Fabrication of graphene-based electrochemical capacitors through reactive inverse matrix assisted pulsed laser evaporation

Ángel Pérez del Pino^{*1}, Mohamed Ahmed Ramadan^{1,2}, Pablo Garcia Lebière¹, Raluca Ivan³, Constantin Logofatu⁴, Ibraheem Yousef⁵, Enikő György^{1,3}

¹ Instituto de Ciencia de Materiales de Barcelona, Consejo Superior de Investigaciones Científicas (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain.

² Faculty of Engineering, Helwan University, Helwan, Egypt

³ National Institute for Lasers, Plasma and Radiation Physics, PO Box MG 36, 77125 Bucharest, Romania

⁴ National Institute for Materials Physics, PO Box MG 7, 77125 Bucharest, Romania

⁵ ALBA Synchrotron, Carrer de la Llum, 2-26, 08290 Cerdanyola del Vallès, Barcelona, Spain

^{*}Corresponding author (Telephone:+34 935801853; E-mail: aperez@icmab.es)

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Abstract

Electrodes constituted by nitrogen-doped reduced graphene oxide (NrGO) in combination with NiO nanostructures were fabricated by means of reactive inverse matrix assisted pulsed laser evaporation technique. The structure-composition of the electrode composites was tailored by laser-inducing chemical reactions of graphene oxide (GO) flakes with different precursor molecules (citric acid, ascorbic acid and

imidazole) during GO deposition. Structural characterizations reveal the formation of wrinkles and nanoholes in the NrGO sheets, besides their coating with NiO nanostructures. Compositional studies disclose that imidazole precursor promotes the synthesis of NrGO with the largest degree of reduction and nitrogen doping (mainly with graphitic and pyridinic N). Electrochemical analyses of the obtained electrodes reveal that NiO nanostructures increase surface charge storage processes (double layer – pseudocapacitive) over diffusive ones, being the imidazole-based electrodes the ones exhibiting the best performance (up to 114 F cm^{-3} at 10 mV s^{-1}). Symmetric and asymmetric electrochemical capacitors were also fabricated showing excellent robustness over 10000 charge-discharge cycles at high specific currents.

1. Introduction

The social necessity of energy storage devices with improved performance is leading the development of new strategies for the fabrication of materials. A particular interest is focused on electrochemical capacitors (ECs), that require new constituent nanomaterials for exhibiting higher power and longer cycling life than batteries, and increasing energy density as close as possible to that of batteries [1, 2]. Due to their technological development, ECs are being progressively used in a wealth of applications as portable electronic devices, hybrid and electric vehicles, as well as industrial energy management [2-9]. Accordingly, nanomaterials with tailored composition and structure showing improved functionalization are being investigated. At present, hybrid materials composed of nanocarbon, i. e. nanotubes or graphene derivatives as reduced graphene oxide (rGO), and electrochemically active nanostructures (as specific metal-oxides) disclose high potential for the fabrication of performant ECs [2, 10-18]. Similarly, heteroatom doping of rGO also displays electrochemical improvement. These compounds exploit both the high conductivity of the rGO material and the high specific capacitance of the electrochemically active (pseudocapacitive) entities, leading to substantial enhancement in terms of energy and power densities. Particularly, rGO-NiO composites and N-doped rGO (NrGO) present interesting functional properties to be used in electrodes [19-25].

The synthesis of graphene materials either doped or decorated with metal-oxide nanostructures is already achieved by conventional routes. The synthesis is generally

based on chemical reactions that frequently use hazardous precursors or reveal chemical incompatibilities, besides thermally-activated processes, through prolonged high temperature annealing, that can impede the use of temperature-sensitive substrates as polymers, paper, etc. Thus, unconventional methods are being also explored for further advance in this technological area. The matrix assisted pulsed laser evaporation (MAPLE) technique represents a promising method for the controlled deposition of functional nanomaterials [26-30]. Particularly, rGO-based thin film composites were obtained in a simple way [31-33], and even partial nitrogen doping of the rGO material was accomplished using N₂ background gas as doping agent. Recently, a variant of MAPLE method, referred to as reactive inverse matrix assisted pulsed laser evaporation (RIMAPLE), has demonstrated to be a simple and versatile strategy for attaining the controlled fabrication of N-doped rGO flexible electrodes with tailored composition for ECs [34]. By adding different types of reactive molecules to the MAPLE target, this method allows the simultaneous chemical transformation and deposition of graphene-based layers by prompting photo- and thermally-induced chemical reactions of graphene oxide (GO) flakes immersed in frozen aqueous dispersions during laser irradiation process.

In this work, we developed hybrid rGO-based electrodes with different compositional and structural properties by RIMAPLE through laser-induced chemical reactions between GO and citric acid, ascorbic acid or imidazole molecules. Citric acid is a weak organic acid with a carboxylic group rich structure, prone to establish non-covalent bonding to functional groups of GO, that has been used in combination with GO for different applications [35-37]. Moreover, citric acid has been also reported to transform to luminescent graphene quantum dots upon conventional pyrolysis [38]. Ascorbic acid, commonly known as vitamin C, is a well-known compound in organic synthesis. Remarkably, ascorbic acid can act as a reducer or oxidizer under illumination [39, 40]. In particular, L-ascorbic acid has been reported to act as photoreductor of quinones [41]. Therefore, the chemical interaction of GO flakes with citric and ascorbic acids during MAPLE experiments could induce a large reduction of GO. On the other hand, imidazole is an aromatic nitrogen-containing compound with unique pharmaceutical and biological activities. The imidazole molecule is highly polar, and hence, it is prone to establish non-covalent bonds. Recently, imidazole molecules were proven as effective N-doping agent of GO upon UV laser radiation [42]. Moreover, thermal annealing of

imidazole-based precursors demonstrated the formation of N-doped graphene [43]. Consequently, MAPLE deposition of GO in presence of imidazole is expected to induce large N-doping of GO. Analogous electrodes containing also NiO nanostructures were synthesized, since NiO material has been reported to exhibit promising electrochemical reactivity for energy storage applications [44]. The electrochemical properties of the obtained electrodes were methodically studied and correlated to their chemical structure. Finally, electrochemical capacitors were assembled with the best electrodes and their performance was investigated.

