Magnetic Properties of Thermally Reduced Graphene Oxide Decorated with PtNi Nanoparticles.

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Abstract

Nanocomposites of reduced graphene oxide (RGO) with PtNi nanoparticles were obtained by in situ thermal reduction of a physical mixture of GO and metallic precursors. RGO and PtNiRGO nanocomposites were studied by differential thermal analysis and thermogravimetry, Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (XRD), as well as scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The method presented here is a one-step thermal reduction procedure that allows the deposition of bimetallic PtNi nanoparticles with tetragonal crystalline structure and particle size ranging from 3 nm to 30 nm on RGO. The magnetic properties of the RGO and PtNiRGO nanocomposites were measured by vibrating sample magnetometry, which revealed that the RGO exhibited diamagnetism at room temperature and paramagnetism at temperatures below 10 K. PtNiRGO nanocomposites show hysteresis and ferromagnetic ordering at room temperature with a Curie temperature of 658 K. In addition, its magnetic properties at low temperature were strongly influenced by the paramagnetic contribution of RGO and the morphology of the bimetallic nanoparticles.

1. Introduction

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In recent years, reduced graphene oxide (RGO) and its nanocomposites have attracted a lot of attention due to their interesting properties such as high surface area, electric conductivity, electrocatalytic activity, and low cost. These features make RGO suitable for many applications, such as functional electrodes, catalytic support, and high-performance adsorbent [1,2]. Several low-cost methods have been developed to produce RGO in large scale by using graphite oxide (GO) prepared by chemical oxidation of graphite as precursor [3]. The resulting RGO obtained by reduction of GO is a two dimensional material similar to graphene obtained by chemical vapor deposition [4], molecular beam epitaxy [5], graphite intercalation catalytic reactions [6] and chemical exfoliation of graphite [3,6]. Nevertheless, their electrical properties and microstructure are strongly influenced by the residual oxygen groups or doping heteroatoms such as nitrogen, that are characteristic of RGO [7]. The thermal reduction technique consists in heating the GO above its exothermal deoxygenation temperature which is usually around 180 to 200 °C [8]. The thermal reduction is very attractive because it yields RGO with high electrical conductivity and does not need any chemical reducing agent or organic solvents, thus is simple and environmentally friendly [9]. Recently, RGO decorated with metallic nanoparticles have been used in new catalytic, catalytic, magnetic and optoelectronic materials. GO can act as a high surface functional matrix that promotes the support-nanoparticle interactions, leading to reduced agglomeration of the nanoparticles. [10,11]. The methods for the attachment of metal nanoparticles to RGO sheets can be classified as *in situ* or *ex-situ* techniques [12,13]. Among RGO nanocomposites with metallic nanoparticles, RGO decorated with platinum has been particularly studied due to their potential electrocatalytic applications whereas some platinum alloy nanoparticles can also display interesting magnetic properties. Zhang *et al.* [14] prepared graphene supported Pt nanoparticles by the simultaneous chemical reduction of GO and chloroplatinic acid using ascorbic acid resulting in a hybrid material with strong electrocatalytic activity for methanol oxidation. Many of the recent works of graphene decorated with metallic and bimetallic nanoparticles have shown outstanding performances, however, their separation involves considerable energy and time consumption. Magnetic separation has emerged as an important solution to recover and reuse hybrid catalysts [15]. Graphene decorated with magnetic nanoparticles has been successfully used as reusable catalyst support for the reduction of 4-nitrophenol [16] and for dye reduction [17]. Besides graphene hybrid materials with magnetic properties have also potential applications in flexible electromagnetic and storage devices, magnetically guided drug delivery systems and magnetic separation [18-20]. Guo *et al.* [21] decorated RGO with bimetallic Pt-transition metal nanoparticles (PtNi, PtCo, FePt) by chemical reduction, providing good magnetic properties besides the catalytic activity increasing the functionalities of graphene nanocomposites. This kind of graphene based hybrid material has also potential application as magnetic electrode for sensing and electrochemical detection [22,23]. On the other hand, theoretical studies have shown the strong effect of the substrate on the performance in oxygen reduction reaction (ORR) of PtNi nanoparticles on Nitrogen doped graphene [24]. Several authors have focused in the preparation of highly loaded RGO sheets with Pt nanoparticles [25,26] many of the methods previously

