Reactive laser synthesis of nitrogen doped hybrid graphene-based electrodes for energy storage

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Abstract

A versatile method based on matrix assisted pulsed laser evaporation (MAPLE) technique was used for the fabrication of graphene-based electrodes for supercapacitors' applications. The simultaneous deposition and chemical transformation of graphene oxide (GO) and GO-NiO nanoparticles was attained by including nitrogen containing chemically reactive compounds (ammonia, urea and melamine) in the aqueous MAPLE targets. Morphological analyses reveal the formation of hundreds of nm to tens of

micrometres thick porous films on both plastic and metallic flexible substrates. Structural and compositional studies, carried out by transmission electron microscopy, and Raman and X-ray photoelectron spectroscopies disclose significant deoxidation and nitrogen doping of the GO material. The electrodes reveal remarkable electrochemical performance, showing a maximum volumetric capacitance of 350 F cm^{-3} (9.5 mF cm^{-2} areal capacitance) in aqueous electrolyte. Symmetric supercapacitors fabricated with these electrodes reveal excellent long-term stability at high specific intensities. From the obtained results, it can be asserted that the reactive inverse MAPLE method stands as a promising technology not only for the adaptable fabrication of flexible graphene-based composite electrodes but also for a wide variety of advanced functional materials for diverse applications.

Keywords: MAPLE, nitrogen doped graphene, NiO, hybrid electrode, laser synthesis, energy storage.

1. Introduction

Electrochemical capacitors, also named supercapacitors (SCs) are attracting high attention due to their capacity to store and supply large amount of electrical energy in short periods of time, providing much higher power and longer cycling life than batteries. SCs, often in combination with batteries, are being increasingly applied in electronic devices as memory back-up systems, electric and hybrid vehicles, as well as industrial power and energy management.¹⁻³ Recently, flexible SCs have received increasing consideration for portable electronic devices, such as wearable electronics, mobile phones, and flexible displays.⁴⁻⁸ Currently, the most commercial supercapacitors

use carbon electrodes due to their excellent temperature and cyclic stability, long lifetime, and relatively low cost. 2D carbon nanosheets as graphene and reduced graphene oxide (rGO) are also excellent candidates to be used in SCs due to their large surface areas and high conductivities.^{6, 9-12} Besides, it has been proven that nitrogen functionalities change the electronic characteristics of neighbouring carbon atoms, leading to modified spin density and charge distribution which induces the activation of regions on the graphene surface.^{13, 14} Thus, significant enhancement of capacitance of graphene-based electrodes when doped with nitrogen species has been reported.¹⁵⁻¹⁷ Furthermore, the energy density of carbon electrodes can be also improved by the presence of active species that contribute to the total specific capacitance by the pseudocapacitive effect.^{18, 19} In particular, electrodes based on graphene decorated with pseudocapacitive transition metal oxides are being studied as hybrid materials with high performance for flexible SCs.^{2, 20-24} The composites take advantage of both the high conductivity of the carbon materials and the high specific capacitance of the pseudocapacitive materials, leading to significant improvements in both the energy density and the power density of SCs. Particularly, carbon-NiO composites present interesting functional properties to be used in SCs' electrodes.²⁵⁻²⁷

Nitrogen-doped and metal-oxide decorated graphene materials have been already obtained by conventional routes. These methods usually induce the chemical reaction of nitrogen-containing molecules such as ammonia, urea or melamine with graphene derivatives.²⁸⁻³⁴ However, the chemical reaction is commonly activated by thermal processes, which hampers the use of thermally-sensitive substrates as polymers. Besides, chemical incompatibilities and the use of hazardous precursors set constraints to conventional methods. A possible alternative can come from the matrix assisted pulsed laser evaporation (MAPLE) technique, which provides a gentle process for

fabricating films of molecular species by means of the vapour phase. MAPLE technique uses a frozen target, consisting of a solution of a molecular compound dissolved in a relatively volatile solvent, being submitted to laser ablation process. Most of the laser energy is initially absorbed by the solvent molecules, which undergo a rapid vaporization process, leading to the transfer of the solute molecules towards a facing substrate. This method allows the deposition of different types of molecules such as polymers or biomolecules³⁵⁻³⁹ as well as nanoentities,⁴⁰⁻⁴³ and prevent them from being damaged by the high energy laser radiation. A variation of this technique, called inverse MAPLE, uses solutions / dispersions of molecules / nanoentities in non-absorbing solvent as water for UV radiation. In this case, the dispersed material absorbs the laser radiation, becomes rapidly heated and provokes the explosive boiling of the surrounding water ice which vapour transports the nanoentities towards the substrate.⁴⁴ In this way, oxides nanoparticles' (NPs) films have been deposited by laser irradiation of aqueous solutions of metal organic precursors.⁴⁵ Furthermore, rGO-based hybrid thin films were synthesized on different types of substrates,^{44, 46, 47} and partial N-doping of the rGO material was achieved by using N₂ background gas as doping agent.

Contrarily to conventional MAPLE, in which a minimum chemical modification of the molecular structure is desired, in this work we illustrate a new strategy for the inverse MAPLE fabrication of graphene-based layers accomplished by inducing chemical reactions of graphene oxide (GO) sheets at the frozen target during the irradiation process. Particularly, laser-induced physicochemical mechanisms led to significant and simultaneous reduction and N-doping of GO material by introducing nitrogen containing compounds (ammonia, urea, melamine) in the aqueous GO dispersion. Besides, the addition of NiO NPs to the MAPLE target showed different chemical pathways and deposition dynamics accounting for different structural characteristics.