2. Experimental

Different aqueous dispersions were synthesized by mixing GO powder, composed of 1-15 layers thick flakes around $1\ \mu\text{m}^2$ in lateral size (NanoInnova Technologies), with chemically active molecules (citric acid, ascorbic acid, and imidazole from Sigma-Aldrich) and deionized water (solvent). Analogous dispersions were also produced by adding NiO nanoparticles (NPs, Sigma-Aldrich) with sizes about 50 nm. The concentration of the precursors was optimized for avoiding precipitation and obtaining high rate deposition process. Table 1 shows the relative concentrations of the precursors present in the dispersions. Next, the dispersions were systematically stirred and sonicated at room temperature. The MAPLE targets were set by filling a 3 mL target holder with the dispersion, being subsequently flash frozen by immersing it in liquid N_2 . Lastly, the targets were located inside the deposition chamber and maintained frozen during the deposition process by means of a liquid N_2 -cooled holder.

MAPLE experiments were executed by submitting UV laser pulses (266 nm wavelength, ~ 5 ns pulse duration, 10 Hz repetition rate) to the frozen targets by using a Quantel Brilliant B Nd:YAG laser system. Flexible copper substrates, $1\times 1\ \text{cm}^2$ in size and 0.5 mm in thickness, were placed in parallel to the target at a separation distance of 4 cm. In addition, 0.1 mm-thick polypropylene (PP) films coated with sputtered Au (20 nm) / Cr (5 nm) layers were also used as conducting flexible substrates. During the experiments, the laser beam scanned the target surface at an incident angle of 45° . The depositions were carried out at room temperature, in 20 Pa N_2 background gas environment after evacuation to a residual pressure of 0.1 Pa. For the deposition of each sample, 6000 laser pulses were submitted to the target at $0.4\ \text{J cm}^{-2}$ laser fluence.

The thickness and the morphology of the composite films was studied by field emission scanning electron microscopy (SEM) by means of QUANTA 200 FEG-ESEM and extreme high resolution (XHRSEM) Magellan 400L microscopes (FEI). Three-dimensional surface morphology maps at the sub-microscale were also obtained through atomic force microscopy (AFM) using a Nano-Observer system from CSInstruments. The topographic maps were recorded by means of intermittent contact mode (silicon tip with less than 10 nm apex; resonance frequency about 200 kHz). Additionally, resistance maps were obtained by using conducting boron-doped diamond tips in contact mode using a Resiscope II electrical characterization module. The resistance maps were recorded applying 2 V between sample surface and grounded tip. The AFM-resistance data was processed with Mountains 7.4 software from Digital Surf. The study of the structural properties was accomplished through high resolution transmission electron microscopy (HRTEM), scanning TEM (STEM) and high angle annular dark field STEM (HAADF-STEM) through a Tecnai F20 equipment (FEI). The chemical composition of the obtained films was investigated by X-ray photoelectron spectroscopy (XPS) by means of a SPECS XPS spectrometer based on a Phoibos 150 electron energy analyser. The system used the aluminium anode (Al K α 1486.74 eV) as a monochromatic X-ray source, being the electron energy analyser operated in constant energy mode. Wide range spectra over 1200 eV binding energies were acquired by means of an analyser pass energy of 50 eV. Additional high resolution spectra were also recorded over 20 eV ranges at 10 eV pass energy with an energy resolution of 0.7 eV. All the measurements were carried out in ultra-high vacuum ($\sim 10^{-7}$ Pa). Furthermore, synchrotron-based trans-reflection mode Fourier transform infrared microspectroscopy (SR-FTIRM) measurements were performed at the infrared beamline MIRAS of ALBA Synchrotron using a Hyperion 3000 microscope coupled to Vertex 70 spectrometer (Bruker, Germany). This microscope is equipped with a liquid nitrogen-cooled mercury cadmium telluride 50 microns MCT-A detector. The microscope used a 36X Schwarzschild objective (NA=0.65) and a matching 36X condenser. All spectra were obtained using a single masking aperture size of $10 \times 10 \mu\text{m}^2$. Single spectra (9 per sample) were collected in the 4000-600 cm^{-1} mid-infrared range at 4 cm^{-1} spectral resolution with 1024 co-added scans per spectrum.

The electrochemical performance of the samples was studied through cyclic voltammetry (CV) in the voltage range of [0, 0.8] V by using a Keithley 2450-EC

Electrochemistry Lab System. The samples deposited on Au/Cr/PP substrates were used as working electrodes (geometrical area of 0.5 cm²) in a three-electrode cell. The measurements were performed with an Ag/AgCl reference electrode (3M NaCl internal solution) and a Pt wire counter electrode in a 1 M Na₂SO₄ aqueous solution at room temperature. Galvanostatic charge-discharge analyses were also performed in the voltage range of [0, 0.8] V at different current densities. Additional studies were carried out by means of electrochemical impedance spectroscopy (EIS) with a Hioki IM3590 chemical impedance analyser. Impedance spectra were acquired in the 0.1 Hz – 200 kHz frequency range at open circuit potential with a perturbation of 5 mV amplitude. An average of 4 measurements per data point was taken for reducing experimental error.

Finally, symmetric and asymmetric electrochemical capacitors were assembled with the best performant electrodes by using stainless steel AISI 316 substrates (1 cm² area, 0.1 mm thickness). The electrodes were separated by glass microfiber filter paper (Prat Dumas) impregnated with 1 M Na₂SO₄ aqueous solution. A few cm long copper contacts were attached to the steel collectors and the system was sealed with adhesive tape.

Dispersion	Composition
GO	GO (10 wt.%)
GO-NiO	GO (10 wt.%) + NiO NPs (5 wt.%)
GO-cit	GO (10 wt.%) + citric acid (5 wt.%)
GO-NiO-cit	GO (10 wt.%) + NiO NPs (10 wt.%) + citric acid (5 wt.%)
GO-asc	GO (8 wt.%) + ascorbic acid (4 wt.%)
GO-NiO-asc	GO (8 wt.%) + NiO NPs (8 wt.%) + ascorbic acid (4 wt.%)
GO-imi	GO (5 wt.%) + imidazole (5 wt.%)
GO-NiO-imi	GO (5 wt.%) + NiO NPs (5 wt.%) + imidazole (5 wt.%)

Table 1. Relative concentration of the precursors in the synthesized aqueous dispersions.

