Reduced graphene oxide/iron carbide nanocomposites for magnetic and supercapacitor applications


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A B S T R A C T

Reduced graphene oxide/Fe$_3$C hybrids were prepared through Fe-based intercalation of graphite oxide (GO). Altering pH (acidic to basic) of aqueous GO dispersion, the immobilization of Fe-based intercalant bearing amino benzoate groups (IFe) was strongly affected following either the nucleophilic substitution (sample: IGO) or ion exchange path (sample: IGO/b). Subsequent pyrolysis of the intercalated materials provided magnetic hybrid materials (samples: r-IGO and r-IGO/b), differing in terms of BET surface area (87 and 163 m$^2$/g), magnetization (70 and 43 J/T/kg), resistance (3 and 3.7 Ohm) and capacitance (5 and 17 F/g) correspondingly, displaying both magnetic and supercapacitor behavior. IFe triggered after thermal treatment in vacuum the formation of Fe$_3$C nanoparticles encapsulated in a graphene shell whose incorporation into the multi-layer reduced graphene oxide (GO) matrix provided multi-functional materials. In these materials, aggregation is prevented in two directions: (a) between adjacent Fe$_3$C nanoparticles, since the graphitic shell offers isolation, and (b) between bundles of neighboring multi-layer graphenes, due to Fe$_3$C nanoparticle interference. The graphitic shell assists cohesion of encapsulated Fe$_3$C nanoparticles with the graphene matrix as well as chemical stability, affording thus materials appropriate for a variety of applications.

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1. Introduction

Nanoparticles possessing magnetic properties embedded in a non-magnetic graphene matrix combine both the benefits of the unique properties of graphenes (e.g. high surface area, electrical conductivity [1], high flexibility [2], mechanical strength, light weight etc.) and magnetization. When these magnetic particles are encapsulated in a graphitic shell, the limits of application are extended since the carbon layers isolate the particles magnetically from each other, provide protection against oxidation and environmental degradation as well as stability in many organic and inorganic media [3,4]. These hybrid materials can open up new prospects in bio-engineering and biomedical applications, such as controlled drug delivery [5,6], magnetic recording media [7], magnetic toners, magnetic resonance imaging, ferrofluids [8], as well as in electrochemical energy storage and supply [9].

The energy applications including supercapacitor and lithium ion batteries require materials exhibiting reversible capacity, high cycle stability, electrical conductivity and active surface area [10].

Considerable efforts have been made towards this goal. Mainly, they include carbonaceous materials such as carbon nanotubes, graphenes and ordered mesoporous carbon [11] in composites with metal oxides (e.g. iron oxides [12,13]) in order to fully utilize the synergistic effects between these two components [14]. Drawbacks like low cycle stability is caused largely by the aggregation of metal or metal oxide particles and leads to the reduction of active surface area and subsequently lowers the efficiency of the active material. To overcome these problems carbon coating of metal oxide nanoparticles has been employed in several cases in order to enhance the electrical conductivity and electrochemical performance [10,15]. Especially, carbon encapsulated nanoparticles have been developed actively by various methods, including arc discharge techniques, chemical vapor depositions and pyrolysis of metal complexes [16].

In the present work the latter method of pyrolysis applied in an iron species-intercalated graphite oxide matrix resulted in a composite magnetic graphene-based material. By exploiting the chemistry of graphite oxide we have introduced functionality between graphene oxide layers. The modification of graphite oxide surfaces based either on grafting reactions or ion exchange has attracted considerable interest [17–20]. Trinuclear iron acetates have been
used in the past for pillaring of graphite oxide, utilizing its ion exchange capacitance [21]. In our case instead of an acetate, an amino benzoate compound such as p-aminobenzoic acid was employed in a modified synthesis of Shova et al. [22] for the preparation of a trinuclear like iron compound that would allow, under appropriate conditions, the intercalation via grafting or ion exchange path. This parent material produces after thermal treatment in vacuum an exfoliated multi-layer graphene material bearing carbon coated magnetic nanoparticles. The major advantages of this route are in terms of: (a) blocking the aggregation between adjacent bundles of multi-layer graphenes, (b) isolation and environmental protection of encapsulated iron carbide nanoparticles and (c) improved cohesion between these two components which is of great importance if it is taken into consideration that a main drawback in the area of magnetic graphene hybrids is the weak interaction between magnetic nanoparticles and graphene.

