Graphene materials from coke-like wastes as proactive support of nickel-iron electro-catalysts for water splitting

M.González-Ingelmo[1], P. Álvarez[1], M. Granda[1], V. G. Rocha[1], Z. González[1], U. Sierra[2], A. Mercado[2], S.Fernandez[2], R. Menéndez[1]

[1]Instituto de Ciencia y Tecnología del Carbono, INCAR-CSIC, C/Francisco Pintado, Fe, 26,Oviedo, 33011, Spain
[2]Centro de Investigación de Química Aplicada (CIQA) Laboratorio Nacional de Materiales Grafénicos, Boulevard Enrique Reyna 140, San José de los Cerritos, C.P. 25294 Saltillo (Coahuila), México

Keywords: coke, graphene.
Presenting author email: par@incar.csic.es

Global demand for energy is increasing rapidly due to economic growth and a worldwide increase of population. Accompanied to that, there is an ongoing transformation of traditional economies and industrial sectors driven by an urgent need to address climate changes. This movements towards decarbonisation is however hard to reach in certain sector, as for example, the well established energy-intensive industries of iron and steel sector. As an example, this later technology is nowadays dependent on coal or coke, not only as an energy source but also for necessary process engineering. The decarbonization of such industries can be faced from different point of view which supports this process in an integrated manner. A possible solution passes through the minimization of the environmental impact of the coke production in the blast furnace.

Several strategies are being proposed for the modification of the coke production, as for example using for example innovative raw with higher reactivity, which enable lower temperature operation of the blast furnace, and establishment of an innovative ironmaking processes. In any case, there is a generation of wastes inherent of this type of industry. One of them is a carbonaceous residue usually formed at the inner upper part of the furnaces that has to be scraped after several cycles. This material exhibits certain characteristics similar to the metallurgical coke, but is not of controlled composition and is usually discarded leading to solid and water environmental contaminations in the area.

With a view to minimize the environmental impact of the process and contribute to increase the fix carbon content of the overall process we propose here the utilization of the carbonaceous residue from the blast furnaces as raw material of graphene. It is an objective of this work to develop a graphene preparation process which avoids the typical graphitization step (thermal treatment at 2500-3000ºC) at which these coke-like material are usually subjected as a initial step (graphite formation). Additionally, taking into consideration circular economy issues, it is also an objective of this work to study the utilization of the as prepared graphenes in green energy production, which can be used in the same type of industry. In particular, the hydrogen (energy vector) production by water splitting is being studied. The oxidation of water to generate protons and oxygen is the hardest step in the water splitting process, and the development of catalysts to accelerate this reaction is therefore essential. In this sense, the use of graphene as proactive catalyst support in these electrochemical reactions is a promising alternative to other materials since offers a high surface area or outstanding chemical stabilities. Among the most used water splitting catalyst to support, we focus in low-cost, earth-abundant, environmentally friendly, efficient, and stable water splitting catalyst (e.g., Ni, Co, Fe, Cu and Mo). In particular, Ni/Fe-based composites are potential substitutes of noble metals for their abundance and electrochemical efficiency. In order to maximize the efficiency of the graphene as support, we focus here in achieving a homogeneous distribution and particle size control, which will lead to the optimization of their electrical conductivity, catalytic performance and maximize their durability. These results will be compared to those obtained with a graphene prepared from commercial graphite under the same experimental conditions.

Materials and methods

A coke-like waste (waste) and a commercial graphene (ALDRICH) were used as raw materials. Graphene oxides were prepared from them (waste-GO and ref-GO respectively) by means of a modified Hummers method (*Sierra* et al. (2015)). Graphenes obtained were characterized by EA, TGA, Raman, XPS and optical methods. Graphene containing Ni/Fe nanoparticles were prepared by a two step method consisting on i): electrophoretic deposition of graphene-like material on Toray Carbon Paper (TCP) and ii) electrodeposition of Ni/Fe nanoparticles. For the first one, TCP acting as working electrode was immersed in an aqueous suspension of graphene-oxide used as electrolyte. A cyclic voltammetry was carried out following the conditions described by Chang *et al* (2020) to coat carbon-fiber with the GO. The electrodeposition of NiFe composites onto TCP was undertaken in the electrolyte containing equal molar (3 mM) of nickel (II) and iron (III) nitrates (Xunyu *et al* (2015)). The synthetized electrodes were tested in at room temperature and under inert atmosphere. Cyclic and linear sweep voltammetry were performance to study their electrocatalytic behavior in KOH 1M as electrolyte.

Results and discussion

According to the elemental analysis, the coke-like waste used as raw material is composed by a 98.5 wt.% of Carbon and less than 1 wt.% of Sulphur. In addition, its Raman spectra shows a Id/Ig ratio of 0.94, which makes it a good candidate for the preparation of graphene. By means of a Hummer procedure, graphene oxide was prepared from this material (waste-GO), which shows, by TEM analysis, its typical morphology (Figure 1A), confirming the feasibility of this material to prepare graphene.

