

Influence of the pH on the Hydrothermal-Assisted Synthesis of Graphene

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Graphene (G) is an allotropic form of carbon which can be described as single sheets of aromatic sp² carbon atoms. From 2004, when Novoselov *et al.* reported its isolation through the so-called scotch-tape method,¹ it has attracted increasing interest, becoming one of the hottest scientific topics to date. Its importance is undoubtedly associated to the sophisticated electronic properties predicted for G sheets. Among them, ballistic transport, high conductivity, extraordinary optical or thermal properties, high surface area or its mechanical resistance, which turns it into one of the strongest materials on earth, justify the current importance devoted to this material, confirming it as a one of the most promising candidates for the future development of technologically advanced applications.²⁻⁵

Concerning the synthesis of G, several physical routes such as the Chemical Vapor Deposition (CVD) or the micromechanical exfoliation of graphite (more commonly known as the scotch-tape method) has emerged as the most exploited synthetic recipes.⁶ Though these routes lead to high-quality G sheets, the scalable production of G in good yields remains one of the main challenges for its potential employment into further technological applications. With this regard, the chemical synthesis of graphene has become as a promising alternative, since it would permit synthesizing large-scale quantities of G. Depending on the chemical nature of the G precursor, these chemical methods can be divided in two general categories: a) Those starting directly from graphite – a layered material built up from the stacking of G sheets through weak van der Waals interactions – and b) Those relying on the sequential exfoliation and reduction of graphite oxide (GO), which is generally prepared in a preliminary stage through acidic oxidation of graphite.⁷ This oxidation promotes an increment of the interlayer space separating the G sheets in the solid state, thus permitting the exfoliation of the layers under continuous cycles of sonication and mechanical stirring. Afterwards, the exfoliated material is subjected to a reduction reaction, necessary to recover the electronic properties of pristine unmodified G. So far, this reduction has been accomplished through several strategies, which typically relied on the use of hazardous reduction agents (i.e. hydrazine, dimethylhydrazine or L-ascorbic acid).^{8,9} Recently, it has been demonstrated that supercritical water may act as a reducing agent for GO in hydrothermal conditions, offering a new and “green” route for the production of graphene.¹⁰

Herein we provide further insights on this biocompatible method for the production of graphene from the exfoliation/reduction of GO (**Figure 1**). GO is obtained by the Hummers method,¹¹ and afterwards reduced *via* a hydrothermal (HT) treatment in water (G_{red}). The effect of the pH on this latter step, which was found to produce different nanocarbon forms with variable reduction degrees, was studied in the 3-11 interval. We will describe the chemical nature of the resulting species on basis of the collective employment of High Resolution Transmission Electron Microscopy (HRTEM), Raman and X-ray Photoelectron Spectroscopy (XPS), amongst other experimental techniques.

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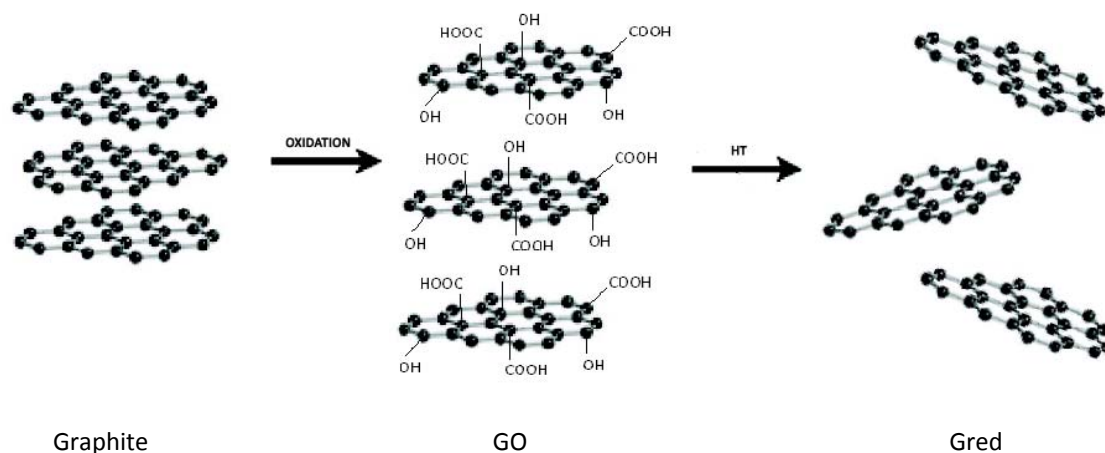


Figure 1. Scheme describing the chemical production of graphene (G_{red}) through the reduction of GO.