The obtained N-doped rGO (NrGO) and NrGO-NiO coatings reveal significant electrochemical performance able to be used in energy storage applications.

2. Experimental section

MAPLE dispersions were synthesized by mixing GO powder composed of flakes about $1\ \mu\text{m}^2$ in size and 1-15 layers in thickness (NanoInnova Technologies) with deionized water for obtaining 10 wt% concentration. Besides, different types of N-containing molecules were added to the GO-H₂O dispersions for inducing chemical reactivity: ammonia (NH₃), melamine (C₃H₆N₆) and urea (CON₂H₄). Their respective concentrations were 4 M, 0.3 M and 2 M, ensuring homogeneous mixing without precipitation. Furthermore, similar dispersions were synthesized with additional mixing of 10 wt% NiO NPs (Sigma-Aldrich) with sizes ca. 50 nm. Afterwards, the dispersions were thoroughly stirred and sonicated at room temperature, and the MAPLE targets were prepared by filling a target holder with the dispersion and flash freezing by immersing the target holder in liquid N₂ at 77 K. Finally, the targets were located on a liquid N₂-cooled holder inside the deposition chamber, for maintaining the target frozen during the deposition processes.

MAPLE experiments were performed in a stainless steel vacuum chamber by irradiating the frozen targets with UV laser pulses through a Quantel Brilliant B Nd:YAG system (266 nm wavelength, ~5 ns pulse duration, 10 Hz repetition rate). The depositions were done in 20 Pa N₂ gas environment after evacuation to a residual pressure of 10^{-2} Pa. During the experiments, the laser beam scanned the target surface over an area of ca. $15\times 15\ \text{mm}^2$ at an incident angle of 45°. A number of 6000 laser pulses at a fixed fluence of $400\ \text{mJ cm}^{-2}$ was applied for the deposition of each sample. 0.5 mm-thick metallic

(copper, AISI 314 stainless steel) substrates of $1 \times 1 \text{ cm}^2$, were placed parallel to the target at a separation distance of 4 cm. The depositions were carried out at room temperature. Copper substrates were previously treated with glacial acetic acid to eliminate the surface native oxide⁴⁸. 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.

The thickness of the films was measured with a Leica DCM 3D confocal microscope. The samples were previously coated with a 10 nm-thick gold film for enhancing their reflectivity. The morphology of the composite films was studied by field emission scanning electron microscopy (SEM) by means of a QUANTA 200 FEG-ESEM microscope (FEI). The structural characterization was accomplished through scanning transmission electron microscopy (STEM), high resolution TEM (HRTEM), high angle annular dark field scanning TEM (HAADF-STEM) and Energy-dispersive X-ray spectroscopy (EDAX) with a Tecnai F20 equipment (FEI). Raman spectroscopy investigations were done by means of a LabRAM 800 system from Horiba Jobin Yvon. The measurements were completed in spots of about 500 nm in diameter by using a 532 nm laser wavelength (1.5 mW). Several spectra were recorded on each sample in the $200 - 3500 \text{ cm}^{-1}$ range, by integrating an average of 3 spectra of 20 s of acquisition time each for improving the signal-to-noise ratio. The chemical composition of the deposited materials was studied by X-ray photoelectron spectroscopy (XPS) by using a SPECS XPS spectrometer based on a Phoibos 150 electron energy analyser. The apparatus used the aluminium anode (Al K α 1486.74 eV) of a monochromatic X-ray source and the electron energy analyser operated in the constant energy mode. Wide range spectra over 1200 eV binding energies were recorded using an analyser pass energy of 50 eV. Additional high resolution spectra were also acquired over 20 eV ranges at 10 eV pass

energy, by using an energy resolution of 0.7 eV. All the measurements were performed in ultra-high vacuum ($\sim 10^{-7}$ Pa).

The electrochemical properties of the samples were analysed by cyclic voltammetry (CV) by means of a Keithley 2450-EC Electrochemistry Lab System. The samples were used as working electrode with a geometrical area of 0.58 cm^2 in a three-electrode cell. The measurements were carried out with an Ag/AgCl reference electrode (3M NaCl internal solution) and a Pt counter electrode in a 1 M Na_2SO_4 aqueous solution at room temperature. The average areal capacitance of the samples was calculated at different scan rates according to the following equation:

$$C_A = \frac{\oint I(V)dV}{2\Delta V v A} \quad (1)$$

where C_A is the areal capacitance, the integral at the numerator represents the area enclosed in CV plot (anodic - cathodic charges), ΔV is the voltage window, v is the voltage scan rate and A is the area of the active material during the measurement. The performance of symmetric supercapacitor devices, assembled inside Swagelok cells, was studied with a Bio-Logic VSP electrochemical workstation system. For the fabrication of the supercapacitors, glass fibre separators and 1 M Na_2SO_4 aqueous electrolytes were used. Cyclic voltammetry and galvanostatic charge-discharge analyses were carried out with electrodes deposited on AISI 314 stainless steel collectors.

