Materials Letters 290 (2021) 129473

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

A comparative analysis of the electrochemical performance obtained for magnetic graphene oxide-based composites

Diana M. Arciniegas Jaimes[a], Paulina Márquez[b,c], Juan Escrig[b,c], Omar Linarez Pérez[d,e,*], Noelia Bajales[a,f,*]

[a] CONICET, IFEG, Av. Medina Allende s/n, 5000 Córdoba, Argentina
[b] Universidad de Santiago (USACH), Department of Physics, 9170124 Santiago, Chile
[c] Center for the Development of Nanoscience and Nanotechnology (CEDENNA), 9170124 Santiago, Chile
[d] Universidad Nacional de Córdoba, Facultad de Ciencias Químicas, Haya de la Torre esq. Medina Allende, 5000 Córdoba, Argentina
[e] CONICET, INFIQC, Haya de la Torre esq. Medina Allende, 5000 Córdoba, Argentina
[f] Universidad Nacional de Córdoba, FAMAF, Medina Allende s/n, 5000 Córdoba, Argentina

ARTICLE INFO

Article history:
Received 15 December 2020
Received in revised form 1 February 2021
Accepted 2 February 2021
Available online 11 February 2021

Keywords:
Carbon materials
Magnetic materials
Composite materials
Electrical properties
Electron microscopy
Raman

ABSTRACT

Low dimensional carbon allotropes are the most used materials in composites. In addition, when magnetic nanostructures are assembled with carbon-based materials, a versatile material for building sensitive electrodes is achieved. Here, we propose a route to obtain magnetic composites based on both graphene oxide and reduced graphene oxide with permalloy nanowires. A comparative analysis of the electrochemical performance for such composites reveals that a relatively small amount of magnetic nanowires leads to an increased conductivity with respect to that of the pristine matrix, being such effect more pronounced for the graphene oxide-based composite. Therefore, the presence of permalloy nanostructures plays a determinant role in the conductive properties of graphene oxide-based materials, providing an attractive alternative for sensing purposes.

1. Introduction

Carbon-based composites arise as advanced materials for a new generation of highly sensitive electrodes [1,2]. In fact, since composites are constituted by two or more components of different physical and/or chemical nature, an integration between any carbon allotrope and other different structures leads to a multifunctional profile in the new hybrid material. In this framework, graphene oxide (GO) as well as reduced graphene oxide (rGO), used as a cheaper alternative source than graphene, can provide a robust platform as building blocks of the composite matrix [3,4]. Furthermore, GO and rGO both supply high surface area and the possibility of obtaining a family of GO and rGO with differentiated conductive properties by controlling the reduction process. This is mainly due to the presence of functional groups that behave as reactive points to anchorage pollutants, which can be furthermore easily removed [5,6]. In addition, the functional groups can also promote a co-operative interaction with magnetic nanostructures, such as nanowires (NWs), inducing an effective assembly with them. These latter present a large surface-to-volume ratio, high shape anisotropy and exhibit different properties in comparison to bulk, which makes this type of materials very attractive for tuning the composite properties [7]. The use of magnetic nanostructures for environmental applications provides advantages over non-magnetic ones, since they can be removed from contaminated waters by applying an external magnetic field [8] or enhance the electrical conductivity to increase the sensitivity in molecular sensors [8,9]. Among magnetic nanomaterials, the alloy $Ni_{80}Fe_{20}$, known as permalloy (Py), has evidenced remarked performance in several technological applications for environmental remediation [10,11].

In this work, we develop an easy synthesis route to prepare novel magnetic GO and rGO-based composites with potential use as electrodes of interest in the environmental remediation field. The morphology of the magnetic nanostructures was characterized by scanning electron microscopy (FE-SEM), while the electrochemical characterization of Py NWs, GO and rGO components as well as of the obtained composites (Py NWs/rGO and Py NWs/GO) were performed by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

---

[*] Corresponding authors at: CONICET, IFEG, Av. Medina Allende s/n, 5000 Córdoba, Argentina (N. Bajales). CONICET, INFIQC, Haya de la Torre esq. Medina Allende, 5000, Córdoba, Argentina (O. Linarez Pérez).