3. Results and discussion

3.1 Structural-compositional study of the electrodes

Previously reported works demonstrated that laser irradiated graphene oxide sheets and NiO NPs immersed in a water-ice target absorb UV laser radiation provoking rapid heating and explosive boiling of the surrounding matrix, and leading to the deposition of rGO-based films [31, 34]. In this work, in which the matrix is composed of a mixture of water and reactive precursors, the simultaneous chemical reaction and deposition of the transformed nanoentities is expected. Two sets of samples, based on GO/reactive precursors and GO/NiO NPs/reactive precursors, are fabricated. The deposited films are stable, adherent to the substrate, flexible and show uniform dark brown - black colour independently on the chemically active molecules or used substrate. As observed in Table S1, the GO set of samples present a film thickness in the 100 – 500 nm range, whereas the GO/NiO films are thicker, about 2.3 – 8.6 μm . Photothermal simulations showed that this difference of thickness is due to the higher absorption coefficient exhibited by NiO NPs as compared to that of GO flakes, leading to the attainment of much greater temperatures in a larger matrix volume and provoking the deposition of larger amount of material [34]. Representative SEM images of the obtained films are shown in Figures 1a, b and Figure S1 (Supporting Material). As witnessed, the films display a rough surface morphology composed of irregular-shaped aggregates of wrinkled GO flakes about hundreds of nanometres to the micron in size. The formation of furrows in GO flakes irradiated with nanosecond UV laser radiation has been observed previously [45, 46]. The origin of the furrows is attributed to the steady deformation of the GO sheets prompted by the creation of structural defects. The GO aggregates are compact, though cavities with tens to hundreds of nanometres in size are also visible between the aggregates (Figure 1a, and Figure S1a, c). GO/NiO films show a similar rough morphology though, besides the GO aggregates, tens of nm-sized droplets are also visible (some of them appear pointed by arrows in Figure 1b). These particulates, not observed in GO samples, may be ascribed to NiO nanostructures. Detailed inspection of GO/NiO films' morphology through AFM reveals that the surfaces are indeed covered by round particulates with sizes about tens to few hundreds of nm (Figures 1c, d). The diameter of the particulates, larger than the initial NiO NPs size, seems to be somehow greater than their height suggesting the existence of melting-coalescence-resolidification processes. Higher magnification topographic maps reveal the presence of particulates with complex features, including geometric shapes, at 100-

500 nm scale (Figure 1e). The existence of geometric shapes also points to recrystallized material formation. The corresponding resistance maps show domains, around tens-hundreds of nm, with very different resistance values ($k\Omega$ to $M\Omega$) varying quite abruptly, in just tens of nm range, even within single particulates (Figure 1f). This fact could be explained by considering (i) adjacent graphene-NiO domains and/or (ii) the particulates are composed of smaller crystalline entities with different resistivity.

Figure 1. XHRSEM images of (a) GO-cit, (b) GO-NiO-asc samples. AFM examination of GO-NiO-cit sample, (c) topographic image and (d) corresponding profile along the indicated line in (c); (e) higher magnification topographic image and (f) corresponding resistance map, taken by applying 2 V between tip and sample's surface. The arrows in panel (b) point to rounded droplets.

Transmission electron microscopy analyses of the deposited GO samples reveal highly crumpled graphene oxide flakes, showing irregular edges and some formation of nanoholes in the inner part of the flakes of GO, GO-cit and GO-asc films (Figures 2a, c). However, GO-imi sample shows higher density of furrows in the GO flakes (Figure 2d) and the formation of larger quantity of nanoholes. It has to be noted that the formation of high quantity of wrinkles and nanoholes has been also observed in reactive MAPLE deposition of GO flakes with N-containing precursors as ammonia, urea and melamine molecules [34]. These results would indicate that molecules containing

nitrogen functional groups, as imidazole, provoke more evident structural alterations to GO flakes during the UV laser irradiation process. Importantly, the presence of defects as nanoholes is assumed to be beneficial establishing electrolyte diffusion channels and interaction to edge atoms that are more electrochemically active than basal ones [47, 48]. Selective area electron diffraction (SAED) patterns of GO samples show concentric rings corresponding to 0.14 and 0.24 nm interplanar distances, which are respectively attributed to (010) and (100) planes of the graphitic structure. The rings appear rather wide pointing to randomly oriented small graphene domains with some distortion of the lattice due to strain and large density of structural defects. TEM analyses of the GO/NiO set of samples reveal the formation of wrinkled GO flakes covered with tens of nm sized round nanostructures (Figure 2b). SAED patterns display rings corresponding to interplanar distances of 0.13-0.15 and 0.24 nm assigned to strained (010) and (100) graphene domains, as well as 0.08 and 0.17 nm which could be ascribed to (511) and strained (220) crystallographic orientations of cubic NiO (Bunsenite; JCPDS 00-047-1049). Some contribution of (220) and (111) NiO planes could be also present in rings corresponding to 0.13-0.15 and 0.24 nm interplanar distance. Many of the recorded planes appear significantly strained as compared to bulk values, pointing to significant mechanical stress developed during strong heating and related structural modification processes. HRTEM analyses reveal that GO/NiO samples are indeed highly covered by nanometric crystals. Figures 2e and f show the same area studied by HRTEM and HAADF-STEM in GO-NiO-im sample. HRTEM image shows the presence of a large amount of nanostructures with dimensions from just 1-2 nm to few tens of nm. The corresponding HAADF-STEM image (Figure 2f), in which the intensity is strongly related to the atomic number, reveals that these crystals are indeed composed of NiO (Ni-rich regions appear with bright contrast). These NiO nanostructures, which are identified as crystals composing the entities observed by AFM (Figures 1c, e), are smaller than the initial NiO NPs (50 nm) suggesting the development of melting-dewetting-recrystallization mechanisms during the laser irradiation-deposition process.

