 and correspondingly the charge capacity is also largest, while waves are less resolved involving a larger capacitive effect from carbon. The catalytic effect of IrOx in oxygen evolution [6] also seems to be enhanced in particular for this hybrid. As expected, the increased intensity effects in n-graphene hybrids correlate in great measure with the thickness of the coating (see Table 3), resulting different for each hybrid electrodeposition process, even under the same conditions. It also correlates with the larger proportions of graphene it is clear that more variables are involved. In terms of charge storage capacities (see Table 3), GOIr had shown [10, 11] the same charge capacity than graphene exfoliated–IrOx hybrid, while the latter was much thinner (see Table 3) and with smaller C content. Here, exfoliated graphene-IrOx (eGIr) and GNIr110 show practically the same thickness, but the latter has much lower surface charge capacity even with larger roughness (and therefore surface area).

For N-graphene oxide hybrids, the largest charge capacity 177 mC/cm² is found for GNIr300 hybrid (1V range in CV), containing nitrogen doped graphene, and it is also larger than that found for GOIr, pristine graphene–IrOx (eGIr) and IrOx. On the other hand, the specific capacity (F/g based on an approximated density of 2 g/cm³ found for carbon and IrOx [8]) suggests that GNIr220 has similar capacity than GNIr300, and similar values to those reported for N doped graphenes, [38] where the largest contribution corresponded to N in graphene basal planes. Those values, however, are lower than for other IrOx hybrids with GO or pristine graphene reported before [10, 11], or even IrOx [8]. It is worth discussing here that neither of both parameters, surface or specific capacity, are fully representative in the hybrid, GNIr220 and GN300 shown in Table 2, derived from a spontaneous larger adhesion of GN220 and GN300 to IrOx. However, of the actual use of the hybrid, since the area exposed at the interface depends on roughness, wettability, while the active
chemical groups being exposed may vary. Furthermore, previous experiments with coatings have shown that surface CSC is a good indicator of the limits of charge delivery before radical formation starts, and cultures of neural cells show that cell response change for charges above or below CSC values [12]. Taking that biological probe as a good indicator of surface electrochemistry helps in giving a significance to each parameter for the electrodes.

As observed in Table 2 and 3, in general, for N-graphene IrO$_x$ hybrids discussed here, the absolute value of CSC is larger in the cases with larger graphene contents, but do not correlate with the increase in total N. That indicates that the crucial role comes from the basal graphene, and that only some type of nitrogen redox behavior adds to the CSC, apparently the type of nitrogen present in GNIr300, doping the graphene basal planes. On the other hand, if we consider the effect per carbon atom (with respect to iridium), the largest CSC value is still the one found for exfoliated graphene (reaching 235 mC/cm$^2$), that does not contribute with any added oxygen (neither N of course) to the hybrid. [11] GNIr220 and GNIr300 have absolute CSC values that almost double the CSC observed for GO and pristine

Figure 5. C1s, N1s and O1s XPS signals for (a) GN300 precursor, (b) GN300Ir hybrid. For easiness of comparison, C1s, N1s and O1s have also been included for the electrochemically cycled coating

Figure 6. Cyclic voltammetry ($10^{th}$ cycle) in sodium phosphate buffer, pH 7.4, of GNIr hybrid coatings in comparison with GOIr and IrO$_x$ coatings (10 mV/s).
graphene hybrids (up to 177 vs 106 mC/cm²), although similar to GOIr if considered per C atom (50-60 mC/cm²). This is due to the larger amount of N-graphene spontaneously attached to IrOₓ in the hybrid. Thus, from a practical point of view these hybrids would be the choice for electrodes of larger capacity, while the correlations among graphene types contribute to the fundamental understanding of the role of nanocarbons in hybrids. The actual increase in carbon content from GNIr100, to GNIr220 and GNIr300, on the other hand must be related to a larger interaction with IrOₓ in the last cases through N groups in the structure, and may be developed further.