Nyquist plots of the capacitor cells with graphene composite materials as well as cyclic voltammetry curves were investigated. In-series resistance and capacitance of the materials were determined, opening thus perspectives for their application as electrodes in supercapacitors. Mössbauer spectroscopy was performed in order to identify the iron species and their content in the sample and magnetization measurements revealed properties that can establish these hybrid materials as candidates appropriate for magnetic applications.

2. Experimental

2.1. Synthesis of graphite oxide (GtO)

GtO was synthesized according to a modified Staudenmeier method [23] where Graphite flakes (Natural, ~10 mesh 99.9%, metal basis) were used as pristine graphite. This procedure was applied twice.

2.2. Preparation of iron intercalant (IFe)

5 mmol p-aminobenzoic acid (99%, Alfa Aesar) were dispersed in 50 ml distilled water and 2.5 mmol K$_2$CO$_3$ (Riedel-deHaën) were added. The solution became transparent and then 2.5 mmol FeCl$_3$·6H$_2$O (Panreac) were added. The whole was left under stirring for 1 h.

2.3. Preparation of intercalated GtO samples (r-IGO, r-IGO/b)

50 mg GtO were dispersed in 50 ml distilled water under sonication for 1 h (pH ~ 2.8). Then IFe solution was added and the whole was left under stirring for 48 h at room temperature. Washing, stirring and centrifugation followed several times (8–9) and finally drying in air (sample: r-IGO).

For the preparation of IGO/b sample 50 mg GtO were initially dispersed in 15 ml distilled water (sonication for 1 h) and 60 mg K$_2$CO$_3$ were added under stirring (pH ~ 9.8). Then it was mixed with IFe solution and an extra amount of 100 mg K$_2$CO$_3$ was added. The whole was left under stirring for 24 h at room temperature. Subsequently it was washed, stirred and centrifuged 3–4 times and finally dried in air (sample: IGO/b).

2.4. Synthesis of reduced graphene oxide/Fe$_3$C hybrids (samples: r-IGO, r-IGO/b)

Thermal annealing of samples IGO, IGO/b under vacuum (9.3 × 10$^{-3}$ mbar) at 800 °C for 2 h (Samples: r-IGO, r-IGO/b correspondingly).

2.5. Characterization

Siemens D500 X-ray diffractometer was used for the XRD measurements. The nitrogen adsorption isotherms at ~196 °C were obtained with the Quantachrome Autosorb-1 MP volumetric apparatus. SEM characterization was performed using a JEOL JSM-7401F field-emission gun scanning electron microscope. TEM analysis was carried out in FEI CM20 transmission electron microscope operating at 200 kV. Raman spectra were obtained using an inVia Reflex (Renishaw) micro-Raman spectrometer using a laser excitation of 514.5 nm. The IR transmittance spectra of the samples (KBr pellets) were measured on EQUINOX 55/5, Bruker instrument. The prepared materials mixed with 10 wt% carbon black and 5 wt% PVDF, used as binder, were deposited as an electrode layer on aluminium foil of 2 cm$^2$ square area used as current collector. Such electrodes were then used to fabricate an electrochemical double layer capacitor (EDLC) cell with 1 M TEABF$_4$/PC electrolyte. The electrochemical properties of the materials were then investigated using impedance spectroscopy in the range 10 mHz–1 MHz and cyclic voltammetry (CV) in a voltage range 0–3 V. Mössbauer spectroscopy was carried out using a constant acceleration spectrometer with a Co$^{57}$ (Rh) source calibrated using a metallic α-iron foil at RT. All isomer shifts are quoted with respect to α-iron at RT. Powdered samples were measured in an Oxford Instruments cryostat at temperatures in the range 78–300 K. Magnetization measurements were carried out in a Quantum Design SQUID magnetometer.

