

Advances in Graphene and Graphene-Related Materials

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In recent years, the investigation into and development of graphene-based materials have been continuing, and have formed the basis of a remarkably large number of the latest publications in the fields of materials science, applied chemistry, and electronics. The interest in graphene-based materials ranges from the synthesis to the modification of them, from the point of view of their practical application in several industrial and research fields. Most applications of GO-based materials and components take advantage of their properties such as capability of rejecting monovalent ions, high salt rejection, high chemical and physical stability, high water permeability, high selectivity, and reduced fouling [1].

The peculiar chemical and physical properties of GO-based materials enable them to form into a variety of shapes. Among others, membrane production takes advantage of the self-assembling behavior of graphene and graphene-related materials, enabling the possibility of producing thin components with controllable selectivity and high permanence [2]. The separation capacity relies on the sieving ability of nanochannels in the membrane, according to molecular size [3]. Accordingly, G- and GO-based membranes have found applications in several areas, such as gas separation [4], organic solvent filtration [5], water purification [6], and desalination [7,8]. The latter topics are of particular interest, as the global water demand has been estimated to continue at a similar growth rate until 2040, projecting a 20 to 30% increase from existing water consumption rates [9]; based on these data, hybrid graphene-based membrane materials may represent a valuable solution for water purification to meet global freshwater demand. The performance and selectivity of G- and GO-based materials can be further increased by properly modifying the chemical properties of the membrane, either via chemical modification [10] or via the addition of a photochemical functionality, by introducing photo-active materials such as titania [11]. In addition to the removal of pollutants, graphene and its derivatives are materials that are well known to be used for water desalination, which represents another valuable approach to the fulfilment of a resilient and sustainable use of water resources [12].

Graphene-based materials have also found a wide range of applications in the field of energy production and storage. In the first case, GO has been investigated as a possible alternative electrolyte in hydrogen-fed fuel cells (i.e., Proton Exchange Membrane Fuel Cells, PEM) at high temperatures and low relative humidity, which would enhance both kinetic aspects and the efficiency of the electrode reaction with respect to what occurs currently with the most widespread electrolyte (i.e., Nafion[®]), operating at 60–80 °C.

GO has attracted a lot of interest due to the easy production of both self-standing [13,14] and hybrid electrolytes, with the latter based on Nafion[®] [15–17] or more thermally stable polymers based on polyimides [18,19] or poly(ether sulfones/ketones) [20,21]. Composites with pure or functionalized GO can show higher mechanical properties as well as enhanced water uptake and proton-conducting behaviors.

The important self-assembling, mechanical, and insulating features of GO are derived from oxygen-bearing functional groups, namely hydroxyl, carboxyl, carbonyl, and epoxide moieties [22], which can lead to the formation of hydrophilic regions separated by



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hydrophobic graphitic domains. The resulting structure may enhance the ion exchange and in particular the transport of protons [23].

Free-standing pure GO membranes have been fabricated and successfully exploited as electrolytes in preliminary tests, showing a higher water uptake compared to Nafion[®] [14,24] as well as better mechanical properties, lower permeability to hydrogen, and promising in-plane proton conductivity. However, a lower open circuit voltage compared to the one exhibited by Nafion[®]-based devices and poor fuel cell performance have been detected, which may be due to both low through-plane conductivity and high-temperature durability. Therefore, innovative procedures to modify GO with alternative functionalities (e.g., sulfonic groups covalently bonded with the basal plane) are needed to enhance ionic conductivity and both the thermal and structural stability of the material.

G and G-related materials also have excellent supporting material properties and the ability to stabilize various electrocatalysts such as metal nanoparticles, metal oxides, and polymers. Such properties, together with a certain electrocatalytic ability for redox reactions, have allowed the use of graphene as a catalytic material for enhanced glucose oxidation in a glucose fuel cell [25].

The aforementioned channeling properties determined by the stacking of graphene layers can also be exploited for the development of hydrovoltaic generators. The latter approach provides a new method for obtaining energy from water that consists of the hydration of the nanochannels, where the overlapping EDLs can exhibit charge selectivity, repelling the co-ions while allowing counter-ions to pass through. This characteristic can enable the generation of electricity via the evaporation of water or directly from moisture. This represents one of the latest extents of graphene-based materials in the field of sustainable energy production [26].

In the case of energy storage purposes, for instance, graphene flakes can be incorporated in metal oxides to be used as electrodes in lithium-ion batteries (LIBs). It has been proven that self-assembled SnO₂-graphene nanocomposite films can easily have Li-ions inserted into their structure, achieving high specific energy density without relevant charge/discharge degradation [27]. Functionalized graphene sheet-sulfur nanocomposites with a 3D layered structure have also been used for LIBs [28], providing high capacity and good cycling stability. Porous graphene networks prepared via CVD have been assembled in LIBs as high-performance anode materials [29], demonstrating high reversible capacity.

Finally, graphene is a valuable candidate for the development of advanced microelectronic components, such as electrochemical sensors. Among others, applications have been reported such as the detection of free chlorine in water using graphene-like carbon-based resistive sensors [30], and, in more general terms, the development of new water quality sensors for the identification of deteriorating water quality [31].

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