Synthesis and characterization of graphenes containing S, N and P. Electrochemical activity toward the oxygen reduction reaction

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Abstract

The discovery of graphene, a single-layer carbon atoms densely packed into a two-dimensional honeycomb lattice, has opened up a new field based in bidimensional materials (2D) [1].The driving forces in the field are the potential technologies associated with graphene and its derivatives, such as nanoelectronics, biolabeling, sensors, energy storage and catalysis [2]. The great interest in the use of graphene as catalysts has its origin in three properties: large surface area, very good conductivity and high mobility of charges. In addition, the graphitic structure gives to the graphene based materials a high chemical and mechanical stability.

Catalysts for oxygen reduction and evolution reactions are at the heart of key renewable-energy technologies including fuel cells and water splitting. The development of the oxygen electrode catalysts with high activity at low cost remains a great challenge despite tremendous efforts. The non-noble metal catalysts based on pyrolyzed carbon and nitrogen precursors have shown good performance toward the oxygen reduction reaction (ORR) [3].

In graphene, the substitution of carbon by heteroatoms or the covalent bonding of functional moieties containing heteroatoms modifies the electronic structure, hydrophobic character and chemical affinity, providing a way to tailor the catalytic properties. Therefore, graphene could be a good system to correlate its catalytic reactivity with chemical properties. Graphene oxide (GO) and reduced graphene oxide (RGO) can be synthesized from graphite using low cost and easily scalable methods (Scheme 1) [4] and then chemically modified [5].

The present work reports the preparation and characterization of modified GO and RGO with the final purpose to study its use as catalyst in the ORR. The synthesis of GO was performed by a modified Hummers method [6]. RGO was obtained by hydrothermal treatment of GO at 90, 150, 200 and 300 °C. Graphene used as reference was synthesized by electrochemical exfoliation of HOPG in aqueous solution [7]. GO and RGO were doped with nitrogen, sulfur and phosphorous by different methods. The materials were purified by a combination of several centrifugation and dialysis steps. Finally, graphenes were characterized by FTIR, Raman, AFM, TEM and EDS-SEM.

Preliminary measurements realized in acid and basic media show good catalytic activity toward the ORR, in agreement with literature data,.

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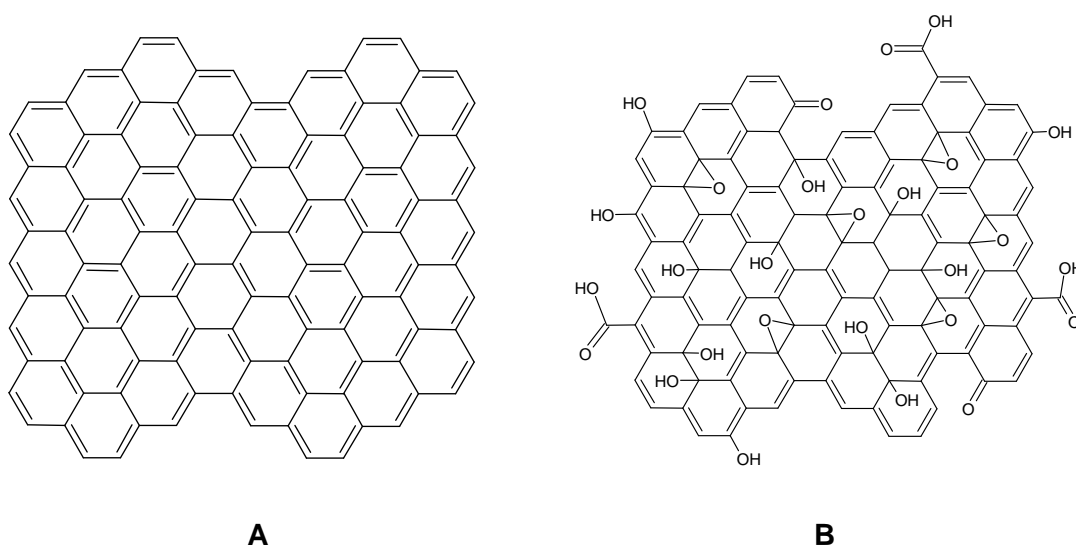
Scheme 1: A) graphene and B) graphene oxide and reduced graphene oxide [5].