The evolution of the electrode hybrid coatings upon electrochemical cycling is of great significance. Two types of behavior are found for the nitrogen–graphene hybrids. (See Figure 7). Upon cycling, CVs still show IrOₓ anodic waves, but the first wave near 0 V vs Ag/AgCl decreases in intensity in all cases with the exception of GNIr100.

The large electrochemical stability found for GNIr300 suggests a large resistance to oxidation that could be crucial in its use as electrode. Examples where carbon electrodes are used despite being oxidized, like in M-Oₓ batteries or in vanadium redox flow cells, would benefit from such an electrode [39-41].

The actual redox processes involved during electrochemical treatment may be envisaged using XPS. Thus, after the 1000 voltammetric cycles (see Figures 3-5 part c) XPS analysis show the same type of deconvolution in N 1s binding energies for GNIr100 and GNIr220, but with larger intensity in peaks from N-O and nitro groups (403 and 405 eV). Both hybrids differ in peaks quantification from GNIr300, that still contains the maximum peak for the lower energy type of behavior than other graphene-IrOₓ hybrids, having a large initial capacity that decreases upon cycling to about 50 to 75% respectively of the original value. GNIr220 detaches from the electrode for each preparation made, possibly through oxidation and CO₂ formation, observed before for oxalate at room temperature during IrOₓ deposition, [8] and suggests that the 50% loss may be due to the smaller amount of material as the cycling progresses in that particular case. Neither GNIr100 or GNIr300 detach however, evidencing a better adhesion to the Pt substrate. Significantly, GNIr300, with a larger capacity than GOIr, also retains after 1000 cycles a CSC value above the maximum value for other hybrids, with large currents in oxidation scans. Curiously, GNIr100 increases its charge capacity during the first few cycles, as it gets oxidized (as described below), and slowly reaches the same CSC than the GNIr220 coating. Such increase must be related to the observed N oxidation described in XPS data, as if the final hybrid in both cases could be similar.

As mentioned above, Ir 4fₓ/₂ and 4fᵧ/₂ doublets remain at the same binding energies with only a slight modification of the asymmetry in the GNIr100 hybrid related to satellite peaks that does not imply any energy shift and or changes in oxidation states. Ir 4f signals are rather insensitive to possible coordination changes and do not yield information on possible modifications in N-Ir interactions. It is known that K⁺ is exchanged in and out of pure IrOₓ without redox processes by immersion in aqueous solutions with no K⁺ ions present, presumably by exchange with H⁺ from the media. On the other hand, several intercalation phenomena are possible in IrOₓ (Na⁺ intercalation and OH⁻ deintercalation at cathodic potentials, K⁺ redox deintercalation at anodic potentials from IrOₓ). In fact, in the hybrids the K content after cycling is lowered to K/Ir 1.3 vs 1.6 in (GNIr100 for example (see Table 2)), and Na 1s and Na KLL signals appear in the spectra only after cycling in sodium containing electrolyte (not
related to direct wetting), evidencing the existing redox reactions in the hybrids, similar to those expected in pure IrOx.

On the other hand, along with K/Ir decrease upon cycling, a depletion is observed for N/Ir ratios for GN100Ir and GN220Ir, the hybrids with originally larger values, while the O/Ir has increased dramatically. The significant decrease of N/Ir ratio, with stable C/Ir ratios, involves oxidation and liberation of nitrogen oxide groups. After cycling, the N/Ir values for these two hybrids GN100 and GN220 gets similar to the observed for GN300, as if only doping N at the basal plane remains. Therefore, N-containing graphene hybrids with IrOx evolve to the most stable N doping found in GN300, possibly through irreversible oxidation of the N groups to an oxidized NO-C type of entity, while other nitrogen species are eliminated.