Finally, thermal simulations were performed by solving the 2D heat equation in idealized GO sheets and NiO NP systems in water ice matrix at 200 K submitted to one laser pulse. The numerical calculations were done by means of COMSOL 5.2 software, using the H_2O , GO and NiO thermophysical properties extracted from Refs.^{44, 46, 49} For the sake of simplicity, the model uses rectangular-shaped GO flakes $1 \text{ }\mu\text{m}$ in length and

1-10 nm in thickness (ca. 1-15 monolayers) and squared-shaped NiO NPs with 50 nm lateral size. Besides, only photothermal effects are considered.

3. Results and discussion

3.1. Structural – compositional study of the films

Due to its rich chemical structure, graphene materials are prone to establish a wealth of noncovalent interactions with molecular entities.⁵⁰ Particularly, it has been proven that melamine molecules act as a non-covalent anchor that indeed keeps water molecules conveniently close to the graphene surface,⁵¹ besides it can bind strongly to the surface of both defect and defect free graphene nanoribbons⁵² and interact with quinones (present in GO) through n- π charge-transfer mechanisms.⁵³ On the other hand, the polarity of ammonia and the tendency of urea for creating hydrogen bonding⁵⁴⁻⁵⁷ allow us inferring that the GO platelets are tightly surrounded by a wealth of ammonia, urea and melamine molecules in the aqueous dispersions.

Figure 1a displays a sketch of the MAPLE deposition process. Water ice, ammonia, melamine and urea do not significantly absorb the 266 nm wavelength radiation.⁵⁸⁻⁶⁰ Consequently, GO sheets and NiO NPs are the entities that absorb the laser radiation at the frozen targets. Figure 1b shows the simulated temperature evolution of GO sheets and NiO NPs as a function of time. As observed, the laser pulse induces very rapid thermal cycles in GO flakes and NiO NPs which also lead to a rapid heating of the surrounding water ice. In the case of GO, the maximum temperature increases with the thickness of the flakes being higher than the sublimation temperature of water ice at 20 Pa (ca. 240 K)⁶¹. The irradiation of 10 nm thick platelets provokes their heating beyond 550 K, which is 85% of the water critical temperature (647 K), leading to the explosive

boiling of the surrounding water matrix.^{62, 63} As a result, the simultaneous thermally-activated chemical reaction of the molecular species and their transportation towards the substrate through the matrix vapour is anticipated (Figure 1a). Noteworthy, NiO NPs exhibit faster heating mechanisms due to higher absorption coefficient, reaching much higher temperatures than GO platelets, even beyond the melting point of bulk NiO (ca. 2230 K) in just few nanoseconds.

Figure 1. (a) Sketch of the MAPLE deposition process. (b) Simulated temperature of GO flakes and NiO NPs submitted to one UV laser pulse of 400 mJ cm⁻². Insets: temperature distribution in 50 nm NiO NP and 10 nm thick GO flake at 3 ns.

Dark brown – black films were obtained in all the cases (Figure S1, Supporting Material), being the ones deposited onto Au/Cr/PP substrates highly flexible and stable upon bending. The measurement of the film thickness clearly reveals different deposition phenomenology depending on the presence or absence of NiO NPs (Table 1). The GO films, deposited from frozen dispersions without NiO NPs, show thicknesses about hundreds of nm to microns, whereas the films containing NiO NPs reveal thicknesses about one order of magnitude higher (tens of microns). Besides, the films developed with urea molecules are the thickest ones at their respective series. The fact that GO / NiO samples exhibit larger thickness than GO-based ones points out to different deposition regimes. This dissimilarity would be related not only to the larger amount of material present in the target (GO flakes + NiO NPs) but mainly due to the high temperature reached by the NPs, which would provoke a massive and energetic explosive boiling of the matrix leading to substantially higher deposition rates (up to 4 $\mu\text{m}/\text{min}$).⁴⁴

Sample	GO	GO-NH₃	GO-Melamine	GO-Urea
Thickness (μm)	0.1	0.1	0.2	4
Sample	GO-NiO	GO-NiO-NH₃	GO-NiO-Mela.	GO-NiO-Urea
Thickness (μm)	7	20	30	40

Table 1. Average thickness of the deposited electrodes.

Electron microscopies analyses of the deposited films reveal different structural characteristics in GO and GO / NiO sets of samples. SEM inspections disclose the

formation of a porous assembly throughout the film in all the cases (Figure 2a). GO films appear to be formed by a matrix of hundreds of nanometre-sized clusters composed by GO sheets connected between them (Figure S2). The size of the clusters and the film porosity seems to vary between the samples, being the GO-Urea film the most compact one. On the other hand, GO / NiO samples show a more compact structure with additional rounded structures, from tens of nanometres to about one micron in size, composed of nickel oxide aggregates probably formed after melting, coalescence and resolidification of NiO NPs (Figures 2b, S3). Furthermore, HAADF-STEM imaging, which is strongly dependent on the atomic number Z , reveals Ni-rich regions (with bright contrast) fully covering the GO surface with sizes as small as 1 nm, smaller than initial NiO NPs (50 nm), what indeed accounts for melting and dewetting processes (Figures 2c, S4a). The presence of Ni is verified by TEM-EDAX analyses, showing the additional presence of C, O and N atoms from NrGO material and Cu from the TEM grid (Figure S4b). HRTEM studies disclose GO sheets with similar dimensions to the raw GO but with evident rippling and the presence of nanometre-sized defects as holes and beams of misoriented planes (Figures 2d, e). The presence of defects as nanoholes is expected to be advantageous since edge atoms are more electrochemically active than basal ones.^{64, 65} The wrinkles can extend over few hundreds of nanometres and appear to be more evident in GO rather than GO / NiO films. Remarkably, the GO-NH₃ material seems to display higher density of holes, rippling and some amorphization. As shown in Figure 2f, the Ni-rich nanostructures are highly crystalline, showing interplanar distances of 0.25 nm, and additional 0.22 and 0.28 nm (not shown) which could correspond to strained (200) (0.22 nm) and (111) (0.25 and 0.28 nm) crystallographic orientations of cubic NiO (Bunsenite; JCPDS 00-047-1049). All the observed planes appear significantly strained as compared to bulk