reported are based on the sequential chemical reduction of graphene oxide followed by that of the metallic precursors. However, these methods sometimes are time-consuming and a large amount of chemical waste usually results from the purification process that typically requires several steps to clean the RGO surface. Gao *et al.*[27] prepared PtNi-RGO nanocomposites by a simple method that consists of simultaneous electrochemical reduction of metal precursors and GO, the resulting nanocomposite exhibited an enhanced electrochemical glucose detection capability. However, the synthesis of bimetallic nanoparticles on graphene by simple and scalable routes is still a challenge. In this work, we studied a one-step synthesis of PtNiRGO nanocomposites by the carbothermal reduction of PtNi nanoparticles during the thermal reduction of GO. The oxygen functional groups of GO most likely enhance the nucleation and growth of PtNi nanoparticles on RGO during the thermal treatment. The structural characterization of PtNiRGO nanocomposites was performed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and transmission electron microscopy (TEM). In addition, magnetic properties of RGO and PtNiRGO nanocomposites were evaluated by magnetization curves at different temperatures.

2. Materials and methods

Thermally reduced graphene oxide (RGO) was prepared by thermal reduction of graphene oxide (GO) obtained by the modified Hummers method[3, 6]. Briefly, 5.0 g of graphite powder were added to 250 ml of concentrated H_2SO_4 , the mixture temperature was kept below 10°C in an ice bath. Then, 30 g of KMnO_4 were slowly added to the mixture under stirring, while maintaining the temperature below 15°C . The mixture was carefully heated at 40°C for 2 h. The reaction mixture turned into a dark green slurry as a result of permanganic acid formation and graphite oxidation. Then, the mixture was cooled to 0°C by using an ice-bath and 1 L of deionized (DI) water was slowly added, keeping the temperature below 10°C . Finally, 25 ml of 30% H_2O_2 were added to the mixture in order to neutralize the residual KMnO_4 . During the peroxide addition, the mixture bubbled vigorously and changed its color to light yellow. The GO was decanted and purified by filtration, followed by washing with 5.0 wt% HCl aqueous solution to remove the reaction by-products and metals ions. The acid was removed by several centrifugation-redispersion cycles with DI water. The GO was exfoliated by sonication in DI water during 3 h (VWR 50D ultrasonic cleaner bath), and finally the exfoliated GO was dialyzed for two days. A GO paper was obtained by pouring a GO dispersion (3.6 mg/ml) in a petri-dish and dried at room temperature for five days. RGO was obtained by thermally reducing the GO paper by heating at 800°C for 2 h using a heating rate of $5^\circ\text{C}/\text{min}$ under N_2 atmosphere. The yield of RGO obtained from GO paper was 40 wt%. GO papers loaded with the PtNi nanoparticle precursor (PtNiRGO) were obtained by dissolving in the GO dispersion used to prepare the GO paper. Similarly, metallic precursors ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{H}_2\text{Cl}_6\text{Pt} \cdot 6\text{H}_2\text{O}$) were added to the aqueous GO dispersion and the mixture was stirred for 72 h. After drying, a GO paper homogeneously loaded with the metallic precursors

was obtained. SEM images show that even on the microscopic scale there is no evidence of phase separation (Supplementary materials Figure S1). The PtNiGO paper was thermally treated at 550°C for 4h under nitrogen atmosphere using a heating rate of 5°C/min. The amount of GO and metallic precursors were adjusted to target RGO:PtNi nanocomposites with a mass ratio of 1:1 considering the mass loss of GO during the thermal treatment. The stoichiometry of Pt:Ni precursors was selected to be 1:1 to promote the growth of nanoparticles with an atomic ratio of 1:1 (Pt:Ni). The schematic illustration for the one-step synthesis of PtNiRGO nanocomposites is shown in Figure 1a. After thermal reduction the samples were chlorine free, as tested by washing with water and testing the water with silver nitrate.