E-mail addresses: olinarez@unc.edu.ar (O. Linarez Pérez), noelia.bajales.luna@unc.edu.ar (N. Bajales).

https://doi.org/10.1016/j.matlet.2021.129473
0167-577X/

2. Material and methods

Anodic aluminium oxide (AAO) of 1 μm wide and pores of (28 ± 2) nm in diameter were obtained by applying a two-step anodization process to aluminium substrates (Alfa Aesar, 99.997%) [12].

Py NWs were synthesized inside the AAO pores, by means of AC electrodeposition, applying a peak-to-peak voltage amplitude (V_{PP}) of 16 V and a frequency of 200 Hz, during 1 min, at room temperature. The electrodeposition process was carried out in aqueous electrolytic bath of salts containing both Ni and Fe cations [12]. AAO templates were coated with Au at the backside to be used as working electrode. The obtained NWs were decoupled from the AAO template by dissolving the template with 1 M NaOH, for 30 min.

Commercial suspension of GO (0.04 mg/mL) from Graphenea was employed. An emulsion constituted by 50 mg of commercial rGO powder (Graphene Supermarket) and 10 mL of isopropyl alcohol (Cicarelli) was prepared, followed by sonication during 1 h. Raman spectra of GO and rGO samples employed for composites are shown in Fig. S1. Sonication was also applied to Py NWs to avoid agglomeration. Sputtered Au on Al was used as substrate (S) for all samples in order to facilitate the handling. The magnetic composites were obtained by sequential steps of dripping the decoupled Py NWs onto the rGO flakes supported on S (S/rGO/Py NWs), on the one side, and Py NWs onto GO layers deposited on S (S/GO/Py NWs), on the other side, up to reach 80 μL of each component for both composites [12].

An 8-nm thick Cr coating was deposited on the surface of the Py NWs sample by means of sputtering, prior to morphological and elemental composition characterization performed by a Field-Emission Scanning Electron Microscope (FE-SEM Zeiss Σigma) with an Energy Dispersive Spectrometer (EDS Oxford of 80 mm^2 of surface).

The electrochemical properties have been characterized by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS), using an AUTOLAB PGSTAT100. A 0.1 M KNO_3 aqueous solution was used as electrolyte, at room temperature. The voltamperograms were measured using a window potential between −0.8 and 0.8 V at 0.01 Vs^{-1}. For EIS, the first and last applied frequency was 10^4 Hz to 2×10^{-2} Hz, respectively, recording 60 frequencies and applying a V_{PP} = 10 mV.

3. Results and discussion

Fig. 1a shows FE-SEM images of Py NWs that were collected over the substrate after decoupling them from the AAO template. This procedure yields ~1 μm long Py NWs as well as of Py NWs arrays that are still embedded inside the alumina membrane. Both Py NWs configurations, individual ones and arrays, are randomly orientated on the substrate and exhibit a serrated morphology, as it is observed in the SEM image. As well, Py NWs of shorter lengths due to the decoupling process are observed. In addition, elemental analysis of the Py NWs carried out by EDS shows the presence of Ni, Fe, O, Al (Fig. 1b). Ni and Fe elements are expected because of the alloy composition of the NWs, while the O signal has probably two contributions, one coming from the residual AAO membrane, and the other due to certain degree of oxidation of the Py NWs [12]. The Al signal corresponds to substrate or undissolved template.

In Fig. 2, CV responses for rGO and GO films display a typical capacitive shape, showing higher currents for rGO than for GO, in good agreement with its conductive properties. On the other hand, the current response for the Py NWs shows the presence of anodic and cathodic peaks at around 0.3 V. This is due to Ni and Fe oxidation and reduction. For the case of S/GO/PyNWs and S/rGO/PyNWs composites, no major changes in the voltamperogram shapes are observed, in comparison to carbonaceous components. In addition, for the GO based composite electrode (Fig. 2b), incipient peaks are observed at around 0.3 V (see arrows), indicating that Py NWs redox reactions take place.