3. Results and discussion

The characteristic groups of IFe, its incorporation in GtO matrix (samples: IGO, IGO/b) and the effect of thermal annealing on the composite material (samples: r-IGO, r-IGO/b) were investigated through FTIR spectroscopy (Fig. 1). The FTIR spectrum of pristine GtO demonstrates the presence of C=O at 1732 cm$^{-1}$ (carboxyl stretching vibration), C=C at 1629 cm$^{-1}$ (in aromatic ring assigned to skeletal vibrations of unoxidized graphite domains), C–OH at 1387 cm$^{-1}$ (stretching) and C–O–C at 1070 cm$^{-1}$ (in epoxide). The peaks at 2928 and 2855 cm$^{-1}$ result from the –CH$_2$ stretching (alkyl groups present in GtO). The wide peak appearing at 3000–3500 cm$^{-1}$ is related to the presence of hydroxyl groups. By taking into consideration that IFe was prepared by a modified method of Shova et al. [22] describing the synthesis of trinuclear iron acetates and the fact that in the present work instead of sodium acetate, potassium p-aminobenzoate salt was employed, there are indications of a trinuclear like structure. The FTIR spectra of carboxylate complexes are usually dominated by two strong bands between 1350 and 1650 cm$^{-1}$ arising from the carbon–oxygen stretching vibrations. The frequency difference (Δν) between the symmetric (ν$_{sym}$(CO$_2$)$_1$, typically between 1400 and 1450 cm$^{-1}$) and asymmetric ν$_{asym}$(CO$_2$), typically between 1550 and 1650 cm$^{-1}$) ν$_{asym}$(CO) vibrations are correlated with the coordination mode of a carboxylate ligand [24]. The observed vibrational frequencies ν$_{asym}$(CO$_2$) (1603 and 1558 cm$^{-1}$) and ν$_{sym}$(CO$_2$)ν$_{sym}$(CO$_2$) (≈1414) for the carboxylate ligands support the presence of bridging coordinated carboxylates in IFe [25]. The band at 624 cm$^{-1}$ can be assigned to the O–C=O out-of-plane deformation mode (π (COO)) [24]. In IFe spectrum the peak at 1019 cm$^{-1}$ indicates the presence of C=N bond (due to amino group) while that of N−H (~1580 cm$^{-1}$) cannot be seen probably because is overlapped by ν$_{sym}$(CO$_2$) which is very intense, indicative of successful incorporation of p-aminocacid in IFe compound [26]. The peak at ~2880 cm$^{-1}$ in IFe was assigned to CH groups of p-aminobenzoic acid, while the peaks between 3200–3500 cm$^{-1}$ are attributed to amino groups and moisture. In
case of IGO, the IFe that bears p-aminobenzoic acid was adsorbed on the surface of graphene oxide sheets, through a strong electrostatic effect between amino group and oxygen functionalities (—OH, C—O—C on the plane and —COOH) of GO. Even after repeated washing of IGO with distilled water, sonication and centrifugation (more than 8 procedures) IFe still remained incorporated in the GO matrix. On the contrary in case of sample IGO/b, prepared in basic aqueous GtO dispersion, pH = 9.8, extensive washing procedures (8–9) resulted in the removal of IFe, and that was the reason that in IGO/b sample, only 3–4 washing steps were applied. Furthermore the epoxy C—O—C (1070 cm⁻¹) peak of GtO in the composite material (IGO) is not visible due to weakened C—O—C and the subsequent formation of C—NH—C— resulting from the reaction of epoxy group and the amino group [20]. By comparison, it is evident that the spectra of IGO, IGO/b samples present the stretching deformation of the benzenoid rings at 1492 cm⁻¹, suggesting that IFe can be successfully deposited on the GO surface [27]. In the thermally annealed sample r-IGO all the functional group peaks diminish, almost disappear, indicating reduction of the IGO. The same holds for r-IGO/b sample (omitted due to similarity with r-IGO).