As previously noted, citric acid has been reported to transmute to graphene material upon thermal annealing [38]. In this work, the incomplete carbonization of citric acid leads to the formation of oxygen-containing graphene quantum dots, whereas complete carbonization produces bulky GO material. Since UV laser irradiation of NiO NPs

provokes the fast and intense heating of the surrounding matrix, we studied the possible laser-induced transformation of citric acid to graphene material by preparing an additional MAPLE sample (NiO-cit) in which the target is composed of NiO NPs (10 wt.%) and citric acid (5 wt.%), without GO powder. The laser parameters for the film deposition are the same as for the rest of samples. Figures S2a, b show the formation of continuous films, mainly composed of NiO, displaying smooth regions and nanometric to hundreds of nm-sized particulates. Interestingly, HRTEM inspection at the edges of the particulates reveals the formation of defective crystallized regions with somehow parallel planes, showing about 0.37 nm interplanar distances, that could be ascribed to graphitic (001) planes. Hence, it could be stated that during the MAPLE deposition, citric acid does chemically react and transforms to graphene-based flakes.

Figure 2. TEM images and corresponding SAED patterns of (a) GO-cit and (b) GO-NiO-cit, (c) GO-asc, and (d) GO-imi samples; (e) HRTEM and (f) corresponding HAADF-STEM images of GO-NiO-imi sample.

The composition of the deposited films is studied by means of wide scan and high resolution XPS. Figure 3a shows a typical XPS survey of GO raw material, in which carbon and oxygen peaks are clearly observed. The atomic concentration of the chemical elements existent in the raw GO and deposited films was calculated from the wide scan spectra. Figures 3b, c present the calculated reduction degree ($\text{at.\% C} / \text{at.\% O}$ ratio) besides the nitrogen doping degree ($100 \times \text{at.\% N} / (\text{at.\% N} + \text{at.\% C})$) of all the samples. It is important to note that, in the GO/NiO set of samples, the concentration of C, O and N in GO material has to be recalculated (closed bars in Figure 3b) from the measured data (open bars) due to the presence of Ni and O atoms from NiO (calculation details in Supporting Material). As observed, GO precursor (raw) displays a low reduction degree (about 2.6) and no presence of nitrogen-containing groups. The deposited films from targets comprising GO-water besides those containing reactive molecules reveal an increase of the reduction degree in all cases, evidencing the simultaneous deoxygenation and deposition of the GO flakes. The rGO-based sample revealing largest reduction degree (8.6) is the one synthesized in presence of imidazole molecules. GO and GO-asc films show a similar reduction degree of 6, whereas GO-cit is the one showing the lowest value (4.2). The GO/NiO films obtained without reactive molecules in the target, and with the presence of citric and ascorbic acids display a reduction degree very similar to that of raw GO. Probably, the presence of highly UV absorbing NiO NPs could provoke a laser radiation shielding effect at GO flakes, lessening the photochemical deoxygenation reactions. Noticeably, and in the opposite way, the presence of imidazole molecules provokes a great deoxygenation process, leading to a reduction degree of 13.7. This fact accounts for a high chemical reactivity during the deposition process, probably driven by thermal mechanisms. Regarding the inclusion of nitrogen into the rGO structure, the samples deposited without reactive molecules in the target (GO, GO-NiO) reveal a modest N incorporation with a respective N-doping degree of 2% and 3% coming from the N_2 gas environment. Further, the presence of citric and ascorbic acids precludes somehow the incorporation of nitrogen from the gas ambient, leading to a pretty low doping degree (1% and 0.4% for GO-cit and GO-NiO-cit, and 0.9% and 0.5% for GO-asc and GO-NiO-asc, respectively). Remarkably, the samples synthesized with imidazole precursor display the largest N-doping degree (7% and 16%, respectively for GO-imi and GO-NiO-imi) mainly due to the additional incorporation of N atoms from imidazole molecules into the rGO structure. Contrarily to the samples obtained with citric and ascorbic acids, the

GO-NiO-imi sample exhibits larger N-doping than its counterpart without NiO. Summarizing, the samples obtained with imidazole precursor are the ones displaying the largest degree of reduction and nitrogen doping of GO material. Citric and ascorbic acids do not induce the expected large reduction of GO and even preclude the incorporation of nitrogen from the environment into the rGO structure.

Figure 3. (a) Wide scan XPS spectrum of raw GO, (b) reduction degree and (c) nitrogen doping degree of all the samples. In (b), open bars are directly obtained from measurements, whereas filled bars correspond to the calculated concentrations by subtraction of NiO contribution.

High resolution XPS spectra allows obtaining information about the nature of the chemical groups present in the surface material. Representative C1s and N1s high resolution XPS spectra of the deposited samples, including the corresponding deconvoluted peaks, are displayed in Figures 4a-d. The C1s signal is deconvoluted in five components (C1-C5) centred at ca. 284.7 eV, 286.9 eV, 288.4 eV, 290 eV and 292 eV (Figure 4a). These peaks are respectively ascribed to sp^2 -bonded carbon atoms (C1), possibly with a minor contribution of sp^3 configuration, as well as carbon-oxygen hydroxyl-epoxide (phenolic-ether, C2), carbonyl (quinone, C3) and carboxylic (C4) groups. The peak located at 292 eV (C5) is associated to a shake-up satellite caused by a π - π^* transition in graphene structure [33]. On the other hand, the N1s spectra deconvolution reveals a mixture of nitrogen containing functionalities since three components attributed to pyridinic N (N1, centred at ca. 398.8 eV), pyrrolic-amine groups (N2, at 399.5 eV), and graphitic N (N3, at 401 eV) are detected (Figure 4d) [34]. Figure 4e displays the integrated area percentage of the deconvoluted C1 peak in all the spectra. The areal percentage of C=C (C1) signal increases in all the deposited samples as compared to raw GO. This effect is clearly witnessed when comparing C1s spectra of

Figures 4a-c, revealing a decrease of carbon-oxygen bonds due to the deoxidation of deposited GO. The percentage integrated area of the deconvoluted C-O peaks of all the samples is shown in Figure S3. As observed, hydroxyl-epoxide (C2) functional group is the most abundant in all the samples, being minor the contribution of the shake-up satellite (C5). It is important to note that some N-containing functionalities would contribute to C2 and C3 signal [49, 50]. Therefore, the C=C integrated area percentage, especially at GO-imi and GO-NiO-imi where high nitrogen doping is present, might be underestimated. Figure 4f displays the integrated area of the N1s deconvoluted components. GO sample exhibits the formation of pyrrolic / amine functionalities (N2), GO-NiO and GO-NiO-cit show the presence of pyrrolic / amine (N2) and graphitic nitrogen (N3), being N2 the most abundant group in GO-NiO and N3 component the most abundant in GO-NiO-cit. The samples GO-cit, GO-imi and GO-NiO-cit reveal the presence of all the functionalities, being N1 and N3 the most abundant ones in, respectively, GO-cit and samples developed with imidazole precursor. GO-asc and GO-NiO-asc display very weak N1s signal and it might be highly influenced by adsorbed N₂.