NiO, accounting to considerably mechanical stress developed during very fast solidification-crystallization processes.

Figure 2. (a) Cross sectional and (b) surface SEM images of GO-NiO-NH₃, (c) HAADF-STEM and (d) HRTEM of GO-NiO sample. (e) HRTEM of GO-Melamine and (f) GO-NiO-Melamine samples. Inset in (f) zoomed image of pointed NiO nanostructure. Also, the arrows point to NiO NPs.

Interestingly, GO-Urea and GO-NiO-Urea films exhibit different structural features as compared to the rest of the samples. As witnessed in Figure 3, GO layers appear somehow stacked and show smooth morphology without wrinkling. High resolution TEM reveals very low concentration of defects at GO structure though, noticeably, the creation of carbon nanotube-like structures is observed in some regions (Figure 3b). SAED patterns reveal rings corresponding to 0.14, 0.25 and 0.35 nm interplanar distances attributed to (010), (100) and (002) planes of graphitic structure (Figure 3a). In addition, all the rings show intensity asymmetries and some elongation along

preferential orientations what account for ordered stacking and anisotropic strain in the assemblies. A proposed cause for this structure, not observed in the rest of samples, could be the creation of a self-assembled urea-based motif structure between the GO sheets by the action of hydrogen bonds between the urea molecules before the GO-urea aqueous target becomes frozen.^{66, 67} The π orbitals located in nitrogen atoms of urea molecules could couple with the π system in the graphene domains of GO allowing the urea to drive the assembly of the GO layers.⁶⁸ The formation of such GO-urea stacked assemblies in the aqueous target would increase their absorption to the laser radiation leading to the development of higher temperatures, and hence larger deposition rates and film thicknesses, as already observed (Table 1). Remarkably, the presence of NiO NPs does not preclude the formation of the GO stacks, which appear decorated with a continuous layer of NiO in addition to the typical nanostructures after their deposition. The covering layer is composed of crystalline domains about tens of nanometres in size (Figure 3d). The observed interplanar distances are mainly 0.25 and 0.28 nm corresponding to a preferential creation of strained (111) NiO, besides 0.17 and 0.22, attributed to strained (220) and (200) planes of NiO (Figures 3c, d). It is worth to notice the great morphological difference between the small randomly oriented NiO nanostructures covering the GO sheets in GO-NiO, GO-NiO-NH₃ and GO-NiO-Melamine films, and the smooth continuous coating grown on GO flakes in GO-NiO-Urea sample. This fact points out to very different recrystallization mechanisms of molten NiO material due to spatial confinement when it is trapped between GO layers.

Figure 3. (a) TEM and (b) HRTEM images of GO-Urea sample. Inset in (a) SAED pattern. (c) TEM and (d) HRTEM images of GO-NiO-Urea sample. Insets in (c) SAED pattern, and (d) HRTEM and FFT of the indicated regions.

Additional structural information of the deposited materials can be extracted by means of Raman spectroscopy. Typical spectra recorded from the films, and the corresponding deconvoluted bands, are shown in Figure 4a. All the spectra show Raman bands corresponding to GO material. Interestingly, GO / NiO samples do not show NiO bands with the exception of GO-NiO-Urea, which exhibits a band centred at around 500 cm^{-1} that is ascribed to one-phonon (1P) scattering.⁴⁹ This fact could be related to the preferential orientation and larger size of the NiO domains in the continuous layer present in GO-NiO-Urea rather than in the rest of GO / NiO films, where smaller