The XRD patterns of graphite, GtO, intercalated GtO, (samples: IGO and IGO/b) are presented in Fig. 2. The patterns of IGO and r-IGO are similar with IGO/b and r-IGO/b correspondingly. The sharp (0 0 2) peak at 26.52° is representative of graphite and corresponds to 0.335 nm interspacing between the graphene layers. The GtO feature peak at 12.02° has a corresponding d-spacing 0.735 nm much larger than that of pristine graphite (0.335 nm) ascribed to the introduction of oxygen-containing functional groups on the GO surfaces. In the case of IGO and IGO/b samples, X-ray powder-diffraction analysis revealed an increase in the distance within the intersheet gallery from 0.735 nm in GtO to 1.213 nm and 1.231 nm in the products (IGO, IGO/b), which is an indicator of the installation of additional functionality on the surface of the basal plane of GO [28]. The enlarged intra-gallery space of GtO corresponds to an interlayer separation of 1.213 nm much larger than that of pristine graphite (0.335 nm) ascribed to the introduction of oxygen-containing functional groups on the GO surfaces. In the case of IGO and IGO/b samples, X-ray powder-diffraction analysis revealed an increase in the distance within the intersheet gallery from 0.735 nm in GtO to 1.213 nm and 1.231 nm in the products (IGO, IGO/b), which is an indicator of the installation of additional functionality on the surface of the basal plane of GO [28]. The enlarged intra-gallery space of GtO corresponds to an interlayer separation of 1.213 nm much larger than that of pristine graphite (0.335 nm) ascribed to the introduction of oxygen-containing functional groups on the GO surfaces. In the case of IGO and IGO/b samples, X-ray powder-diffraction analysis revealed an increase in the distance within the intersheet gallery from 0.735 nm in GtO to 1.213 nm and 1.231 nm in the products (IGO, IGO/b), which is an indicator of the installation of additional functionality on the surface of the basal plane of GO [28]. The enlarged intra-gallery space of GtO corresponds to an interlayer separation of 1.213 nm much larger than that of pristine graphite (0.335 nm) ascribed to the introduction of oxygen-containing functional groups on the GO surfaces. In the case of IGO and IGO/b samples, X-ray powder-diffraction analysis revealed an increase in the distance within the intersheet gallery from 0.735 nm in GtO to 1.213 nm and 1.231 nm in the products (IGO, IGO/b), which is an indicator of the installation of additional functionality on the surface of the basal plane of GO [28].

Even though the estimated available space of ~0.6 nm is lower than even the smallest calculated dimension of a trinuclear-like Fe complex conformation ~1.1 nm (Fig. 3), and its accommodation in the above interlayer distance would be inconsistent, there are cases recorded in the literature referring that complexes adopt a squeezed conformation in the confined nanospace different from the ideal structure adopted in a solution [29]. Urged by this argument and the XRD analysis results, the intrusion of IFe in the

<table>
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<th>Sample</th>
<th>2θ</th>
<th>d₀₀₂ (nm)</th>
<th>Lc (nm)</th>
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<tr>
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interlayer space of GtO, cannot be excluded [20]. Definitely further investigation is needed both on the crystal structure of the IFe and on the changes that undergoes during its incorporation in the GtO matrix, but this lies beyond the scope of the present work. After thermal annealing in vacuum for 2 h at 800 °C a low intense broad peak at 2θ = 26.44° and 26.23° for r-IGO and r-IGO/b samples appears corresponding to the (0 0 2) reflection of graphene. The fact that this peak is very broad suggests that the sample is very poorly ordered along the stacking direction. The spacing of graphene layers in r-IGO and r-IGO/b samples is slightly greater than in the ideal graphite lattice denoting a turbostatic structure. The mean number of graphene sheets stacked along the c-axis is 17 and 18 for r-IGO and r-IGO/b samples (Table 1) and that is an indication that the delaminated structure of IGO, IGO/b was preserved after thermal treatment, and in any case multi-layer graphenes were formed. In parallel, thermal annealing induces reduction of the majority of functional groups such as carbonyl, epoxy and hydroxyl which affect the d-spacing values. Furthermore, the IFe acted as a precursor of Fe3C particles (cementite) attributing magnetic properties to r-IGO, r-IGO/b materials without destroying the graphene structure [30]. The above interpretation is consistent with FTIR analysis, where annealing led to the removal in significant extent of all functionalities. In order to explain the formation of the trinuclear-like Fe complex, taking into consideration the studies of Shova et al. [22] and Ciavatta et al. [31] the following equilibrium was assumed:

$$3\text{Fe}^{3+} + 4\text{H}_2\text{O} + 6\text{H}_2\text{NC}_6\text{H}_4\text{COO}^- \rightarrow [\text{Fe}_3\text{O}(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_6\cdot 3\text{H}_2\text{O}]^{2+} + 2\text{H}^+$$

The pH value of the IFe aqueous solution was ~3. On heating the intercalated samples IGO, IGO/b in vacuum the complex decomposes producing a residue that consists of iron, carbon (which acts as an additional to GO carbon source), hydrogen, nitrogen and chlorine (counter ion of trinuclear Fe complex). Between 500° and 600 °C occurs the formation of cementite (Fe3C) [32] according to:

$$3\text{Fe} + \text{C} \rightarrow \text{Fe}_3\text{C}$$  \hspace{1cm} (1)

Thermal annealing in vacuum at 800 °C for 2 h and cooling down to room temperature (also in vacuum), insures the formation and preservation of Fe3C nanoparticles.