3. Characterization

X-ray diffraction (XRD) analysis for all samples was performed using a Rigaku Multiflex powder diffractometer with Cu K α radiation. The diffraction patterns were acquired in 2 θ mode, between 5° and 90°, with a scan rate of 0.5°/min. Infrared Spectroscopy (IR) measurements were carried out in a Thermo Scientific Nicolet 6700 FTIR spectrophotometer with a wavenumber range from 4000 cm⁻¹ to 400 cm⁻¹. The samples were mixed with KBr and pressed into pellets and analyzed in transmission mode. Raman spectroscopy analyses were carried out in a Thermo Scientific XDR Raman microscope using a 532 nm laser excitation. Differential thermal analysis and thermogravimetry (DTA/TGA) analysis were carried out using a SETARAM with CS32 controller, the temperature range was from 25°C to 800°C, a heating rate of 5°C/min under N₂ flow. Scanning electron microscopy (SEM) characterization was performed in a FEI NOVANO SEM 200. The samples were observed at 10 kV accelerating voltage and at 5 mm working distance. The sample was prepared by attaching a piece of GO paper and the RGO powders to silicon wafer using carbon tape. Elemental mapping analysis was carried out using a SEM Tescan, model Vega II SBH equipped with EDAX detector. Transmission electron microscopy (TEM) and scanning transmission electron microscopy analyses were performed in a FEI Titan G2 80-300 TEM with an accelerating voltage of 300 kV. A drop of either RGO or PtNiRGO aqueous dispersion was dried onto a lacey silicon monoxide film on copper grid. Magnetic measurements were carried out using a vibrating sample magnetometer (VSM) mounted onto a “Cryogenics” platform for magnetic measurements with a superconducting magnet of 14 T, a vibration frequency of 20 Hz, sensitivity of 10⁻⁶ emu with preamplifier and 5 s average and a temperature control of 2 K to 325 K. Moreover, a homemade VSM, with a temperature control from 300 K to 1000 K and a sensitivity of 10⁻⁵ emu with a magnetic field up to 1.8 T was also used.

Results and discussion

Figure 1a shows the scheme for the synthesis of PtNiRGO nanocomposite by the simultaneous thermal reduction of GO with metallic precursors (PtNiGO). DTA/TGA measurements for the GO, the RGO and the PtNiGO samples were carried out (figure 1b). Control GO and PtNiGO loose *ca.*10% of its mass between room temperature and 100 °C due to the release of intercalated and adsorbed water. In addition, a weight loss occur at 200°C indicating the evolution of CO₂, CO and water molecules eliminated during the thermal reduction of GO [28]. The DTA curve confirms the reduction reaction by the exothermic nature of this stage due to the removal of the oxygen functional groups, such as carboxyl, hydroxyl, carbonyl, ethers and epoxy groups [29]. In addition, another exothermic stage is observed at 500 °C, due to the reduction of metal precursor that leads in the formation of PtNi phase as was expected in accord with the Pt-Ni phase diagram [26,30]. On the other hand, the TGA curve of RGO sample shows a gradual weight loss instead of an abrupt weight loss, and exothermic peak is observed. The weight loss is usually attributed to the loss of residual solvent and the decomposition of residual oxygen based functional groups of RGO. This is consistent with the thermal behavior of RGO in N₂ atmosphere [19]. In addition, the PtNiRGO composites contain about 50 Wt% of PtNi nanoparticles, which was estimated by the inorganic residuals during the TGA of PtNiRGO and RGO in air flow (Supplementary materials Figure S2).

