Green way to clay-supported graphenes

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Abstract

This contribution introduces recent results reporting on the achievement to prepare graphene-like materials from resources as common as carbohydrates (e.g., table sugar) and proteins (e.g., gelatin) supported on diverse porous solids (clays, silica, zeolites,..). These transformations are conducted at relatively moderated temperatures (below 800ºC) in absence of oxygen and, surprisingly, without requiring the presence of reducing agents.

Among other porous solids, clay minerals of different topologies, i.e. from layered silicates of the smectite type to fibrous sepiolite, have been used as porous substrates to produce nanostructured carbonaceous materials using diverse molecular and polymeric organic precursors [1-3]. Although the carbon-clay materials may have interest per se, most of the carbon-clay precursors are used as source of nanostructured carbons provided with electronic conductivity useful for diverse applications such as electrode materials for secondary battery electrodes and supercapacitors [4]. Nevertheless, few reports on the use of the carbon-clay intermediates without removal of the porous substrate have been reported, though the presence of the clay substrate may provide additional advantageous features [5,6].

The present contribution will introduce recent results pointing out the possibility to prepare supported graphene-based materials from natural resources, such as sucrose or caramel and two types of clays, i.e. layered clay (montmorillonite) and fibrous clay (sepiolite). Figure 1 shows a schematic representation of the synthetic approaches using sepiolite as porous support. Intermediate clay-caramel nanocomposites can be prepared either by microwave (MW) irradiation of sucrose-clay precursors or by direct silicate impregnation with water-caramel suspensions. The resulting graphene-clay supported materials were obtained by further heating at 700-800 ºC, under nitrogen flow (Fig. 1).

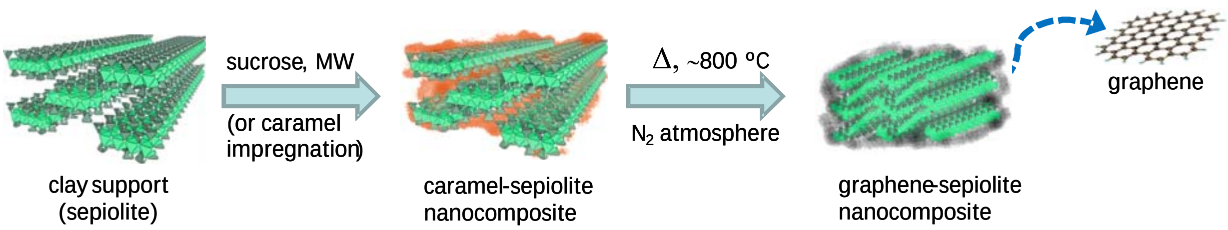

Fig. 1. Schematic representation of the preparation route of supported graphenes on the magnesium silicate sepiolite using sucrose or caramel as precursors.

The carbon content in the resulting powder samples determined from CHN elemental analyses is around 35% (w/w), which corresponds to graphene-like compounds assembled to the clay support. Deconvoluted C1s peak in the XPS spectrum of thermally treated caramel-clay samples shows that the main contribution corresponds to C=C bonds, which are present as an intense, sharp and very narrow component of graphene-like material. Raman spectrum confirms the graphene formation through the G-band at 1595 cm^{-1} (sp^2 carbon) and the D-band at 1360 cm^{-1} (disorder in sp^2-hybridized carbon) (Fig. 2).

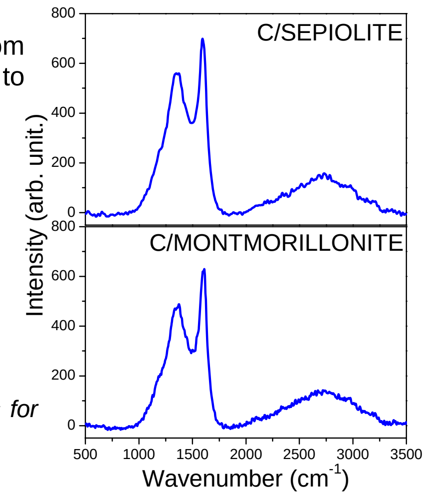

Fig. 2. Raman spectra of graphene-clay materials showing similar features for the both types of clay substrates, montmorillonite and sepiolite.

The graphene-clay supported materials show interesting characteristics such as simultaneous conducting behavior, together with chemical reactivity and textural features provided by the silicate backbone, of interest for diverse high-performance applications [7]. In this way the resulting supported-graphenes based on sepiolite act efficiently as electrodes for lithium-batteries without the usual requirement of conductive additives, and the preliminary results open also the way for applications as components in supercapacitors. However, it is necessary to optimize these systems to improve them in the light of possible real-world applications.

The procedure here reported for the synthesis of clay-supported graphenes can be considered as a remarkable eco-friendly approach deserving a relatively low-cost and promising large scale way for graphene-like materials production, especially when comparing with the Hummers's method and related procedures using graphite as precursor.

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