Figure 4. Deconvolution of XPS high resolution C1s spectra of (a) raw GO, (b) GO-asc, and (c) GO-NiO-imi samples. (d) Deconvoluted N1s spectrum of GO-NiO-imi sample. Ratio of (e) sp² C=C bonds (C1) and (f) N1s components of all samples.

For attaining a deeper insight into the composition of the samples, synchrotron trans-reflection mode-FTIRM studies were carried out and representative spectra are shown in Figure 5a. Raw GO powder does not reveal characteristic bands probably due to high absorption or scattering, though a band located at ca. 890 cm^{-1} , assigned to C-O-C is clearly observed. The deposited films display reflection bands centred at ca. 810 cm^{-1} that could be attributed to C-H and/or C-O-C groups, besides bands at about 980 cm^{-1} and 1640 cm^{-1} assigned to C=C at graphene domains, 1090 cm^{-1} indicating the presence of C-O, as well as bands at ca. 1230 , 1260 and 1325 cm^{-1} ascribed to C-OH with some contribution of C-O-C groups. Additional bands located at around 1490 and 1770 cm^{-1} could be assigned to C-H alkyl and / or N-H, and C=O chemical groups respectively [42, 51-53]. The small bands located at around 2350 cm^{-1} are assigned to CO_2 . As witnessed, the band located at ca. 1490 cm^{-1} (C-H / N-H) clearly appears in GO-asc, GO-NiO-asc, GO-cit and NiO-cit, in some of them also appears the band centred at 810 cm^{-1} (C-H / C-O-C) possibly accounting for the formation of C-H alkyl chains, whereas GO-asc, GO-NiO-asc and GO-imid clearly show the band located at 1325 cm^{-1} (C-OH). GO-imid also displays an important contribution of 1150 cm^{-1} band which is related to in-plane stretching of imidazolium ring [42]. Summarizing from the XPS and FTIR results, it can be stated that the rGO flakes deposited without precursor molecules and in presence of citric and ascorbic acid exhibit the presence of hydroxyl, ketone (probably quinone-like), epoxy and carboxylic oxygen-containing groups, as well as low quantity of N-containing functionalities (pyridinic, pyrrolic, amine and graphitic), besides some presence of structures associated to alkyl chains. Figure 5b displays a scheme showing illustrative chemical structures. The relative amount of the different types of chemical groups varies at each type of sample. The GO material deposited from imidazole-based targets reveal similar structure with higher degree of deoxidation and doping with nitrogen (mainly graphitic and pyrrolic).

Figure 5. (a) FTIR spectra of the obtained samples, (b) scheme of the resulting structures after laser irradiation of GO and reactive molecules.

3.2 Electrochemical study of electrodes

The electrochemical properties of electrodes deposited on Au/Cr/PP substrates were studied by cyclic voltammetry in the range of sweep rates between 10 and 150 mV s^{-1} . All the voltammograms show highly symmetric rectangular-like shape without the presence of pronounced peaks (Figure S4). The peak recorded at the highest potential is caused by oxygen-evolution reaction processes at the aqueous electrolyte. Representative curves obtained in the whole range of sweep rates, belonging to GO-imi and GO-NiO-imi electrodes, are shown in Figures 6a, b. In general, the samples deposited with NiO NPs reach current densities greater than their counterparts without

NiO, accounting for higher charge storage. No evidence of features' potential variation with sweep rate, characteristic of kinetic irreversibility, is perceived. However, a progressive symmetry deviation in the voltammograms with increasing sweep rate is witnessed at the voltage limits (0, 0.8) V, which is caused by kinetic limitations during the voltage reversal at each cycle. The rectangular-like shape, without marked redox peaks, and the kinetic reversibility of the voltammograms mainly point out to a capacitive behaviour (surface mechanisms) in the electrodes [54, 55].

Figure 6. Cyclic voltammetry plots of (a) GO-imi and (b) GO-NiO-imi samples at different sweep rates. (c) Percentage of surface/bulk charge storage, and (d) b-parameter of all the samples calculated between 0.1 V and 0.7 V vs Ag / AgCl. The inset in (d) shows the plot of log(i) vs log(s) of GO-NiO-imi at 0.1 V.

As already demonstrated in Section 3.1, the NrGO that constitute the electrodes contains oxygen- and nitrogen-based functionalities that would indeed enhance the charge storage capability of the electrodes. Two main mechanisms of charge storage are

expected to occur in the obtained electrodes: double layer and pseudocapacitive caused by redox (faradaic) reactions. Ideally, the formation of an electric double layer is expected at the interface between graphitic domains and electrolyte. It is worth noting that remaining oxygen-containing chemical groups of rGO would impart a polarity to carbon atoms, which interact with polar water molecules at the electrolyte provoking an increase of wettability [56]. In these conditions, the equilibrium reaction at the positive electrode during charging would be simply presented as:

being C_x the carbon structure of the electrode and A^- the anion molecules of the electrolyte. An analogous mechanism, but implying cations, occurs in the negative electrode. Additionally, oxygen- and nitrogen-containing chemical groups are also expected to add pseudocapacitance through different redox reactions. Quinone oxygen groups as well as pyridinic and pyrrolic nitrogen (present in graphene edges and with negative charge) were reported to have the most noticeable influence on the capacitance due to their redox reactions [56, 57]. Graphitic nitrogen, which is not on the edge but within the graphene sheet, was reported to enhance the capacitance due to its positive charge that improves electron transfer and adds n-type nature to the material [56-61]. Furthermore, NiO-containing electrodes would exhibit additional charge storage processes being the result of oxidation of NiO to NiOOH (charging) and reduction of NiOOH to NiO (discharging) processes, respectively. This process is described in the following reaction [62]:

being z the fraction of nickel sites. Double layer and pseudocapacitive charge storage are inherently surface processes. However, diffusion-limited (semi-infinite or bulk) electrochemical processes can also occur depending on the structure-morphology of the electrode material. Therefore, complex systems composed of different types of nanomaterials can display pseudocapacitive (surface) or battery-like (bulk) behaviour even having the same chemical composition. A typical case is NiO-based nanomaterials, which have been reported to show different electrochemical behaviour depending on their nanostructure [44, 62-64]. Usually, however, NiO exhibits plateaus at galvanostatic charge-discharge curves pointing to significant contribution of diffusion-limited mechanisms. The study of the electrochemical nature (battery-like or

pseudocapacitive) of our NrGO-based electrodes was carried out by analysing the current measured in CV as a function of sweep rate, since the response current produced by capacitive (surface) processes is proportional to sweep rate but the current generated by diffusion-controlled (bulk) processes is proportional to the square root of the sweep rate [55]. First of all, the percentage of surface / bulk charge storage is calculated through the method developed by Ardizzone et al. [65] and is presented in Figure 6c. As witnessed, the charge storage in surface sites is dominant, about 55-82%, being always higher in the GO/NiO samples as compared to their counterparts without NiO. This fact could indicate that either NiO nanostructures, that are located on the surface of rGO sheets, increase the distance between rGO sheets leading to an increase of the effective surface exposed to electrolyte (increase of porosity) or/and NiO nanostructures exhibit pseudocapacitive behaviour due to their small size. The electrode with lowest surface contribution is GO-cit, whereas the highest one corresponds to GO-NiO-imi. As stated, in CV analyses the current required to charge the double layer and to initiate fast faradaic reactions on the exposed electrode surface (i_{cap}) is proportional to sweep rate (s), whereas the current related to the slow diffusion-limited process (i_{dif}) is proportional to $s^{1/2}$. An empirical description of this behaviour, calculated at a certain voltage applied to the electrode (V), is:

$$i(s, V) = i_{cap} + i_{dif} = as^b \quad (1)$$

$$\log(i(s, V)) = \log(a) + b \log(s) \quad (2)$$

being both $a(V)$ and $b(V)$ adjustable parameters. Hence, linear fits of $\log(i(s, V))$ versus logarithm of sweep rate allow us to calculate b -parameter (slope). A b value of 1 signifies a pure capacitive contribution to charge storage (double layer and pseudocapacitance), whereas a b value of 0.5 indicates the occurrence of slow faradaic processes controlled by diffusion (bulk). Intermediate b values, between 0.5 and 1, describe a transition state between capacitive and battery-type material in which the lower values of b -parameter account for larger contribution of diffusion-controlled mechanisms. To the contrary, the b -parameter is assumed to increase with greater contribution of capacitive (surface) processes. Figure 6d displays the calculated b -parameter of all the deposited electrodes. As witnessed, “average” b -parameter appears greater in GO/NiO electrodes as compared to their counterparts synthesized without NiO. This fact totally supports the calculations obtained by Ardizzone’s method (Figure

6c). Remarkably, the b-parameter displays a tendency to decrease with applied voltage in all the samples except in those synthesized with imidazole molecules, in which b-parameter increases with the applied voltage. It must be reminded that GO-imi and GO-NiO-imi samples present the highest rGO reduction degree and N-doping of their respective series (Figure 3). Previously reported CV analyses show a current increase at potentials lower than 0.2 V vs saturated calomel electrode (SCE) that is ascribed to pseudocapacitance contribution from pyridinic and pyrrolic nitrogen groups, whereas reversible redox reactions of quinone-type oxygen are specified to contribute to current between 0.2 and 0.4 V (versus SCE) on the CV curves [66]. Further, redox reactions of NiO have been reported to appear at about 0-0.1 and 0.25-0.4 V vs SCE [63]. Thus, we could consider that the change of b-parameter at different applied voltages indeed reveals the occurrence of different types of redox reactions between the electrode material and electrolyte ions. The electrodes composed of NrGO with higher concentration of oxygen-containing groups and lower nitrogen functionalities reveal a decrease of b-parameter at high voltages. To the contrary, the materials composed of greater reduced and nitrogen-doped rGO exhibit a decrease of b-parameter at low voltages. These results would indicate that the reduction/oxidation reactions activated in NrGO material are, to some extent, diffusion-controlled in nature.

Figure S5 displays representative galvanostatic charge-discharge curves of GO-cit, GO-NiO-cit, GO-imi and GO-NiO-imi samples at 1, 2, 4 and 8 mA cm⁻². It is worth noticing that, given the very low mass loading of the films (about few µg cm⁻²), the corresponding specific currents are very high, about kA g⁻¹. The curves show highly triangular profile without the presence of plateaus, revealing a quasi linear dependence of voltage with time. This behaviour is distinctive of electrochemical capacitors. As observed, the charge/discharge time decreases with the magnitude of applied current density, being higher at GO/NiO electrodes than their counterparts without NiO. Moreover, the samples synthesized with imidazole reveal larger charge-discharge times than the respective ones obtained with citric acid. The areal capacitance (C_A), calculated by equation (3) and showed in Figure S5e, reveals values in the range of ca. 2-7 mF cm⁻² that decreases about 10% with increasing the applied current density in the range of 1-8 mA cm⁻².

$$C_A = I_d \frac{\Delta t}{\Delta V} \quad (3)$$

In this equation, I_d is the discharge current density, Δt is the discharge time and ΔV is the voltage window (0.8 V) in galvanostatic charge-discharge measurements. Furthermore, the average areal/volumetric capacitance of the samples is also calculated from cyclic voltammetry data at different scan rates according to the following equation:

$$C_X = \frac{\oint I(V)dV}{2\Delta Vsk} \quad (4)$$

where C_X is the areal (C_A) or volumetric (C_v) capacitance, the integral at the numerator represents the area enclosed in CV plot (anodic - cathodic charges), ΔV is the voltage window, and s is the voltage sweep rate. $k = A$ is the area or $k = A \times t$ is the volume of the active material during the measurement, being t the thickness of the film. Figure 7a shows the calculated areal capacitance of all the electrodes as a function of the sweep rate. As observed, the areal capacitance slightly decreases with the sweep rate due to the kinetic limitation of the electrolyte ions to flow in and out of the pores of the electrode material. This effect can be further analysed from CV data. As discussed above, the capacitive and diffusive components of the recorded current are, respectively, proportional to s and $s^{1/2}$. Therefore, equation (1) can be also expressed as [55]:

$$i(s, V) = i_{cap} + i_{dif} = k_1 s + k_2 s^{1/2} \quad (5)$$

Hence, the parameters k_1 and k_2 can be calculated by fitting of $i(s, V)/s^{1/2}$ versus $s^{1/2}$. These parameters allow establishing the percentage of capacitive or diffusive contribution to the capacitance. Figure S6 presents characteristic plots of the areal capacitance as a function of sweep rate with the intrinsic capacitive and diffusive contribution. As expected, the diffusive contribution to the capacitance decreases in all cases with sweep rate. Moreover, the capacitive (surface) component is larger in GO/NiO electrodes as compared to their counterparts without NiO, in concordance to the results showed in Figures 6c, d.

