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Review

Graphene production via electrochemical reduction of graphene oxide: Synthesis and characterisation

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HIGHLIGHTS

- We highlight the graphene production via electrochemical reduction of GO.
- We review two different routes for electrochemical reduction of GO.
- Experiment setup and conditions for both electrochemical routes were reported.
- Highlight of several spectroscopy characteristic properties of the graphene.
- The graphene produced from both routes showed similar characteristic properties.

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ABSTRACT

A considerable amount of research has been devoted to the synthesis of graphene materials via graphene oxide (GO) precursor during recent years due to the fact that it is ease in processing, versatile, and scalable for mass production. Nevertheless, GO needs to be reduced in order to recover the unique properties of pristine graphene. Of the various reduction approaches, the electrochemical method provides a facile, fast, scalable, economic and environmentally benign pathway to the production of desirable quality graphene materials. The electrochemical approach can be undertaken via two different routes: the one-step route which involves direct electrochemical reduction of GO in suspension onto the substrate electrode whereas the two-step route requires pre-deposition of GO onto the substrate electrode prior to electrochemical reduction process. This paper first reviews the preparation methods and various properties of graphene oxide. This is followed by a discussion on the working parameters of the two different electrochemical routes and the associated electrochemical techniques used to produce graphene. This paper also provides reviews on the characteristic properties of the electrochemically reduced graphene through the analysis of various spectroscopic techniques, such as X-ray photoelectron spectroscopy, Raman spectroscopy, infrared spectroscopy, X-ray diffraction and electron microscopic.

Contents

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1. Introduction

Graphene is a carbon allotrope that consists of a flat monolayer of sp^2-carbon atoms bonded and arranged in a honeycomb lattice. Since the discovery of graphene in 2004, this single atomic layer carbon material has garnered tremendous attention from researchers around the world because of its remarkable properties, such as high surface area [1,97], strong Young's modulus [2,3], good thermal conductivity [4,98], outstanding electrical conductivity [5,6], and optical transparency [7,99]. Because of these fascinating properties, graphene has found its way into various applications, including energy conversion and storage (e.g., fuel cells [8] and capacitors [9]), sensors [10], electrocatalysis [11,102,103] and electronic devices [12].

Several approaches have been developed for the synthesis of graphene, such as mechanical cleavage [13,14], epitaxial growth [15,16], chemical vapour deposition [17,18], electrochemical exfoliation of graphite [111,113,114,117] and reduction of graphene oxide (GO) that derived from chemical exfoliation of graphite [19]. Recently, non-covalent exfoliation of graphite by sonication in liquid phase has also been reported [115,116]. Of all these approaches, the reduction of GO is regarded as one of the most promising routes for the mass production of graphene at a low cost and high yield, albeit only partially restore the properties of pristine graphene. Thus, the product obtained from this approach has been given various names and it is more frequently known as reduced graphene oxide (RGO), as it possesses properties that are different from pristine graphene. The graphene oxide is hydrophilic [20] and electrically insulating [21] because of the disruption of the sp^2 bonding network in its carbon basal plane whereby a significant fraction of the sp^2 carbon network is bonded with oxygen-containing functional groups during chemical exfoliation of the graphite. Thus, the graphene oxide has to be reduced to restore the unique properties found in the pristine graphene. Despite the difference in the quality of the reduced graphene oxide from that of pristine graphene, the product from the reduction process could be further modified and used for a wide range of applications.

There are a number of routes for the reduction of GO, such as chemical reduction [22,23], thermal reduction [24,25], photocatalytic reduction [26,27] and electrochemical reduction. Typically, the chemical reduction of GO route involves the use of reducing agents, such as hydrazine [71,99], dimethylhydrazine [106], metal hydrides [104,105], and hydroquinone [22]. The excessive use of reducing agents could contaminate the resulting product [28] and even be harmful to human health and the environment [29]. Moreover, some oxygen functionalities in GO are selective and could not be removed completely with only one reductant treatment [30,31]. On the other hand, the thermal reduction route involves the use of high temperature to remove the oxygen functionalities, which would result in high production cost in addition to tedious control of experimental conditions. Meanwhile, the photocatalytic reduction of graphene oxide depends heavily on the presence of photoactive materials under ultraviolet (UV) irradiation. In contrast, the electrochemical reduction of GO is a relatively simple, economic, fast and environmentally benign method [28,32] to reduce GO to the graphene material on a large scale compared to the aforementioned methods. This approach is often compared with electrochemical exfoliation approach due to the similarity of exploiting the external power source to yield graphene in solid form and occurring in solution phase. However, it should be noted that the electrochemical reduction of GO approach is aimed at restoring some of the original properties of pristine graphene and exploit new functionalities of the RGO, along with other nanoparticles or compounds whereas the electrochemical exfoliation approach is focused on preservation of the properties of pristine graphene. The graphene produced from this approach is more appropriately known as electrochemically reduced graphene oxide (ERGO) as its properties differ from that of pristine graphene because of several residual oxygen functionalities on the carbon basal plane, while it retains some of the graphene structures [33]. Typically, the electrochemical reduction of GO can be carried out using a standard electrochemical cell in the presence of a non-hazardous aqueous buffer solution at room temperature. An external power source (applied potential) is used to drive the reduction process, and the oxygen functionalities in GO are removed with concomitant deposition of conductive solid films onto a working electrode surface. The properties of the ERGO can be tuned by controlling the electrolysis parameters and electrolyte [34].

In this review, we discuss the graphene, ERGO, which is produced from a GO colloid suspension precursor via the electrochemical approach. The focus of this review will be on the different electrochemical synthetic routes used to convert GO to the desirable properties of the ERGO. This review will also give an overview of the GO precursor used in the electrochemical reduction process. A summary of the characteristic properties of ERGO is provided through the analysis of several spectroscopic techniques, such as X-ray photoelectron spectroscopy, Raman spectroscopy, infrared spectroscopy, X-ray diffraction, and electron microscopy.

2. GO precursor

GO is typically derived from the chemical exfoliation of graphite oxide. GO is generally similar to graphite oxide [35] in terms of its chemical structure, which contains plenty of oxygen functionalities on its carbon basal plane. However, the physical structure of GO is different from graphite oxide as the latter retains a stacked structure [36] similar to that in graphite. In general, the GO is exfoliated into a single-layer or few-layered carbon sheets. The precise structure of GO is still elusive and remains under debate as the coverage of oxygen functionalities that exist on the GO varies widely with the different synthetic procedures [37,38]. However, the generally accepted structural model of GO, which was proposed by Lerf et al. [39,40], depicts the hydroxyl and epoxy groups as dominant functional groups residing mainly on the basal plane of the GO sheets while the carbonyl and carboxyl groups accommodate the edges of the GO sheets (Fig. 1).

The first step in the synthesis of GO in a stable colloidal suspension begins with the oxidation of graphite to graphite oxide. Subsequently, graphite oxide is exfoliated in the solution phase into individual GO sheets to form an aqueous GO colloidal suspension. Presently, the Hummers [41] and the modified version of this method [42,43] are the most commonly used methods for the oxidation of graphite. All of these methods involve the oxidation of graphite in the presence of strong oxidants in acidic media. In Hummers' method, the graphite is oxidised using $KMnO_4$ and