randomly oriented nanostructures are grown. GO broad bands appear around 900 – 1800 cm^{-1} and 2300 – 3400 cm^{-1} . The first broad band was deconvoluted in five peaks located at around 1200 cm^{-1} (I), 1350 cm^{-1} (D), 1500 cm^{-1} (D''), 1590 cm^{-1} (G) and 1680 cm^{-1} (D'). The broad band located at 2300 – 3400 cm^{-1} would be composed by 2D and D+G contributions.⁶⁹ G peak is characteristic of carbon materials and is produced by the relative motion of sp^2 -bonded carbon atoms. The D peak is ascribed to the defect-activated breathing mode of hexagonal carbon rings, whereas I, D'' and D' peaks are also related to disordered or amorphous carbon.⁷⁰⁻⁷³ The content of structural defects of graphene materials can be evaluated by D/G intensity ratio. As observed in Figure 4b, the average I(D)/I(G) ratio of all the samples is very similar, in the range of 0.85 – 0.90, and all of them are lower than that of raw GO (0.93 ± 0.05). On the other hand, the FWHM of G peak always augment with disorder, so the regime of disorder of the GO material can be distinguished by the evolution of I(D)/I(G) versus FWHM(G).⁶⁹ As observed in Figure 4b (inset), I(D)/I(G) ratio of all GO-based films (without NiO) decrease with FWHM(G), what accounts for a high defect density regime. Besides wrinkling and some hole formation, no large structural defects or amorphization are perceptible by TEM analyses, suggesting that the most abundant defects would come from the sp^3 -bonded carbon-heteroatom structures. Interestingly, the decreasing tendency in I(D)/I(G) versus FWHM(G) correlation is not recognised in GO / NiO films, pointing to simultaneous and opposing contributions of defects and influence of NiO nanostructures on sp^2 carbon bonds. The average graphitic domain size, considered as the mean distance between defects (L_D), and the corresponding density of structural defects (average number of defects per unit area, n_D) are also calculated from the I(D)/I(G) ratio.^{69, 74} Figure S5 shows the calculated L_D and n_D of all the films. L_D values are very similar in all the deposited films, about 1.15 nm, similar but lower than that of

raw GO (1.2 ± 0.3 nm). The n_D values corresponding to GO, GO-Melamine and GO-Urea are very similar, ca. $2.45 \times 10^{13} \text{ cm}^{-2}$, though GO-NH₃ reveals lower density of defects 2.38×10^{13} . It is convenient to recall that this sample reveals higher amount of holes, corrugations and some amorphization at HRTEM. On the other hand, GO / NiO samples exhibit an increasing value of n_D values from GO-NiO, to GO-NiO-NH₃, GO-NiO-Melamine and GO-NiO-Urea in the range $(2.35 - 2.44) \times 10^{13} \text{ cm}^{-2}$. It must be remarked that all these values are higher than that of raw GO $(2.27 \pm 0.02) \times 10^{13} \text{ cm}^{-2}$, accounting for the creation of structural defects in GO flakes after the laser irradiation process. Furthermore, the GO films show larger density of structural defects than their counterparts in GO / NiO set, what would account for a somehow protective behaviour of GO flakes from laser radiation being mainly absorbed by NiO NPs (shielding effect).

Figure 4. (a) Raman spectra of GO-NiO-Urea and GO-NiO-NH₃ (inset) with their corresponding deconvoluted peaks. (b) (D/G) intensity ratio of all the samples. Inset: (D/G) intensity ratio versus FWHM(G). The open symbols refer to the samples synthesized with NiO NPs and the lines indicate the fitted curves.

Wide scan and high resolution XPS allow studying the composition of the obtained samples. Figure 5a presents the atomic concentration of the chemical elements existent in the films, calculated from the wide scan spectra. As observed, GO-based films are composed of carbon, oxygen and nitrogen elements. It appears clear that, by comparison

with the raw GO precursor (reference, marked as “Ref”), carbon concentration increases after deposition contrarily to oxygen concentration pointing out to a deoxygenation process. The calculated reduction degree (at.% C / at.% O) of raw GO is 3.4. Figure 5b reveals that GO material becomes partially reduced after deposition in all cases, so we consider it a rGO. The most reduced GO is obtained in GO-Melamine film (reduction degree of 9.5), whereas the other films exhibit intermediate values (about 5.6-6.1). On the other hand, nitrogen doping is evident in the deposited films, being the GO-Melamine sample the one with the highest nitrogen concentration (ca. 15%) and nitrogen doping degree (at.% N / at.% C + at.% N) of about 0.17 (Figure 5b). As observed, N-doping degree of GO-Urea (0.1) is larger than those of GO-NH₃ (0.06) and GO (0.02), being nitrogen totally absent in raw GO. Therefore, it can be stated that the introduction of nitrogen containing molecules in the target provokes considerably higher N-doping of rGO as compared to the conventional method using just N₂ gas background (GO sample). Regarding the GO / NiO set of samples, the presence of Ni and O atoms from NiO force us to recalculate the concentration of C, O and N in GO material (open bars in Figure 5a) from the measured data (solid bars) (see Supporting Material for calculation details). As expected, after subtraction of the NiO contribution, the increase of C and N concentrations and the decrease of O is revealed. Noticeably, the reduction degree of all GO / NiO samples is lower than their counterparts in GO set, being the GO-NiO-Urea the most reduced film (5.3). Indeed, GO-NiO and GO-NiO-Melamine show lower reduction degree than raw GO, pointing out to a possible oxidation process. The GO-NiO-Urea film also shows the largest inclusion of nitrogen in the rGO structure (22.1%), followed by GO-NiO-Melamine (16.5%), GO-NiO-NH₃ (4.5%) and GO-NiO (1.7%). Their corresponding N-doping degrees are 0.25, 0.22, 0.06 and 0.02. Summarizing, the inclusion of NiO NPs provokes less deoxygenation of GO

flakes but much higher N-doping in targets containing melamine and urea molecules. As discussed earlier, the presence of NiO NPs could probably lead to a laser radiation shielding effect at GO sheets, though also the development of higher temperatures favouring the development of thermally-activated chemical reactions rather than photochemical ones. The largest reduction and N-doping degrees of GO-NiO-Urea film would be provoked by larger absorption of radiation and development of temperatures caused by their self-assembling into thicker aggregates before irradiation. Nevertheless, it should be noted that, due to precipitation constraints, the melamine concentration in the MAPLE targets (0.3 M) is much lower than that of urea (2 M) and ammonia (4 M). Therefore, melamine appears as the most efficient precursor for provoking the reduction and N-doping of GO material.