In general, GO/NiO electrodes display larger areal capacitance than GO-based ones (Figure 7a). GO-NiO-imi electrode reveals the maximum areal capacitance (ca. 6.3 mF cm⁻² at 10 mV s⁻¹), followed by GO-NiO-cit, GO-NiO-asc and GO-NiO. Regarding GO-based electrodes (without NiO) GO-imi, discloses the largest areal capacitance (4.9 mF cm⁻²) of the set of samples, even larger than GO-NiO-asc capacitance. Therefore, the results indicate that the electrodes composed of the most reduced and N-doped rGO

material display the largest values of areal capacitance of each set of samples. Taking into account the mass loading of the active material (ca. $\mu\text{g cm}^{-2}$), the specific capacitance of the obtained films can be estimated in the range of 1 kF g^{-1} . Importantly, the thickness is different at each electrode (Table S1) leading to the contribution of different amount of material to the areal capacitance. In order to evaluate the performance of the electrodes materials in a normalized way, the volumetric capacitance of the samples is calculated (Figure 7b). As observed, the GO-based set of electrodes exhibit higher volumetric capacitance than the GO/NiO set of samples by a factor of 5-10. This fact could be caused by the lower compactness of GO/NiO-based films provoked by the enlarged distance between NiO-coated rGO sheets. Besides, NiO is a p-type semiconductor that has been reported to act as hole-transport electron blocking material in p-n junctions [67]. As already indicated, graphitic N-doped rGO behaves as a n-type material. Therefore, the NrGO flakes coated with NiO nanostructures would contain p-n nanojunctions exhibiting rectifying effects that could impede charge storage processes. It is also worth to note that the performance of very thin electrodes, as GO-based ones, should not be directly extrapolated to thicker films. The thin electrodes' characteristics will not scale up linearly with the thickness due to microstructural rearrangements that influence in electrolyte diffusion and interaction with active material [68]. At both GO and GO/NiO set of electrodes, the maximum value of capacitance belongs to the film synthesized with imidazole precursor (GO-im with 114 F cm^{-3} and GO-NiO-im with 19 F cm^{-3} ; both at 10 mV s^{-1}) confirming the improved performance after high reduction and N-doping of rGO.

Figure 7. (a) Areal and (b) volumetric capacitance plots of all the samples as a function of sweep rate.

Additional electrochemical impedance spectroscopy measurements were carried out for studying the AC performance of the electrodes. Representative Nyquist plots of GO-cit, GO-NiO-cit, GO-imi and GO-NiO-imi electrodes are presented in Figure S7. As witnessed, the EIS curves show the characteristic shape of carbon-based porous electrodes containing a quite straight line at low frequencies and a partial semicircle at high frequencies [69, 70]. The curves were fitted by using a modified Randles equivalent circuit shown in Figure S7c. This circuit contains an equivalent series resistance (ESR, R1), which accounts for the intrinsic resistance of the electrodes'

materials, besides electric contacts and electrolyte. This resistance is set in series with a two constant phase elements (CPE) in parallel configuration. The impedance of a CPE is commonly described by

$$Z_{CPE} = \frac{1}{Y(j\omega)^n} \quad (6)$$

The exponent n equals to 1 in ideal capacitors. In this case, Y would represent the capacitance. Values of n lower than 1 indicate that the properties of the electrodes are not homogeneous or exhibit some dispersion: highly contorted and rough surfaces, varying thickness or composition of the film, and nonhomogeneous redox reaction rates [71, 72]. In our circuit, CPE1 represents the impedance built up from double layer charge storage processes, whereas CPE2 denotes the pseudocapacitance generated by reduction-oxidation mechanisms. In series to CPE2 is included a charge-transfer resistance (R_2), related to redox reactions, and in parallel to CPE2 a leakage resistance (R_3). Table S2 summarizes the fitted values of such parameters. As observed, all the electrodes exhibit similar ESR, about 20 Ω , and lower n exponent in CPE1, about 0.5-0.6, than in CPE2 (0.9). This means that double layer charge storage mechanisms are more influenced by the material imperfections than pseudocapacitive ones. Interestingly, the electrodes with greater reduction degree and nitrogen content in NrGO material reveal higher charge transfer resistance (R_2) than their counterparts. Moreover, the value of the leakage resistance (R_3) increases orders of magnitude in NiO-containing samples, probably due to the lower compactness of the material and the low electrical conductivity of NiO (p-type semiconductor), which would hamper electron percolation between NrGO flakes.

3.3 Device fabrication and performance study

The electrodes fabricated with imidazole molecule, which exhibit larger reduction degree and N-doping in NrGO flakes, disclose the best electrochemical properties at both GO and GO/NiO set of samples. GO-NiO-imide electrode displays the best areal capacitance whereas GO-imide shows the best volumetric capacitance with an areal capacitance close to that of GO-NiO-imide electrode even having about 10-fold lower thickness (Figure 7, Table S1). The performance of such electrodes in working devices was investigated by assembling symmetric and asymmetric electrochemical capacitors