The chemical structure of GO and RGO was studied by FTIR, the spectra are shown in Figure 1c. The GO spectrum shows a band at 3409 cm⁻¹ due to the -OH stretching modes and the bands associated to the oxygen-containing functional groups of GO at 1727, 1635, 1401, and 1068 cm⁻¹ particularly assigned to the vibrational modes of C=O, aromatic C=C, carboxy C-O, epoxy C-O and C-O groups [25,31]. After annealing at 800°C most of the bands associated with oxygen groups diminished notably, this confirmed the decarboxylation reaction of carboxyl groups and loss of hydroxyl groups. After thermal reduction it can be seen a weak absorption band at 1727 cm⁻¹ due to the residual C=O groups. The other remaining oxygen groups could be ethers, ketones and 1,3-benzoquinones supported by the presence of C-O-H and C-O absorption bands (1401, and 1068 cm⁻¹) [29]. Therefore, the FTIR results confirmed the presence of oxygen functional groups on the RGO structure. The Raman spectroscopic study (Supplementary materials Figure S3) shows two vibration bands at 1350 cm⁻¹ and 1580 cm⁻¹ in samples, which are attributed to the D and G bands. These bands are attributed to the disordered and graphitic domains of carbonaceous materials, respectively [32]. The ratio of I(D)/I(G) for GO and PtNiGO samples show that they are highly disordered due to the presence of oxygen functional groups on basal plane and edges of graphene whereas, after thermal treatment, most of the functional groups were eliminated in RGO and PtNiRGO samples. These results are in agreement with the FTIR analysis, where oxygen functional groups remain in RGO leading a disordered structure.

Figure 1d shows the XRD patterns obtained for GO, RGO and the simultaneous reduced GO with metallic precursors (PtNiRGO) samples. The XRD pattern of the as-prepared GO paper (Figure 1b) shows a sharp peak

at 10.5° of 2θ related to the (001) reflection of GO, with a interlayer spacing of 8.46 Å indicating the large interlayer spacing due to the intercalated water and oxygen-containing functional groups on GO layers and unlike of graphite, it only shows one diffraction peak. Whereas, after thermal treatment, the XRD pattern of RGO sample shows a diffraction peak at 26.7° of 2θ attributed to the turbostratic ordering of RGO, exhibiting maximum intensity at the interlayer spacing of 3.4 Å very similar to that observed for the bulk graphite (3.35 Å), which agree with the results of slow thermal annealing of GO due to the carbon atoms in the basal plane may rearrange during annealing at low heating rate ($5^\circ\text{C}/\text{min}$) [9], unlike of violent reduction-combustion of GO [8]. The change can be associated to the loss of functional groups and interlayer water molecules. However, the diffraction peak at 26.7° is broad, unlike that of (002) plane in bulk graphite XRD pattern, suggesting a highly disordered structure. Besides, the number of layers of RGO (N_{Gp}) is around eight, which were calculated from the Scherrer equation using the relation $N_{\text{Gp}} = D_{002}/d_{002}$ [30,33], where the RGO thickness (D_{002}) is about of 25.4 Å and the interlayer spacing (d_{002}) is 3.4 Å. On the other hand, all peaks in the XRD pattern of PtNiRGO nanocomposites (Figure 1d) can be indexed to the tetragonal crystalline structure of PtNi (JCPDS: 03-065-2797). The diffraction peaks are broadened owing to the small sizes of the bimetallic PtNi nanoparticles. The average particle size obtained from the Scherrer equation was 2.5 nm. Moreover, the diffractogram of PtNiRGO shows a reflection at 26.2° which is related with the turbostratic order of RGO and the (001) reflection of PtNi nanoparticles.

