

# Sustainable production of graphene-anchored NHC-iridium catalyst for water splitting by using coke-like wastes: Investigation of different chemical synthetic routes.

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There is nowadays an increasing global demand for energy driven by the increase of economic growth and population. Additionally, the urgent need to address climate change is transforming the traditional economies and industrial sectors, moving towards a decarbonization scenario. This is the case of the well established energy-intensive industries of iron and steel sector. For such industries it is necessary to face the environmental issues while ensuring the actual production.

In the case of the iron and steel sector, a possible solution passes through the minimization of the environmental impact of the coke production in the blast furnace. Among the several strategies that can be proposed to that end, we focus herein in valorizing one of the main residues inherent of this type of industry. That is a carbonaceous residue usually formed at the inner upper part of the furnaces. This material must be scraped after several cycles of usage and is subsequently stored. Industrial characterization indicated that this material exhibits certain characteristics similar to the metallurgical coke, but its composition is not controlled and is usually discarded, leading to solid and water environmental contaminations in the area.

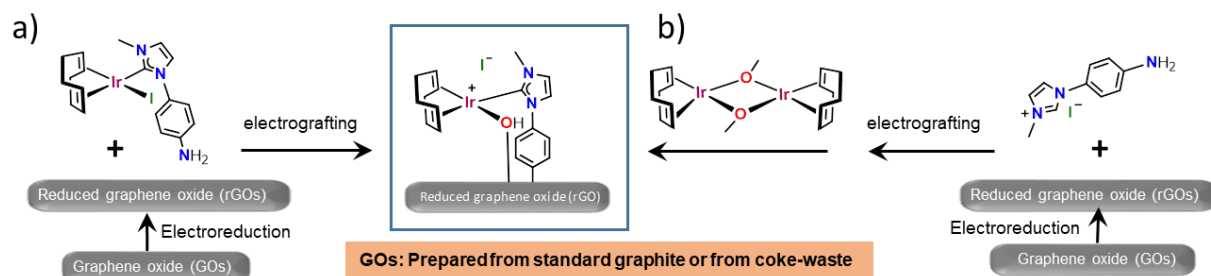
Our proposal to minimize this impact and contribute to increase the fix carbon content of the overall process is to use the carbonaceous coke-like residue from the blast furnaces as raw material of advanced carbon nanomaterials as graphenes, which can be subsequently chemically modified for different applications. In this regard, we demonstrated recently the effectiveness of the chemical route to produce graphene materials (graphene oxide -GOs- and reduced graphene oxides -rGOs-) from graphites or even from cokes (Sierra et al., **2015**). Our objective herein is to adapt and optimize this via to the utilization of a coke-like waste. Moreover, considering circular economy issues, we propose herein the utilization of the materials prepared from that waste in green energy production via the green hydrogen (energy vector) production by water splitting. This water splitting process is a crucial electrochemical reaction to produce sustainable hydrogen directly from water. However, the bottleneck of this process is the oxygen evolution reaction (OER) due to its large overpotential and slow kinetics. This is solved by the utilization of a catalyst, being the most effective of them iridium and ruthenium (Sanchez-Page et al. **2020**,Nieto et al. **2019**). For a large-scale use of these catalysts, also considering their high price, their immobilization via covalent attachment is a requirement, since improves their efficiency and robustness. As support, graphene materials, as reduced graphene oxide (rGO), offers high surface area and chemical stability. The synthetic procedure of producing the hybrid graphene/ir materials has to be exhaustively controlled to ensure adequate chemical environment of the monoatomic catalyst. In general terms, the goal is to developed efficient vias to immobilize the catalysts onto the graphene surface while maintaining or even increasing the catalytic efficiency of the newly formed hybrid material.

In this work, we do not only prepare graphene materials from a coke-like waste but also study and compare two different synthetic routes of covalent functionalization of rGOs with iridium (I) complexes. Both routes are (a) direct graphene electrografting of the previously synthesized imidazolium-Ir(I) complex making use of the aryl diazonium salt chemistry(Fortgang et al. **2016**) and (b) a two-steps sequence comprising initial electrografting of the imidazolium ligand and subsequent chemical anchoring of the Ir(I) precursor. Additionally, we study herein the performance of the hybrid materials prepared as catalyst in the OER reaction.

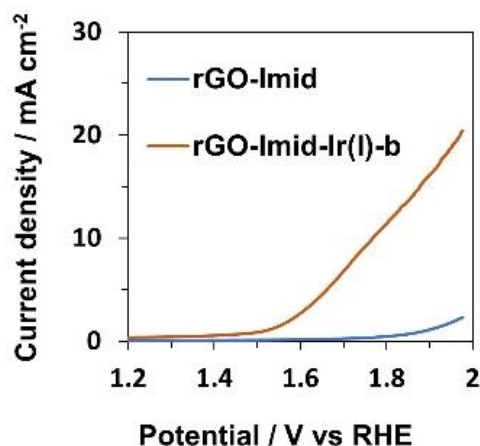
## Results and discussion

The coke-like waste and a standard graphite used as comparative purposes, were used to prepare graphene oxides (GOs) via a modified Hummers method (Sanchez-Page et al. **2020**,Nieto et al. **2019** ). Their characterization (XPS, AFM) demonstrated the feasibility of the coke-like waste as graphene raw material. The GOs so prepared were drop casted over carbon rod electrodes and subject to electro-reduction formation of partially reduced graphene oxides rGOs).

The rGOs were used to produce in situ the hybrid graphene-Iridium materials. These were obtained via the chemical routes a) and b) depicted in **Figure 1**. All hybrid species and intermediates were exhaustively characterized using different techniques (XPS, EXAFS, EA, ICP-ms). The results confirmed the expected structures depicted from each synthetic route. Of particular interest is to confirm not only the presence of the nitrogenated imidazolium ligand (imid) linked to the graphene material (from standard graphite and from coke-like waste) but also the oxidation state of the linked iridium atoms (Ir(I)) as well as their chemical environment (mainly via XPS and EXAFS analysis). The characterization of the resultant materials demonstrated the effectiveness of using a coke-like waste a starting material of graphene oxides via the chemical route.



**Figure 1.** Scheme of the two routes used to prepare the imidazolium-Ir(I) complex on reduced graphene oxide prepared via chemical route (GO) from a standard graphite or a coke-waste.



**Figure 2.** OER polarization curve ( $1\text{mVs}^{-1}$ ) of the catalysts.

The electrochemical performance in OER of all the hybrid-Ir (I) catalyst prepared was studied by using the correspondent polarization curves. The results demonstrated the efficient catalytic activity of the supported imidazolium Ir(I)/graphene hybrid materials prepared. As an example, in the case of using the two step sequence of the route b, the results obtained (Figure 2) shows that the attachment of the Ir(I) complex after the imidazolium grafting increase substantially the current density obtained (**Figure 2**).

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