In Fig. 4 Raman spectra of GtO, IGO and r-IGO samples are illustrated. The G and D bands are associated with the ordered sp2 carbon and disordered effects and edge carbons, respectively. The D peak is disorder-induced and arises only in the presence of defects, such as sp3 carbon. After the intercalation of GtO and subsequently annealing, the G band shifts to lower frequency region (1601 → 1598 → 1592 cm\(^{-1}\)), confirming gradual reduction [33]. Peak 2D (sometimes named as G’) and the disorder-induced combination mode (D + G) peaks can also be observed at ~2719 and ~2937 cm\(^{-1}\) correspondingly. The D band is attributed to edges
and functional groups existing in IGO which remained in r-IGO as well as to amorphous carbon which may also contribute to the peak. Moreover, the intensity of the D band compared to the G band has reduced slightly from \( I_D/I_G = 0.9 \) (igo) to 0.8 (r-IGO), indicating that the resultant material has fewer defects. In the annealed sample 2D peak is observed at \( \sim 2703 \text{ cm}^{-1} \). The intensity of the disorder-induced combination mode band \((G + D)\) is reduced. The 2D band in Raman spectra is widely used in the literature for estimating the number of layers in the graphene samples [34]. Nevertheless, the relation between the number of layers and the 2D band line-shape is only relevant for graphene samples where AB Bernal stacking occurs and not in the case of turbostatic graphite where the stacking of graphene layers is rotationally-random along the \( C \) axis, and electronic coupling between graphene layers may not occur [35]. Raman spectra of IGO/b, r-IGO/b samples due to similarity with those of IGO, r-IGO samples were omitted.

TGA data were recorded in air atmosphere at a heating rate of 5 °C / min (Fig. 5). The weight loss (1.12 wt% and 0.92 wt% for r-IGO and r-IGO/b samples correspondingly) is due to the thermal desorption of water (till 100 °C) and release of adsorbed gases till \( \sim 230 \) °C [36]. Close to \( \sim 270 \) °C elimination of the remaining functional groups occurs (since in the annealed r-IGO and r-IGO/b samples, the majority of these groups were removed). Further decomposition of the multi-layer reduced graphene oxide material takes place between 400 °C and 700 °C. Fe₃C is stable at temperatures below 200 °C. Above that temperature it decomposes to Fe which undergoes oxidation and instead of weight loss, an increase in the weight is noticed with maxima at 360 °C (r-IGO) and \( \sim 385 \) °C (r-IGO/b) due to formation of iron oxide. The final residue left after burning is attributed to Fe₂O₃ formation and allows the estimation of iron percentage, which is 38.6 wt% for r-IGO and 35.95 wt% for r-IGO/b [21,36].

Fig. 7. TEM images (left) and the corresponding HRTEM images (right) for the samples: IGO (a, b), r-IGO (c, d), r-IGO/b (e, f). HRTEM images (d, f) illustrate Fe₃C particles being wrapped by a graphitic shell.
Fig. 6 shows typical scanning electron microscopy (SEM) images of r-IGO (6a, 6b) and r-IGO/b (6c) samples. Fe$_3$C particles deposited on the external surface of the graphene material r-IGO can be seen in Fig. 6a. A closer look (Fig. 6b) indicates a porous surface of the carbon material, as well as a porous carbon shell covering the Fe$_3$C particles, which is attributed to the removal of oxygen functional groups during thermal annealing at 800 °C. These particles are quite large with dimensions up to a hundred nm or more. Interestingly, in sample r-IGO/b (Fig. 6c), the Fe$_3$C particles are scarcely observed. By taking into consideration that the iron content for both samples is very close it can be concluded that in the case of r-IGO/b sample, particles are almost buried and separate multilayer graphenes, justifying thus the higher BET surface area (Fig. 6d) of r-IGO/b which is 163 m$^2$/g in comparison to 87 m$^2$/g corresponding to r-IGO sample. This remark denotes a better dispersion of Fe in the initial GtO matrix in case of IGO/b than in IGO.

