Outstanding performance as proactive support in catalytic green hydrogen production of sustainable graphene synthesised from a macroalgae waste.

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Graphene materials find nowadays application in multiple research areas, due to their outstanding properties such as elevated chemical and mechanical robustness, advanced permeability, as well as large specific surface area. This makes them useful in several applications, as in green energy production. Conventional ways of graphene preparation use graphite or fossil fuel derivatives as starting material, which represents an environmental concern. The replacement of these fossil fuel derivatives by a biomass source constitutes a sustainable approach to that end, and a few examples are already reported recently. Our first goal in this work is the development of a new procedure to prepare and fully characterized a graphene-like material from an Agar–Agar industry macroalgae "Gelidium Sesquipedale" waste and to evaluate the differences encountered with the characteristics of a graphene material obtained similarly but from a standard graphite. Moreover, our ultimate goal will be also to evaluate the capability of this material to be used as proactive support of electrocatalytic green hydrogen production by water splitting. In this regard, the oxidation of water to generate protons and oxygen (oxygen evolution reaction OER), 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 on 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. We will study herein the performance of algae-derived graphene as catalysts support, focusing on aspects as possibility to obtain an homogeneous distribution and particle size control of the catalyst and their proactive catalytic effect. The results will be also compared to those obtained using a standard graphene from graphite similarly prepared.

Materials and methods

The macroalgae waste was generated from the industrial processing of *Gelidium sesquipedale* macroalgae for the production of Agar–Agar in a company in the northern Spain, which is the largest European producer of this polysaccharide. The graphene oxide material obtained from the macroalgae waste (waste-GO) was prepared by a sequential procedure as follows: Firstly, the residue is carbonized in an inert atmosphere at 1000°C and subsequently ground and sieved below 75 μm. This material is purified before undergoing chemical exfoliation. Purification involves basic treatment with 1M KOH followed by 40% HNO_3. This pre-treatment serves to remove any possible contaminants present in the biochar that could lead to high reactivity in the subsequent reaction. Chemical oxidation is carried out using the modified Hummers method for 3 h at 35°C in the presence of H_2SO_4, $NaNO_3$, and $KMnO_4$. After stopping the reaction with 3% H_2O_2, the material is washed using distilled water by centrifugation. After that, material is exfoliated in ultrasound for 8 h, obtaining the desired GO-like material as an aqueous suspension. As comparative purposes a graphene oxide from commercial graphite was synthesized in a similar way and labelled as ref-GO.

The method to prepare the electrodes for OER consists of two steps: deposition of graphene-like material on Toray Carbon Paper (TCP) and then electrodeposition of Ni/Fe nanoparticles. For the first one, TCP was immersed in an aqueous suspension of graphene-oxide (2000 ppm) followed by a treatment at 400°C. This coating is supposed to enhance the distribution of nanoparticles and their electrochemical activity. 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 Teflon home-made three-electrode cell at room temperature and under inert atmosphere. Cyclic and linear sweep voltammetry were performance to study their electrochemical behavior in KOH 1M as electrolyte.

Results and discussion

Graphene oxides were successfully prepared from an algae-derived waste by a modified Hummers method. The characteristics of the GOs obtained were determined (AFM, XPS, etc.) and compared to those

exhibited for a GO from standard graphite. In particular, the AFM shows the presence of few layers graphenes with an average height of 6 nm and an average lateral size of 200 nm.

The algae-derived graphene (waste-GO) was used to prepare TCP-based electrodes for electrocatalytic water splitting, in particular to study the OER semireaction (see experimental section). Characterization of the electrode (SEM, EDX, RX, XPS) was performed after every sequential step (graphene coating and reduction and further electrodeposition) confirming the presence in the electrode of the reduced graphene species as well as de Ni/Fe nanoparticles in electrodes, demonstrating the capability of the waste-GO sample to perform similarly to the ref-GO. The as prepared electrodes were used in OER, by determining the cyclic and linear sweep voltammetry curves (**Figure 1**). Additional studies with bare TCP and without the presence of graphene (TPD-NiFe) were also conducted as comparative purposes. The sample without graphene (TCP-NiFe) presents a higher overpotential value. In this regard, TCP without nickel and iron result shown no catalytic activity, demonstrating its bare activity towards OER. On the other hand, the presence of graphene on the electrode (TCP-ref-GO-NiFe and w TCP-waste-GO-NiFe) caused a decrease in the potential needed to initiate the reaction (TCP-NiFe), confirming the proactive performance of these nanomaterials in the reaction. Moreover, an improvement in the catalytic performance is observed when using graphene from algae-waste (TCP-waste-GO-NiFe) when compare compared to the electrode with graphene from graphite (TCP-ref-GO-NiFe). The overpotential at 10 mA/cm^2 is about 310 mV for TCP-waste-GO-NiFe and 330 mV for TCP-ref-GO-NiFe, a value comparable to other NiFe composites (Li *et al* (2019)). These promising results evidence the possibility of using algae-derived waste and transform it into a value-added carbon material with application in green hydrogen production.

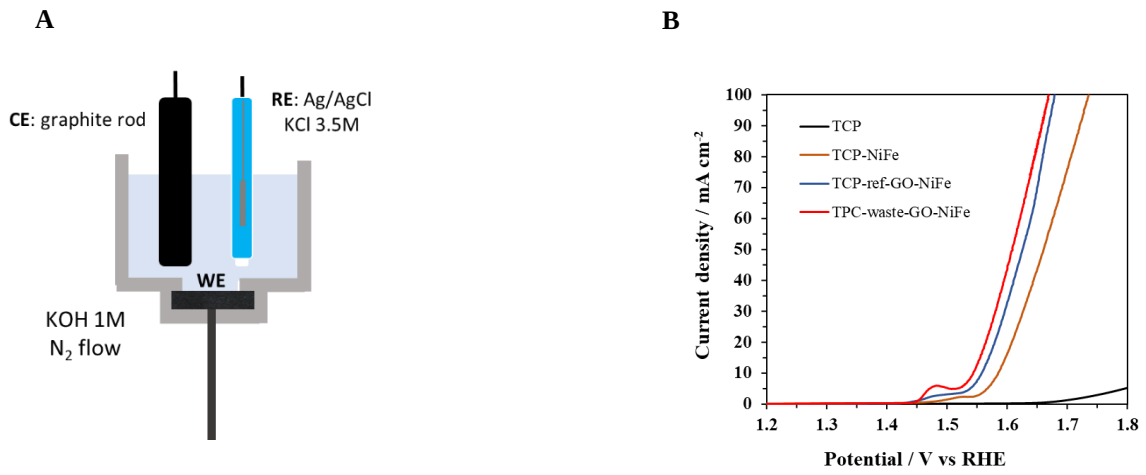

Figure 1. **A)** Schematic Teflon home-made three-electrode cell using a graphite rod and Ag/AgCl KCl 3.5M as counter and reference electrode respectively and **B)** linear sweep voltammetry at 1mV/s of the different synthetized samples and the bare electrode.

Acknowledgement

The authors thank the Spanish Ministry of Science and Innovation (MICINN) (project PID2019-104028RB-I00) and Spanish Council for Research (Icoop program, COOPB22006) for their financial support. Mrs. M-González-Ingelmo acknowledges his fellowship from the Asturias Regional Government (FICYT, Severo Ochoa Program BP20-168).

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