Fig. 3a and b show the Bode representation of the EIS responses for both composites as well as for individual components. For all samples, the double-layer capacitive behaviour is obtained in the 0.1–100 Hz frequency region, meanwhile at very low frequencies the impedance extrapolates to the resistive comportment of the electrodes. Fig. 3c depicts the trend for each electrode resistance at very low frequencies.

A conductivity 20 times higher than that of GO film is obtained for the S/GO/Py NWs composite, evidencing the noticeable contribution of the Py NWs, even at low amounts in comparison to the massive carbonaceous matrix. Comparatively, the contribution of the Py NWs to the conductivity of rGO matrix is ~2.5 times, indicating that the conduction is mainly through the rGO matrix. This latter behavior hints that Py NWs have lower global effect in the S/

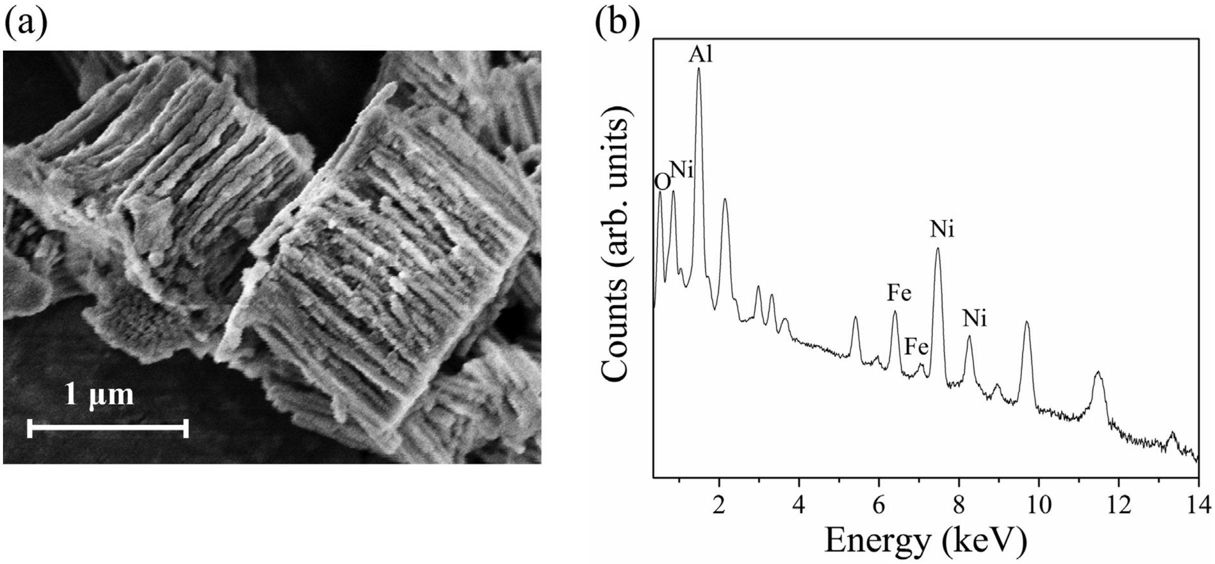

Fig. 1. Py NWs: (a) FE-SEM image of decoupled NWs and (b) EDS spectrum of the elements. The unlabeled peaks correspond to the Au of the substrate and Cr coating.