Table 3. Thickness of coatings, roughness (RMS) and cathodic charge capacities (CSC) observed during the first cycling effects. (IrOx-graphene hybrids reported before and rechecked here). CSC in F/g assume a density of 2g/cm³ as expected for amorphous IrOx and Graphene [8, 10, 11]. CSC per carbon atom are also included.

| Sample   | Thick n. (µm) | RMS (µm) | N/Ir | CSC₁ (F/cm²) | CSC₂ (F/g) | CSC₃ (F/g) |
|----------|---------------|----------|------|---------------|------------|------------|
| GN100    | 0.7           | 2.2      | 2.3/ 2.3 | 21.6         | 5.5        | 110.4/28  |
| GN220    | 2.9           | 5.3      | 1.3/ 2.5 | 132.7         | 53         | 163.4/65  |
| GN300    | 4.0           | 4.1      | 0.7/ 0.7 | 176.5         | 63         | 157.6/56  |
| IrOx [8] | 0.00          | 2.2/0    | -1.7/ -1.7 | 108.6         | 64         | 257.1/151 |
| GOIr [10]|               |          |       |               |            |            |

Figure 8. Cathodic CSC evolution during cycling for IrOx (blue), GOIr (grey), GN100 (yellow), GN220 (green) and GN300 (red). O 1s XPS spectra after cycling also shows a significant shift towards lower binding energies, with the maximum at the signal corresponding to OH (531 eV) and also coherent with the oxidation and elimination of some C-O and C=O, COO⁻ groups (as CO₂ or other soluble species) for which larger shifts had been observed.

In summary, although anodic formation of the hybrid involves oxidation for all hybrids, the lower temperature cases, GN100 and GN220 have further oxidation changes in N signals during electrochemical cycling, while the GN300 phase remains closer to the original material and maintains the highest values of CSC. All processes involved suggest a large span of states in the oxidizing range.

Conclusions

Chemical interaction between iridium oxo species and N-containing graphene oxide, allows anodic deposition of IrOₓ-N-graphene hybrids, in different extents and with different Cₓ per atom/Ir ratios, depending on the graphene precursor used. The hybrids show up to 7 times larger charge storage capacity than IrOₓ and the higher values correspond to the larger content of N-graphene in the hybrid, and also to the largest oxidation to nitro groups. The anodic hybrid formation is responsible of the stability of nitro-graphene oxide in the final material and modulation of the redox state of N after cycling. The most stable hybrid, among those tested, corresponds to the one with the largest amount of N doping in the graphene structure, and large graphene relative amounts, i.e. GN300. It actually contains pyridinic, pyrrolic, graphic N and remaining oxygen. The CSC values for GN300 remain high after 1000 cycle electrochemical sweeping, still above any other hybrid tested previously and in this work. In terms of the contribution of carbons in hybrids, if calculated per carbon atom, pristine graphene hybrids...
with $\text{IrO}_x$ still show the highest CSC$_{\text{c}}$, but N-doped graphene oxide (GNR300 here) forms the hybrid with larger carbon amounts, and results in the largest increase in absolute CSC$_{\text{c}}$ value. The observed roughness correlates directly with the particle size of precursor N-graphenes, and does not define charge capacity. Lower temperature treatment in N-graphenes yields hybrids with redox states available from N, that are oxidized during formation and during electrochemical treatment, without reaching the final CSC of the GNR300 hybrid. In all hybrids, oxidized nitrogen and nitro groups are present, which correlate with a large resistance to oxidation in GNR300, and stable CSC$_{\text{c}}$ values, after 1000 cycles. The redox modulation observed during preparation of the hybrid material and during electrochemical cycling evidences a large stability of nitro groups present in the hybrid, involving a remarkable finding that opens a new path in the chemistry of graphene.

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**Conflicts of interest**

There are no conflicts to declare.

**Authors contributions:** EP has performed most of the hybrid material electrodeposition and XPS studies, GT, AF and SS have designed and prepared the Graphene precursors, NC did start the first hybrid within the frame of her PhD thesis. NCP has directed the main work of hybrid formation and electrochemical work. GT and NCP have handled the preparation of the manuscript

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