with them (Figure 8a). Symmetric ECs were assembled by using pairs of both GO-imi and GO-NiO-imi films. Asymmetric assemblies were composed of GO-imi/GO-NiO-imi pair electrodes working with opposite polarities (+/- and -/+). Galvanostatic charge-discharge voltage plots of all the devices display characteristic triangular-like profiles (Figure 8b). As observed, the duration of the charge-discharge cycles, about seconds, decreases with the applied current density. The corresponding areal capacitance of the ECs was calculated by using equation (3) and is shown in Figure 8c. Remarkably, and despite the small loading of active material on its electrodes, symmetric GO-imi assembly exhibits significantly larger areal capacitance, with a maximum of ca. 3.6 mF cm^{-2} , than the rest of devices at the lowest current densities. The assemblies containing GO-NiO-imi electrodes display similar values, about $1.0 - 1.5 \text{ mF cm}^{-2}$, at the studied current density range. This behaviour of symmetric GO-imi EC versus the rest of devices is also identified through the areal capacitance calculated from cyclic voltammetry (Figure 8d). The areal capacitance of GO-imi EC is larger than that of the rest of devices, being the capacitance difference reduced with increasing sweep rate. As observed, the maximum areal capacitance of GO-imi device is ca. 5 mF cm^{-2} (at 10 mV s^{-1}), which is larger than the one recorded in a single electrode configuration (Figure 7a). Certainly, symmetric GO-imi EC was expected to have lower capacitance than GO-NiO-imi and asymmetric ones since GO-imi single electrode exhibits lower areal capacitance than GO-NiO-imi (Figure 7a). The origin of this effect will be studied in future since goes beyond the scope of this work. Many mechanisms could contribute to this behaviour in such complex hybrid electrodes, composed of electrochemically active n-type NrGO flakes and p-type NiO nanostructures that can undergo a wealth of electrochemical reactions. As an example of the complexity of the problem, and trying to study the influence of the polarity on the electrodes performance, additional experiments were carried out. Figure S8 shows the ratio of areal capacitances of GO-imi and GO-NiO-imi electrodes, calculated from CV data obtained in the voltage ranges $[0, 0.8] \text{ V}$ (positive) and $[0, -0.8] \text{ V}$ (negative). As observed, GO-imi electrodes show higher capacitance in the negative range of voltage at low sweep rates (capacitance ratio lesser than 1) but becomes lower by increasing the sweep rate. On the other hand, GO-NiO-imi electrodes display higher capacitance in the negative range of voltage at all the sweep rates. Nevertheless, we expected higher capacitance in the positive range of voltage, not the negative, since NrGO functional groups and NiO are reported to endure pseudocapacitive charge storage at positive voltages [63, 66]. This fact points to a rich

phenomenology in these types of complex materials that is not well understood yet and should be further investigated.

Figure 8. (a) Image of an assembled EC device. (b) Galvanostatic charge-discharge curves of symmetric GO-NiO-imi device at different current densities. (c) Areal capacitance of the devices at different current densities calculated from galvanostatic charge-discharge data. (d) Areal capacitance of the devices at different sweep rates calculated from CV data. Inset: characteristic CV loop obtained at 100 mV s^{-1} from asymmetric GO-NiO-imi (+) device. (e) Ragone plot of the assembled ECs. (f) Capacitance retention and coulombic efficiency (inset) of the devices obtained from cycling experiments.

The Ragone plot (volumetric energy vs power densities), shown in Figure 8e, allows evaluating the overall performance of the ECs. The calculation of the volumetric energy and power densities is described in the Supplementary Material. The total volume of active material in the assemblies was used for the calculation. As witnessed, symmetric GO-imi device exhibits significantly higher power and energy densities, about 4 mWh cm^{-3} and 5.4 W cm^{-3} respectively, as compared to those containing NiO-based electrodes. Indeed, asymmetric ECs show slightly better performance than the device composed by only GO-NiO-imi electrodes. The stability of the devices was also studied

by galvanostatic charge-discharge cycling at 1.5 mA cm^{-2} current density. The devices containing GO-NiO-imi electrodes disclose similar excellent behaviour in which the capacitance retention and the coulombic efficiency remain unaltered (ca. 100%) after 10000 cycles. In these devices, NiO nanostructures may provide structural stability by means of mechanical strength and adhesion to the electrodes. Nevertheless, the symmetric GO-imi capacitor displays a continuous fading of the coulombic efficiency and tolerates less number of cycles (ca. 5000), probably due to the much higher specific current density that the active material of the electrodes has to bear (much lower mass loading) and lower mechanical strength (absence of NiO). In general, the performance of the studied ECs is comparable to the published one of analogous devices [34]. Finally, Figure 9 shows the Nyquist plots recorded from all the devices through EIS analyses. The equivalent series resistance, obtained from the intercept of the plot on the real axis, is quite low in all the cases, about 2.0, 0.3, 0.8 and $1.1 \text{ } \Omega \text{ cm}^{-2}$ for symmetric GO-imi and GO-NiO-imi, and asymmetric GO-imi/GO-NiO-imi (+/- and -/+), respectively. The characteristic time constant of the ECs, calculated as the inverse of the frequency in which the phase is -45° (Figure S9), is about 130 and 0.5 ms for symmetric GO-imi and GO-NiO-imi, and ca. 7 ms for asymmetric ECs. The large dissimilarity of characteristic time constant between symmetric GO-imi and the other devices accounts for the great difference of power/capacitance between them (Figures 8c, d).

Figure 9. Nyquist plot acquired by EIS studies of the assembled ECs. Inset displays the zoomed region of the plot corresponding to the high frequency range.

4. Conclusion

The reported results point to reactive inverse MAPLE as a promising method for the fabrication of functional graphene-based hybrid composites to be used in electrochemical capacitors. Through a combination of high energy photothermal and photochemical processes, the UV laser-induced reactivity between GO sheets and precursor molecules allows depositing nanocomposites with different degree of reduction and N-doping of GO, leading to a tuning of the functional properties in a quite simple and versatile way. Particularly, NrGO and NrGO/NiO composites synthesized in this work show a very rich phenomenology that should be further investigated, besides an interesting functionality that can be enhanced by varying target composition and increasing the mass loading (just by application of larger number of pulses). N-doped rGO films show high volumetric capacitance (up to 114 F cm^{-3} in sample obtained with imidazole precursor), with mixed surface and diffusive charge storage mechanisms. The films composed of NrGO coated with NiO nanostructures reveal less volumetric capacitance (up to 19 F cm^{-3} in sample obtained with imidazole precursor), but higher capacitive contribution to charge storage and more steadiness on charge-discharge cyclability (100% of capacitance retention and coulombic efficiency after 10000 cycles). The obtained results also point out complex interactions between NrGO and NiO that significantly influence on the material performance as a whole.

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