Figure 5. (a) Atomic concentration of the chemical elements present in the samples obtained from the wide range XPS spectra (solid bars). The open bars correspond to the calculated concentrations by subtraction of NiO contribution. (b) C/O (reduction degree) and N/(N+C) (nitrogen doping degree) atomic ratios.

Representative high resolution C1s and N1s XPS spectra of the raw GO (Ref) and deposited films, including the corresponding deconvoluted peaks, are shown in Figure 6. The C1s signal is deconvoluted in five components (C1-C5) centred at 284.5 eV, 285.9 eV, 286.6 eV, 287.5 eV and 288.9 eV. These peaks correspond respectively to sp^2 -bonded carbon atoms (C1), probably with some contribution of sp^3 bonding; as well as carbon-oxygen hydroxyl (C2), epoxide (C3), carbonyl (C4) and carboxylic (C5) groups.^{75, 76} The GO film obtained in N₂ gas background shows an additional small peak centred at 293 eV associated to a shake-up satellite caused by a π - π^* transition (not shown). The N1s spectra are deconvoluted into four components ascribed to pyridinic N (N1, centred at 398.4 eV), pyrrolic-amine groups (N2, at 399.8 eV), graphitic (quaternary) N (N3, at 401.5 eV) and pyridinic nitrogen oxide (N4, at 402.4 eV).^{76, 77} In order to get additional information of the materials composition, Figure S6 shows the integrated area percentage of all the deconvoluted peaks. The simultaneous augment of the relative amount of sp^2 carbon (C1) and decrease of carbon-oxygen groups (C2-C5) in the deposited films is observed as compared to raw GO, accounting for a significant deoxygenation of GO films. Depending on the type of N-containing molecule used for doping, the relative amount of the different carbon-oxygen groups differs though still retain all of the moieties present in raw GO. The proportion of all the oxygen groups decrease after deposition excluding the hydroxyl group (C2) which seems to remain in similar proportion in all the samples except for GO-Urea, where the initial proportion persists for carboxyl group (C5). In contrast to the atomic concentration results (Figure 5), the reduction of the carbon-oxygen groups in the GO / NiO samples is also evident, though much less noticeable than in GO set of samples. The increased atomic concentration of oxygen in this case could be ascribed to N-O and water molecules

adsorbed on the rGO layers' surface, given the ability of GO to adsorb water molecules.⁷⁸ Moreover, GO / NiO films show noticeably larger relative amount of carboxyl groups than their counterpart without NiO (Figures 6, S6). The analysis of the nitrogen components reveals that the amine – pyrrolic (N2) groups are the most abundant in all the samples. In the GO set of films, the graphitic N (N3) is the next functionality in abundance, followed by the pyridinic group (N1). The relative amount of graphitic N is quite similar and close to amine – pyrrolic one, though the quantity of pyridinic N in GO-Urea and GO-Melamine is noticeably higher than in GO-NH₃ and GO films. The GO / NiO films show a rather different proportion of nitrogen functionalities except for GO-NiO-Urea which is similar to GO-Urea. GO-NiO and GO-NiO-NH₃ samples show additional pyridinic N⁺-O⁻ (N4) contribution, which does not appear in any other sample. Besides, GO-NiO-NH₃ and GO-NiO-Melamine films reveal a more prevalent amine - pyrrolic component than in the rest of samples. GO-NiO-NH₃ does not contain graphitic N and, similarly to GO-NiO-Urea, holds the maximum percentage of pyridinic N.

In summary, the reactive inverse MAPLE deposition has been proven to allow the simultaneous reduction and significant N-doping of the rGO flakes (NrGO) showing different combination of chemical groups depending on the nitrogen containing molecule used in the target's dispersion. The use of melamine and urea seems to provoke a larger incorporation of nitrogen in the rGO structure. Though the development of larger temperatures is expected to provoke greater reduction of GO sheets,⁷⁹ the incorporation of NiO NPs, which reach much larger temperatures than GO when irradiated with laser, leads to the deposition of rGO material with lower reduction degree (Figures 5, 6, S6). This fact would point out to direct laser-driven reduction at GO sheets (caused by a combination of photothermal and photochemical mechanisms)

as more effective process than NiO-mediated thermal one, being GO flakes predominantly shielded from direct laser radiation. Additional explanations would be: (i) that only a small matrix region around the NiO NPs actually reaches very high temperature and, then, most of the GO flakes would be indeed shadowed and submitted to lower temperatures; and (ii) the development of different chemical pathways at GO sheets due to the catalytic mediation of NiO. Molecular simulations would help to unveil the hidden mechanisms during the laser irradiation of the frozen target. Conversely, the N-doping degree of rGO sheets significantly increase with the presence of NiO NPs, pointing to either thermally or catalytically-driven chemical reactions.⁸⁰⁻⁸² There are two possible pathways for nitrogen inclusion into GO structure. The first pathway would be via chemical reactions of the N₂, NH₃, melamine and urea molecules with GO surface oxygen containing functional groups, contributing to the incorporation of N into the graphene lattice.⁸³⁻⁸⁷ Another possible pathway for N-doping would be the production of carbon nitride by the decomposition of the N-containing precursors, acting as an intermediate for the formation of a N dopant in the NrGO.^{30, 88}

Figure 6. Typical high resolution XPS spectra with corresponding deconvolution peaks.