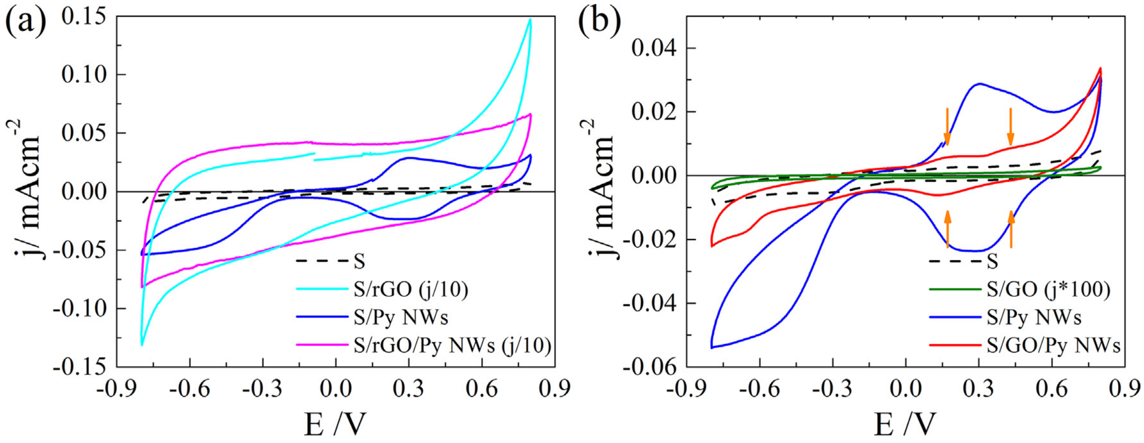

Fig. 2. CV response at 0.01 V s^{-1} for (a) S, S/rGO, S/Py NWs and S/rGO/Py NWs composite, and (b) S, S/GO, S/Py NWs and S/GO/Py NWs composite.

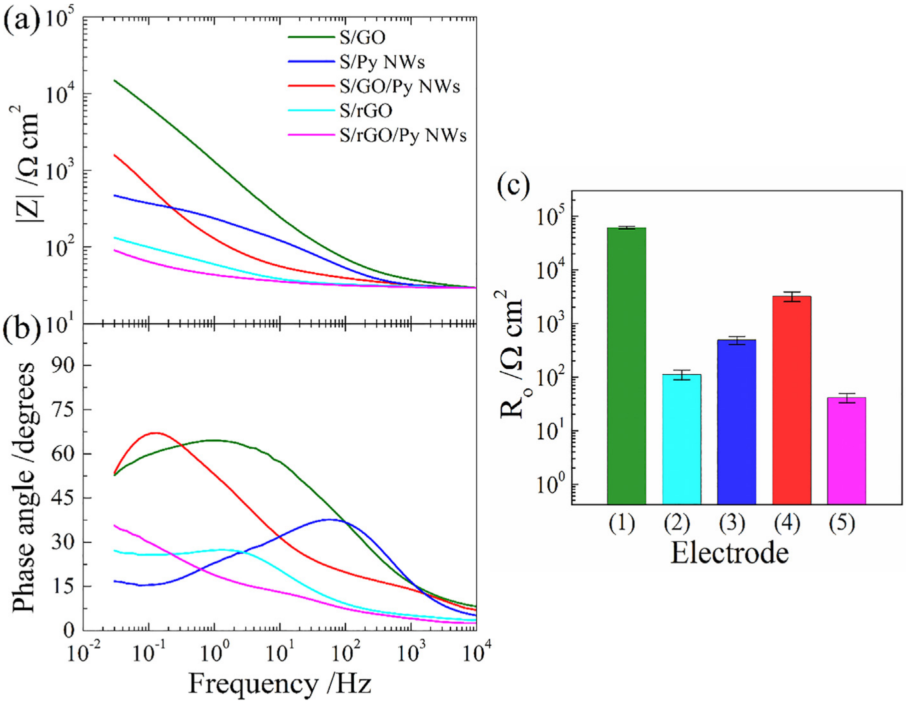

Fig. 3. Electrochemical Impedance Spectroscopy response of individual and composites samples of (a) impedance module and (b) phase angle. (c) Bar graphs corresponding to the resistance, R$_o$, at very low frequencies for the different systems: (1) S/GO, (2) S/rGO, (3) S/Py NWs, (4) S/GO/Py NWs and (5) S/rGO/Py NWs. The error bars are the uncertainties of the resistances.

rGO/Py NWs composite compared to the case of the GO-based one. These results are in good agreement to VC response discussed above.

4. Conclusions

Here we developed a method that allows performing magnetic composites constituted by GO and rGO with Py NWs. A comparative analysis between electrochemical results unveils that Py NWs play a remarkable role in the increased conductivity observed for both GO and rGO-based composites with respect to that of the pristine matrix in each case, being significantly higher for GO than for rGO case. Therefore, both composites show enhanced electrochemical performance, which make them promising materials to be explored as electrodes for sensing devices.