The morphology of the GO, RGO and PtNiRGO nanocomposites was studied by SEM. Figure 2a shows the cross-section of GO paper, where it can be observed a dense layered structure. However, after thermal treatment of GO, an expanded structure resulted from the exothermic removal of oxygen-based functional groups and water molecules during thermal reduction (Figure 2b), which is accompanied of water vapor and CO_2 evolution. The morphological change suggests that the RGO was successfully obtained [31]. On the other hand, the figure 2c and 2d show the SEM images for the PtNiRGO nanocomposites, where RGO sheets with 5 μm of lateral size can be observed, also the presence of PtNi nanoparticles on the RGO sheets can be confirmed. Figure 2d shows the BSED image of the PtNiRGO nanocomposites, where the presence of bimetallic nanoparticles on RGO layers can be evidenced based on the differences in the image contrast due to the large difference in the atomic numbers between C and Pt and Ni. Nanoparticles are anchored homogeneously on the RGO sheets both at the surface and in the edges. It is well known the edges of GO contain a higher density of functional groups however, the very high amount of nanoparticle precursor (50 wt %) guarantees that all GO sample is in contact with the precursor. In addition, the sample is dried which minimizes the effect of ionization of the functional groups and enhance the distribution of the precursor by capillary filling effect within the slit-shaped GO galleries. [34]. Both, theoretical and experimental works have shown that after reduction of RGO, remaining oxygen functional groups such as carboxyl (R-COO) and hydroxyl (R-OH) accompanied with vacancies are excellent binding sites for anchor nanoparticles [35, 36].

After reduction PtNi nanoparticles remain attached to RGO via non covalent interaction most likely through a combination of van der Waals and electrostatic interactions[22,37].

Transmission electron microscopy studies were carried out to study the morphology and structure of the RGO and PtNiRGO nanocomposites. The TEM image of RGO (Figure 3a inset) shows the crumpled carbon sheets of graphene with lateral size larger than 0.5 μm . Furthermore, the HRTEM image of RGO obtained by the thermal reduction of GO paper shows a few-layer graphene (Figure 3a). The distance observed between fringes in the HRTEM image of RGO is about of 0.36 nm, which is in agreement with the results obtained from the fit of XRD data. Although the interlayer spacing is only about 10 % larger than that of bulk graphite, the RGO structure is highly disordered. These results indicate that the functional groups and water molecules eliminated by the thermal treatment of GO, promoted the compaction of RGO sheets and resulted in the decreased of interlayer distance. The TEM analysis of PtNiRGO nanocomposites is shown in figures 3b and 3c. PtNi nanoparticles with several shapes and a broad particle size distribution can be seen distributed irregularly on RGO sheets. The figure 3c inset shows the selected area electron diffraction (SAED) pattern that reveals a polycrystalline-like structure of the PtNiRGO nanocomposites due to the high amount of small particles. The (202), (002) and (111) planes of the tetragonal structure of PtNi were identified in the respective SAED. In addition, the diffraction rings related to RGO are unseen in the SAED of nanocomposite, most likely due to the disordered structure of RGO resulting from the previous oxidation reaction. Thus, the figure 3d shows the HRTEM image of PtNi nanoparticles with monocrystalline structure and an interplanar spacing of 0.218 nm, which match the (111) plane of tetragonal PtNi. The simultaneous synthesis method allows the diffusion of metal atoms through the slit galleries between the GO sheets resulting in the nucleation and growth of bimetallic alloy nanoparticles with a wide particle size distribution resulted from the annealing process, where the growth of bimetallic nanoparticles through sintering was promoted. The elemental mapping images of PtNiRGO nanocomposites were acquired for C K, O K, Pt M and Ni K. The results suggest that in spite of the wide particle size distribution and high nanoparticle loading there is no segregation or clustering of the metallic phase. Indeed, both Pt and Ni are homogeneously distributed on the RGO surface (Supporting material figure S4). In addition, nanoparticle composition in both, small and larger nanoparticles remain unchanged. No single metal nanoparticles or phases were observed in TEM images or XRD diffraction patterns. No phase separation was observed within single nanoparticles, indeed, the chemical microanalysis from two representative areas show the composition of bimetallic PtNi nanoparticles is shown in Figure 4a and 4b and no elemental segregation was observed. These results are in agreement with the XRD analysis from the samples and with the of Pt-Ni phase diagram where, in order to obtain Pt and Ni nanoparticles the annealing temperature should be higher than 700°C [30].