A) **B)**

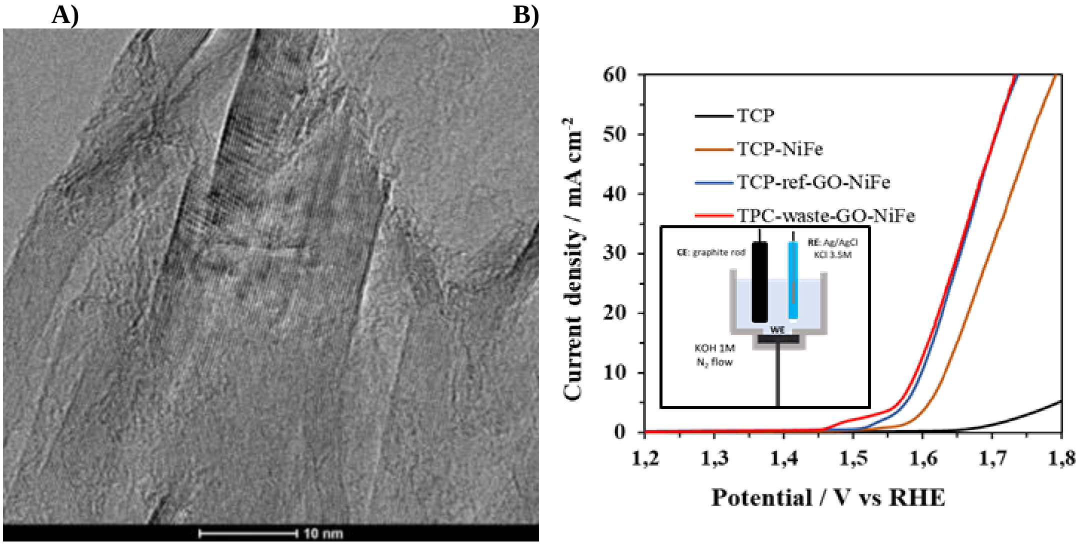

Figure 1. **A)** TEM images of waste-GO. **B)** Linear sweep voltammetry at 1mV/s of the different synthetized samples and the bare electrode. **B Inset**: Schematic Teflon home-made three-electrode cell using a graphite rod and Ag/AgCl KCl 3.5M as counter and reference electrode respectively.

Ni-Fe np were electrodeposited onto these waste-GO previously electrodeposited onto TCP to form the working elkectrode of the water splitting catalytic system (TCP-waste-GO-NiFe). This coating is supposed to enhance the distribution of nanoparticles and their electrochemical activity. The catalytic behavior of the hybrid coke-like/Ni-Fe np material was tested in a Teflon home-made three-electrode cell and compared to that of a GO prepared from commercial graphite (TPC-ref-GO-NiFe) and the working electrode with the electrodeposited NiFe np in absence of graphene (TCP-NiFe). As observed in **Figure 1 B**, in all cases the NiFe np are active catalyst in the oxygen evolution reaction. However, the presence of graphene on the TCP caused a decrease in the potential needed to initiate the reaction (higher overpotential value (400 mV)), and confirms its proactive effect onto the catalytic system. Comparing the catalytic activity of the hybrid materials form coke-like waste and from graphite, no substantial difference are noted in its OER activity. The overpotential at 10 mA/cm^2 is about 350 mV for TCP-ref-GO-NiFe and for TCP-waste-GO-NiFe, a value which is comparable to other NiFe composites (Li *et al* (2019)). These promising results evidence the possibility of using waste coke-like materials to prepare a value-added product useful for greenenergy generation.

Acknowledgement

The authors thank the Spanish Ministry of Science and innovation (MICINN) (PID2019-104028RB-I00) and Spanish council for research (icoop program, COOPB22006) for their financial support. Dr. M-González-Ingelmo acknowledges his fellowship from the Asturias regional Government (FICYT, Severo Ochoa Program BP20-168).

References:

Sierra, U., Álvarez, P., Blanco, C., Granda, M., Santamaría, R., Menéndez, R. New alternatives to graphite for producing graphene materials. *Carbon*, 2015, 93, 812-818.

Chang, Y., Venton, B. J. Optimization of graphene oxide-modified carbon-fiber microelectrode for dopamine detection. *Analytical Methods*, 2020 12(22), 2893-2902.

Li, C., Chen, J., Wu, Y., Cao, W., Sang, S., Wu, Q. Enhanced oxygen evolution reaction activity of NiFe layered double hydroxide on nickel foam-reduced graphene oxide interfaces. *International Journal of Hydrogen Energy*, 2019, 44(5), 2656-2663.

Lu, X., Zhao, C. Electrodeposition of hierarchically structured three-dimensional nickel–iron electrodes for efficient oxygen evolution at high current densities. *Nature communications*, 2015, 6(1), 1-7.