Fig. 7a is a transmission electron microscopy (TEM) image of IGO sample, illustrating the intercalated layers of GtO and Fig. 7b that is a High Resolution TEM (HRTEM) image demonstrates its multi-layer structure. The same material when undergoes thermal treatment in vacuum (sample: r-IGO) at elevated temperature shows a more exfoliated structure than the parent material (Fig. 7c) and also contains Fe$_3$C nanoparticles dispersed throughout the reduced GO layers. A similar picture holds also for r-IGO/b sample (Fig. 7e). In both samples the Fe$_3$C nanoparticles are wrapped in multilayered graphitic sheets (Fig. 7d and f). Such shells made of carbon are airtight and protect the entrapped materials from oxidation [7] offering high chemical and thermal stability [16]. Moreover the encapsulated Fe$_3$C nanoparticles are isolated and therefore their aggregation is hampered.

In the case of IGO the insertion of the Fe bearing p-aminobenzoate, in GtO matrix can occur by the following possible ways: (i) hydrogen-bonding interactions between the amine molecules and the oxygen-containing functional groups of GtO (C—OH ··· H$_3$N—R), (ii) protonation of the amine by the carboxylic groups of the GtO layers (—COO— + H$_3$N—R), and (iii) chemical grafting of the amine
to the GO surfaces via nucleophilic substitution reactions on the epoxy groups of GO [17]. Alternatively, in the case of IGO/b where the GtO suspension is treated with K$_2$CO$_3$ before the addition of the IFe, GtO exhibits ion-exchange ability similarly to clay minerals and the intercalation process proceeds through ion-exchange interaction between the interlayer cations and the positively charged iron species of IFe [21], which act as counter cations with regard to the de-protonated oxygen groups of GtO. An important difference between IGO and IGO/b samples supporting the aforementioned consideration was that in the case of IGO/b after repeated washing procedures (>8) a gradual IFe drain from the solid came about; on the contrary the IGO sample remained unchanged under the same conditions. These remarks denote a stronger binding of IFe in the case of IGO supporting a nucleophilic substitution reaction in comparison with the IGO/b sample where the adhesion was weaker indicating ion exchange (Fig. 8). Afterwards it can be concluded that the intercalation in IGO/b proved to be more efficient than in IGO since it resulted after thermal annealing in I-FeO/b material with an almost double BET specific surface area than that of r-IGO. Similar binding mechanism for the preparation of GO nanocomposites based on negative-positive electrostatic attraction is recorded in recent literature by Zhang and Choi [37].

The performance of the fabricated EDLC cells based on the prepared materials was analyzed using electrical impedance spectroscopy and cyclic voltammetry. The measured Nyquist plots and specific capacitance curves of the cells are given in Fig. 9a and b, correspondingly. The Nyquist plots show the frequency response of the EDLC cells and are a plot of the imaginary component (Zim) of the impedance against its real component (Zre). Each data point is taken at a different frequency. The lower left part of each curve corresponds to the higher frequencies. The capacitance of the cell is determined as $C = \frac{(2\pi f Z_{in})}{m}$, where $f$ is the frequency at each datapoint. The more vertical the curve on the right hand side, the more closely the cell corresponds to an ideal supercapacitor. According to Fig. 9a, the cells based on r-IGO and r-IGO/b materials approach better the ideal supercapacitor behavior. It is interesting to observe supercapacitor behavior of these cells up to high frequencies, 1000 Hz, whereas similar supercapacitors based on activated carbon materials operate in supercapacitor mode only up to frequencies of 1–8 Hz [38]. The intersection of the linear part of Nyquist plot with the x-axis represents an internal cell resistance including the equivalent series resistance (ESR) and the charge transfer resistance of the cell. The inset of Fig. 9a, which is an enlargement of the higher frequency part of Nyquist plots, permits a direct determination of the cells’ ESR. The calculated internal resistance values for the r-IGO, r-IGO/b and IGO/b containing cells are equal to 3.0 3.7 and 6.5 Ohm, correspondingly, demonstrating the increase in conductivity of the IGO reduced samples (r-IGO and r-IGO/b) due to the reduction of oxygen containing groups causing imperfections in the graphene lattice. However, it is interesting that the r-IGO/b based cell has a little higher internal resistance than the r-IGO based cell, which may be attributed to the higher porosity of IGO/b which has double the BET of r-IGO (163 and 87 m$^2$/g, respectively). The specific capacitance of the cells was calculated performing integration over the measured CV loops (Fig. 9b). The obtained values of the specific capacitance are 5, 17 and 6 F/g for the cells r-IGO, r-IGO/b and IGO/b, respectively. It can be seen that the sample r-IGO/b has a resistance value (3.7 Ohm) by ~43% lower than that of sample IGO/b (6.5 Ohm). This denotes higher conductivity attributed to the re-establishment of sp$^2$ hybridization and diminishing of defects related to functional groups of Go during thermal annealing. Since conductivity is one of the major factors that influence decisively the capacitance values, the almost three times higher capacitance of r-IGO/b sample (17 F/g) compared to r-IGO (6 F/g) can be ascribed to its enhanced conductivity. Then, sample r-IGO/b has a slightly higher resistance (3.7 Ohm) from r-IGO sample (3.0 Ohm) while its BET surface area (163 m$^2$/g) is almost double that of r-IGO sample (87 m$^2$/g). Therefore, the enhanced BET surface area gives rise to increased capacitance value of sample r-IGO/b (17 F/g) compared to r-IGO (5 F/g). To this end, Fe$_3$C nanoparticles prevent reduced GO sheets from re-stacking after thermal annealing. That was one of the aims of introduction of IFe complex in Go matrix. This way higher BET surface area can be achieved as well as improvement of the capacitance values.