The magnetic properties of RGO were investigated by magnetic measurements of the samples. RGO sample exhibited diamagnetism at room temperature with mass susceptibility $\chi_m \approx -2.17 \times 10^{-5} \text{ m}^3/\text{kg}$. The diamagnetic behavior of RGO at room temperature is caused by the change of orbital angular momentum by applying the magnetic field. However, the magnetic hysteresis loops of the RGO at 2K, 10K and 30K, shows that the diamagnetism decreased when the temperature decreases from 30K to 2K, exhibiting a paramagnetic behavior at low temperature ($\approx 10 \text{ K}$) (figure 5a). The paramagnetic behavior is due to the interactions between the orbital angular momentum of the electrons around the nucleus and the spin of the electrons, which causes the free magnetic moments to weakly align with the magnetic field. Such a temperature dependent magnetic behavior of RGO was previously observed in graphene sheets obtained by direct exfoliation of graphite [33,38] and also in annealed GO samples [39]. Then, it is possible that the magnetic behavior is independent of the surface modification of graphene with oxygen-based groups. Figure 5b shows the fit of the magnetization data to the Brillouin function Eq.1.

$$M = NgJ\mu_B \left[\frac{2J+1}{2J} \text{ctnh} \left(\frac{(2J+1)x}{2J} \right) - \frac{1}{2J} \text{ctnh} \left(\frac{x}{2J} \right) \right] \quad (1)$$

where $x = gJ\mu_B H / k_B T$, μ_B is the Bohr magneton, k_B is the Boltzman constant, J is the angular momentum number, N is the number of present spins and the factor g . Assuming $g=2$, the $J=5/2$ value provides the best fit and the number of present spins is $N=5.2 \times 10^{18} \text{ g}^{-1}$. The number of free spins could be strongly influenced by some structural features such as vacancies and edges of RGO induced by the synthesis method. This agrees with theoretical studies suggesting that characteristics related with atomic scale, as the arrangement of the atoms in the edges of graphene sheets, can induce a magnetic moment [13,40]. Using these values of J and N ; $M(T)$ was calculated by the Curie Law $M / H = (NJ(J+1)g^2\mu_B^2)/(3k_B T)$, obtaining a very good fit as is shown in figure 5b inset. The results indicate that the observed paramagnetism results mainly from the RGO material rather than from reaction by-product of the synthesis. This was also confirmed by the free electron value of $J=2.5$ obtained, whereas no good fit was possible for $J=1/2$, the expected value for vacancies and adatoms [38]. In addition, a magnetic moment ($\mu = gJ\mu_B$) of $5\mu_B$ per 10,000 carbon atoms was calculated by assuming that the paramagnetism is due to a single species of noninteracting spins with a concentration of approximately 100 ppm. However, RGO materials may possess minimum amounts of magnetic impurities of traces of Mn^{2+} ions [15,41] due to the oxidizer (KMnO_4), which could also contribute to the paramagnetic behavior observed at low temperature ($< 30 \text{ K}$).

Magnetic measurements of PtNiRGO nanocomposites were carried out in order to understand the magnetic behavior of RGO layers decorated with nanoparticles of PtNi (figure 6). The magnetic results at room temperature (figure 6a) indicated a saturation magnetization (M_s) of $0.8 \text{ Am}^2/\text{kg}$, a remanence (M_r) of $0.19 \text{ Am}^2/\text{kg}$ and a coercive field ($\mu_0 H$) of 0.11 T . These features are attributed mainly to the contribution of the PtNi nanoparticles, as the RGO is diamagnetic at room temperature (Figure 6b). The very low saturation moment indicates weak itinerant ferromagnetism, which has been observed before in PtNi systems [19,20]. Based on the band theory, this behavior is due to the extremely small exchange splitting of the band [15]. Figure 6b shows the evolution of the magnetization with the temperature under an applied magnetic field of 50 mT up to 750 K . The curve suggests a ferromagnetic ordering of the PtNi nanoparticles with a Curie temperature of 658 K . In addition, Zero-Field Cooling and Field Cooling measurements were also carried out at a lower field of 5 mT (Figure 6c). The blocking temperature, T_{max} , is observed as a wide curve, which is in agreement with the existence of several superparamagnetic relaxation processes. [41,42]. This is consistent with a nanoparticles system of wide distributions of sizes, anisotropies and shapes (see figure 3). On the other hand, the increase of magnetic moment at temperatures below 25 K can be attributed to the paramagnetic contribution of the RGO. The Figure 6d shows the hysteresis curve at 2 K , 150 K and 300 K of the PtNiRGO nanocomposites for the range of magnetic fields of 10 T to -10 T . The magnetization and the coercive field (Figure 6d inset) for the curve at 2 K , besides the weak itinerant ferromagnetic contribution from the bimetallic nanoparticles, are also influenced by the paramagnetic contribution of RGO at low temperature, and the different magnetic anisotropy effects of the system due to the wide particle size distribution (Figure 3c). At low temperature (2 K) the magnetic behavior is strongly affected by the surface anisotropy of smaller particles [39]. In addition, the high nanoparticles concentration promotes the direct contact between particles, which can lead to the existence of an exchange interaction between them. The particle size, morphology and distribution of particles on the sheets of RGO are important parameters to consider in the study of magnetic properties of nanocomposites materials. In this case, it is possible that magnetic interactions between nanoparticles and sheets of RGO occur freely in the system due to any surface modification resulting from the synthesis method.