3.2. Analysis of electrodes' functional properties

The electrochemical properties of the electrodes were studied by cyclic voltammetry using 1M Na₂SO₄ aqueous electrolyte. Several tests were performed on each sample at scan rates in the 10 – 150 mV s⁻¹ range. For comparison, Figure S7 shows the current density vs voltage plots recorded at 150 mV s⁻¹ of all the samples. As observed, the samples deposited without NiO NPs reach current densities lower than their counterparts with NiO. The maximum difference is observed in GO / GO-NiO samples whereas the GO-Melamine / GO-NiO-Melamine pair show similar current densities. The shape of the voltammograms resemble to rectangular-one being more clear in NiO-containing samples, pointing out to enhanced pseudocapacitive behaviour. Besides, anodic-cathodic peaks are also visible in some of the obtained voltammograms. These

peaks are generally attributed to surface redox reactions at the functional groups of NrGO material.¹⁷ However, we have observed that these peaks only appear on some samples even if they have been deposited in the same conditions. Figure S8 shows additional voltammetry cycles of GO and GO-NiO samples which do not show any redox peak, contrarily to the voltammograms presented in Figure S7. This result would point to the contribution to the electrochemical behaviour of (i) adsorbates or soluble components and/or (ii) slight compositional differences of the electrode's material. Anyhow, the concentration of soluble molecules in the electrolyte / electrodes' compositional variations might be very low since they are not visible by FTIR analyses. Moreover, the contribution of the corresponding anodic-cathodic peaks to the capacitance value is negligible.

Figure 7a shows the films' areal capacitance calculated from the cyclic voltammograms. As observed, the capacitance of the electrodes decreases with the scan rate due to the increasing difficulty of the electrolyte molecules to flow through the pores of the film as scan rate augments. The GO set of samples show a maximum areal capacitance from 2-3 mF cm⁻² in GO and GO-NH₃ electrodes to 7 mF cm⁻² in GO-Melamine at 10 mV s⁻¹. Consequently, this result reveals an increase of the areal capacitance with the reduction and N-doping degrees of the GO deposited films (Figure 5b). Furthermore, there is a notable increase of the capacitance with the incorporation of NiO material, with the exception of GO-Melamine and GO-NiO-Melamine, which display similar capacitances. Remarkably, the highest values, about 9 mF cm⁻² are reached by GO-NiO and GO-NiO-NH₃ electrodes which show the lowest reduction degree and nitrogen incorporation of the GO / NiO set of samples. The obtained specific capacitances can be considered high, roughly 1000 F g⁻¹, taking into account that the mass of the deposited films is about few μg cm⁻², and are excellent for flexible micro-supercapacitor

devices.⁸⁹ Besides, it has to be reminded that the electrodes exhibit very different thicknesses and, therefore, different amount of material exposed to the electrolyte. In order to have a figure of merit about the inherent performance of the deposited materials, the volumetric capacitance was calculated by dividing areal capacitance by the film thickness (Figure 7b). The highest capacitance values, about 200 – 350 mF cm⁻³ at 10 mV s⁻¹, are obtained with the GO set of electrodes with the exception of GO-Urea which exhibits a maximum of ca. 12.5 mF cm⁻³. As previously reported, the capacitance increases with the micropore volume, i. e. electrode's effective surface⁹⁰ being the pore distribution essential for a final performance.^{91, 92} In our case, the GO-Urea reduced value of capacitance would be caused by the self-aggregation of NrGO sheets leading to more compact film which obstructs the exposition of NrGO surface to electrolyte molecules (Figures S2, 3). Regardless the large influence of morphology in electrochemical properties of GO-Urea, the rest of samples exhibit larger volumetric capacitance as the reduction degree and nitrogen incorporation increase in NrGO structure, being GO-Melamine the electrode with best intrinsic performance (350 mF cm⁻³). These values are high as compared to those obtained in rGO-based electrodes fabricated by conventional and laser processing methods.^{89, 93, 94} We attribute such high performance mainly to the extent and quality of N-doping. As already explained, XPS analyses reveal that the rGO sheets are functionalized with pyrrolic / amine, graphitic and pyridinic nitrogen groups. It has been previously evidenced that amine and graphitic N-doping induce a n-type nature, leading to a reduction of the intrinsic resistance of graphene that benefits the electron transfer through the active material and improves the capacitive performance.^{28, 83, 95, 96} Moreover, graphitic and pyridinic N exhibit large dipole moments that can greatly improve the wettability of graphene material in the aqueous electrolyte solution provoking a capacitance enhancement.⁹⁷ Besides, pyridinic

and pyrrolic nitrogen groups as well as quinone oxygen groups are electrochemically active and can participate in redox reactions with H₂O in alkaline aqueous solution.^{87, 98}

As witnessed in Figure 7b, the GO / NiO set of electrodes reveal about one order of magnitude lower volumetric capacitance than GO-based electrodes. These poorer values, comparable to GO-Urea, would point to less performant material due to (i) larger compactness of the films caused by enhanced aggregation induced by molten NiO; and/or (ii) lower degree of reduction of rGO, i. e. larger amount of sp³ C-O groups, which difficult the electron transport between graphene domains. These results demonstrate that, regardless a high N-doping or decoration with capacitive NiO nanostructures, high deoxidation and porous structure of GO material are essential for fabricating electrodes with the electronic and ionic conductivity necessary for good performance.