CRediT authorship contribution statement

Diana M. Arciniegas Jaimes: Investigation, Methodology, Data curation, Writing - original draft, Writing - review & editing. **Paulina Márquez:** Investigation, Methodology, Data curation. **Juan Escrig:** Supervision, Conceptualization, Investigation, Methodology, Writing - review & editing. **Omar Linarez Pérez:** Project administration, Supervision, Conceptualization, Investigation, Methodology, Writing - review & editing. **Noelia Bajales:** Project administration, Supervision, Conceptualization, Investigation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors thank LAMARX for the SEM and EDS facilities. D. M. Arciniegas Jaimes thanks CONICET for the fellowship granted. Fondecyt 1200302 and 3200392, Dicyt-Usach 051831EM_DAS and Basal AFB180001 provided financial support in Chile to this project.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2021.129473.

References

[1] M.M. Baig, S. Zulfiqar, M.A. Yousuf, I. Shakir, M.F.A. Aboud, M.F. Warsi, $Dy_xMnFe_{2-x}O_4$ nanoparticles decorated over mesoporous silica for environmental remediation applications, J. Hazard. Mater. 402 (2021) 123526.

[2] T.B. Nguyen, C.P. Huang, R.-A. Doong, C.-W. Chen, C.-D. Dong, CoO-3D ordered mesoporous carbon nitride (CoO@mpgCN) composite as peroxymonosulfate activator for the degradation of sulfamethoxazole in water, J. Hazard. Mater. 401 (2021) 123326.

[3] D.J. Gengzang, W.J. Chen, Q. Chen, G.H. Zhang, C.R. Limao, X.J. An, Down to ppb level ethanol detection based on heterostructured SnO/rGO composites, Mater. Lett. 284 (2021) 128987.

[4] P. Ranjan, S. Agrawal, A. Sinha, T.R. Rao, J. Balakrishnan, A.D. Thakur, A low-cost non-explosive synthesis of graphene oxide for scalable applications, Sci. Rep. 8 (2018) 12007.

[5] C.R. Minitha, V.S. Anithaa, V. Subramaniam, R.T. Rajendra Kumar, Impact of oxygen functional groups on reduced graphene oxide-based sensors for ammonia and toluene detection at room temperature, ACS Omega 3 (2018) 4105–4112.

[6] S. Wang, H. Sun, H.M. Ang, M.O. Tadé, Adsorptive remediation of environmental pollutants using novel graphene-based nanomaterials, Chem. Eng. J. 226 (2013) 336–347.

[7] S. Raviolo, A. Pereira, D.M. Arciniegas Jaimes, J. Escrig, N. Bajales, Angular dependence of the magnetic properties of Permalloy nanowire arrays: a comparative analysis between experiment and simulation, J. Magn. Magn. Mater. 499 (2020) 166240.

[8] B. Jiang, L. Lian, Y. Xing, N. Zhang, Y. Chen, P. Lu, D. Zhang, Advances of magnetic nanoparticles in environmental application: environmental remediation and (bio)sensors as case studies, Environ. Sci. Pollut. Res. 25 (31) (2018) 30863–30879.

[9] A. Saljooqi, T. Shamspur, A. Mostafavi, A sensitive electrochemical sensor based on graphene oxide nanosheets decorated by Fe_3O_4@Au nanostructure stabilized on polypyrrole for efficient triclosan sensing, Electroanalysis 32 (6) (2020) 1297–1303.

[10] J.L. McCrea, G. Palumbo, G.D. Hibbard, U. Erb, Properties and applications for electrodeposited nanocrystalline Fe-Ni alloys, Rev. Adv. Mater. Sci. 5 (2003) 252–258.

[11] Y. Sun, Z. Liu, Z. Fei, C. Li, Y. Chun, A. Zhang, Synergistic effect and degradation mechanism on Fe-Ni/CNTs for removal of 2,4-dichlorophenol in aqueous solution, Environ. Sci. Pollut. Res. 26 (9) (2019) 8768–8778.

[12] D.M. Arciniegas Jaimes, P. Márquez, A. Ovalle, J. Escrig, O. Linarez Pérez, N. Bajales, Permalloy nanowires/graphene oxide composite with enhanced conductive properties, Sci. Rep. 10 (2020) 13742.