4. Conclusions

Nanocomposites of PtNiRGO were obtained in-situ by thermal reduction of GO and metallic salts precursors, due to the simultaneous synthesis method used, the diffusion of metal atoms through GO sheets was promoted, causing the nucleation and growth of bimetallic alloy nanoparticles. The RGO was constituted by eight graphene sheets with an interlayer spacing of $3.4 \text{ \AA}$, which is maintained even with the presence of nanoparticles. The PtNi nanoparticles obtained presented a tetragonal crystalline structure, besides several geometric morphologies, a wide particle size distribution and a non-uniform distribution on the RGO sheets' surface. Moreover, the RGO is

diamagnetic at room temperature and presented a paramagnetic behavior at temperatures below 10 K, which is in agreement with magnetic properties of graphene obtained by direct exfoliation of graphite. The value of 2.5 for the angular momentum number indicates that the paramagnetic behavior of RGO is due to the structure of RGO, which could be directly related with the atomic arrangement in the edges of the sheets. The PtNiRGO nanocomposites are ferromagnetic at room temperature with a Curie temperature of 658 K, however, the behavior of hysteresis loop at temperatures below 10 K suggests the paramagnetic contribution of RGO.

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Figure Captions

Figure 1. a) Schematic illustration of synthesis of PtNiRGO nanocomposites, b) DTA-TGA curves of GO, RGO and GO with metallic precursor of PtNi (PtNiGO), c) FT-IR spectra of GO and RGO samples, d) XRD patterns of GO, RGO and PtNiRGO nanocomposites.

Figure 2. SEM images of a) the cross-section of GO paper, b) RGO sheets, c) PtNiRGO nanocomposites, d) BSED image of PtNiRGO nanocomposites

Figure 3. TEM images of a) high and low resolution of RGO, b) PtNi nanoparticles on RGO sheets, c) SAED of PtNiRGO composites, d) high resolution of PtNi nanoparticles with monocrystalline structure.

Figure 4. STEM images and EDS spectra of PtNiRGO nanocomposite; a) area with small particle size and b) area with large particle size.

Figure 5. Magnetic response of RGO. a) Hysteresis loop at 2 K, 10 K and 30 K, b) Fits of the data using the Brillouin function with different values of J . The diamagnetic background was subtracted. Inset: $M(T)$ measurements at a field of 1 T, the Curie law calculated is self-consistently with $J=2.5$ ($N=5.2 \times 10^{18} \text{ g}^{-1}$).

Figure 6. Magnetic response of PtNiRGO nanocomposites. a) Hysteresis loop at room temperature for magnetic field up to 2 T, b) Temperature dependence of magnetization at a field of 50 mT, c) ZFC and FC measurements at a lower field of 5 mT, d) Hysteresis loops at 300 K, 150 K and 2K for magnetic field up to 10 T. Inset: Zoom of coercive field.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6