Figure 7. (a) Areal and (b) volumetric capacitance of the deposited electrodes. The open symbols refer to the samples synthesized with NiO NPs.

Symmetric aqueous supercapacitors were also fabricated using GO-Melamine and GO-NiO electrodes, which are the best performing electrodes with the absence and presence of NiO nanostructures, respectively. As observed in Figure 8a, the SCs' cyclic voltammograms show similar quasi-rectangular loops in both GO-Melamine and GO-NiO devices, indicating electric double layer and pseudocapacitance behaviour, respectively. As expected, higher current densities were found for the GO-NiO device. The capacitive performance was further investigated with galvanostatic charge-

discharge cycling experiments at different current densities (Figure 8b). On the basis of the discharging curve line, the capacitance was assessed (Figure 8c). The selected range of current density is $0.5 - 2 \text{ mA cm}^{-2}$. Taking into account that the active material per electrode is below $10 \text{ }\mu\text{g}$, the specific currents applied to the devices are about hundreds of A g^{-1} . The recorded values, with capacitance in the range of $20\text{-}40 \text{ }\mu\text{F}$ and $750\text{-}1000 \text{ }\mu\text{F}$ for GO-Melamine and GO-NiO SCs, respectively, indicate an excellent performance of the SCs at such high specific currents. The corresponding Ragone plot of these devices (Figure 8d) shows volumetric values similar to those of microsupercapacitors previously obtained by conventional techniques.^{10, 99} The cycling stability of the SCs was also tested at constant current density (Figure 8e). GO-NiO electrodes have revealed to be more stable than GO-Melamine, probably due to the improved mechanical strength and adhesion supplied by NiO nanostructures. GO-Melamine devices can endure 20000 cycles, whereas GO-NiO SC tolerates more than 50000 cycles. Both types of devices display similar capacitance fading with excellent long-term cycling stability, about 90% of the initial capacitance is retained at 20000 cycles (in both SCs) and 84% at 50000 cycles (in GO-NiO SC).

Figure 8. Electrochemical characterization of GO-Melamine (red) and GO-NiO (black) supercapacitors. (a) Cyclic voltammetry profiles, (b) galvanostatic charge-discharge curves at different current densities (area of electrode = 1 cm²), (c) Capacity as a function of current density, (d) corresponding Ragone plot, and (e) long-term cycling stability (0.5 mA cm⁻² for GO-Melamine; 1 mA cm⁻² for GO-NiO),.

The obtained results point to reactive inverse MAPLE as a promising method for the fabrication of graphene-based micro-supercapacitors for highly-integrated electronic devices as self-powered sensors, etc. This method, similar to the pulsed laser deposition (PLD) technique (already used at industry) shows interesting features as compared to conventional fabrication methods: the film deposition is carried out at room temperature and is independent on the substrate, so even temperature sensitive materials can be coated; no chemical incompatibilities appear during deposition; it shows higher deposition rate than PLD and conventional MAPLE; it is easy, versatile and innovative method implying a combination of high energy photochemical and photothermal

mechanisms, usually out of thermodynamic equilibrium and not present in conventional processes, that allows obtaining materials with different composition-structure.

4. Conclusion

In this report, a method consisting on introducing reactive molecules in the MAPLE target for inducing GO transformation besides its deposition has been proven. In particular, the deposited GO material becomes reduced and highly doped with nitrogen by using ammonia, urea and melamine as reactive molecules. The morphology and composition of the NrGO layers strongly depend on the target configuration. Hybrid N-doped rGO / NiO films have been also fabricated by introducing NiO NPs in the target dispersions. The presence of NiO NPs in the target provokes a more energetic deposition regime, which leads to considerably thicker nanocomposite films (tens of micrometers) and larger content of nitrogen in rGO structure (up to 22 at.% in GO-NiO-Urea). Flexible electrodes have been manufactured by deposition onto metallic and gold-coated polymer substrates. The obtained electrodes and symmetric supercapacitors fabricated with them reveal significant electrochemical charge storage performance as well as outstanding long-term charge-discharge stability. As a conclusion, the reactive inverse MAPLE method can be considered as a simple and cost-effective methodology with enormous versatility for obtaining functional coatings based on high-quality graphene derivatives for varied applications. Indeed, this technology would have potential to achieve doping of reduced graphene oxide with different heteroatoms. For instance, doping with boron or phosphorus, which are highly interesting for supercapacitor applications, could be performed by adding boric and orthophosphoric acids to the target dispersions, respectively. Though the obtained results would principally point to micro-supercapacitor applications, it should be noted that the use of

high repetition rate laser sources (kHz regime) would allow the development of high mass loaded electrodes ($> 1 \text{ mg cm}^{-2}$) for high power-energy applications.

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Conflicts of interest

There are no conflicts of interest to declare.

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