Mössbauer spectra of the r-IGO/b (Fig. 10a) and r-IGO (Fig. 10c) samples at 300 K showed the iron containing phases of the sample to be composed of greater than 85% and 80% Fe$_3$C respectively. In the r-IGO/b sample this phase is fitted with two components with isomer shifts of 0.19 mm/s, hyperfine fields of 20.9T and 19.8T, and negligible quadrupole interactions. In the r-IGO sample the spectrum is fit with a single broadened line with a hyperfine field of 20.5T and an isomer shift of 0.19. These values are in agreement

Fig. 10. Mössbauer characterization of the r-IGO/b and r-IGO samples. Spectra of sample r-IGO/b at (a) 300 K, (b) 78 K and sample r-IGO at 300 K and (c) showing evidence of a majority of Fe$_3$C phase and the presence of α-Fe inclusions. These spectra show a constant content of magnetic Fe$_3$C (ca. 86–88%) in case of r-IGO/b and (ca. 81%) in case of r-IGO sample.
with published data for the Fe$_3$C phase. Metallic $\alpha$-Fe was also found: 3% of the total iron in the r-IGO/b sample and 8% in the r-IGO sample. Small amounts of a nonmagnetic phase were also observed. In addition, a second nonmagnetic phase with an isomer shift of 0.27 mm/s is observed in both samples. This may be a superparamagnetic Fe$_5$C$_2$-type phase. The spectrum of the r-IGO/b sample at 78 K (Fig. 10b) shows this phase has been reduced to 4%, a reduction expected for superparamagnetic behavior. The samples display saturation magnetization values at 300 K of 43 J/T/kg (r-IGO/b) and 70 J/T/kg (r-IGO) in keeping with the larger amount of $\alpha$-Fe found in the latter sample, Fig. 11a and b, as would be expected from the existence of the magnetic $\alpha$-Fe and Fe$_3$C phases.

4. Conclusions

Pillaring of GtO with iron trinuclear-like complex IFe can be achieved by two modes, in presence of an excess K$_2$CO$_3$ or not, indicating two different mechanisms: (a) cation exchange and (b) nucleophilic substitution, correspondingly. In both cases after thermal annealing in vacuum iron carbide doped few layer graphenes are produced. These iron carbide particles are encapsulated in a graphene cage that protects them from agglomeration or being detached under certain processes, assuring their stability in environmental conditions. In the case of GtO dispersion pretreated with base the initial dispersion of the iron complex seems to be better as it gives rise after thermal annealing to the formation of higher BET surface area exfoliated graphene-based material and has better performance in terms of capacitance, showing perspective for possible supercapacitor application up to high frequencies (1000 Hz). Both materials exhibit magnetic properties opening thus a new avenue for possible magnetic applications.

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