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Review

Modifications in development of graphene oxide synthetic routes

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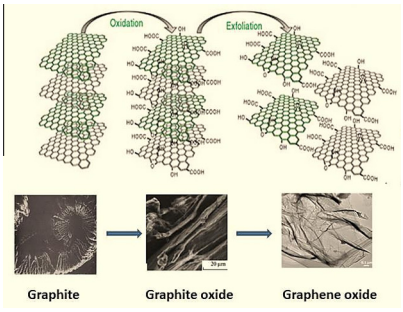
HIGHLIGHTS

- Advances in graphene oxide synthesis routes are explored.
- Conventional routes are studied in comparison with modified routes.
- Synthetic recipe is developed to attain specific morphologies.
- Specific morphologies are achieved for particular applications.

GRAPHICAL ABSTRACT



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ABSTRACT

The synthesis of graphene oxide is discussed in this critical review. Particular emphasis is directed towards the conventional methods for the synthesis of graphene oxide (GO), their draw backs and modifications to enhance the efficiency of conventional synthetic routes. Moreover, this review covers the comparison of all the existing techniques for the graphene oxide synthesis. This review will be of value to the researchers interested in this emerging field of material science for developing the synthetic recipe in order to attain specific morphologies of GO for particular applications.

Contents

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1. Introduction

Nanomaterials are cornerstones of nanoscience and nanotechnology. Some nanomaterials have natural occurrences, but engineered nanomaterials are of particular interest [1]. Among all engineered nanomaterials, carbon based nanomaterials have undergone an explosion of interest in recent years due to their unique combinations of chemical and physical properties [2,3]. Carbon based nanomaterials have shown their importance in every field of technology [4] including energy sources [5]. These nanomaterials are largely exploited in material science for their mechanical, electronic, optical and magnetic properties in the field of biomedical applications and particularly in the new discipline of nano medicine [6,7]. Among all the carbon based nanomaterials, two dimensional graphene, reduced graphene oxide (GO) or GO-supported materials appeared as the hot topic of interest to researchers because of its unusual and exotic properties [8,9]. GO is comparable to graphene in certain aspects with oxygen moieties and holds a remarkable position independent of graphene in the research field [10]. Graphene's boom started in 2004 when Geim, Novoselov and co-workers published the deposition and characterization of single sheets of graphite on solid supports. They were honoured with Nobel Prize in Physics in 2010 [11–14]. Therefore, it is being explored with great eagerness particularly due to challenges in determining its structure and electronic properties [15]. GO is a very promising material as it is easy to process, low cost of manufacture, good colloid condition, high surface area [16], unique mechanical properties [17], low molecular weight, optical electronic and magnetic properties [18], water-dispersible and chemically versatile due to the presence of oxygenated groups on its surface [19–22].

GO presents researchers with the opportunity to explore the solid-state analogue of a polycondensed and conjugated molecule. Since GO can be derived chemically from graphite, it is an abundant and in expensive natural source of carbo-catalyst [23,24]. Several unique features make this material superior to all other carbon based nanomaterials. First the presence of oxygen-containing functional groups allows GO to act as a green oxidant or solid acid as well as to swell and disperse in H_2O [25,26]. Second aromatic scaffold having hole defects [27,28] gives a template to anchor active species such as organocatalysts or photo catalysts. This material is an oxidized form of graphene which is produced with the aid of the reaction of graphite with strong oxidizers [29,30]. It is an electrochemically hybrid material that features both conducting pi states from sp^2 carbon sites and a large energy gap between the sigma states of its sp^3 bonded carbons [20,31–34].

Various structural models of GO have been presented that improved with the passage of time due to advancement in characterization techniques. The first model of GO was presented by Hofmann and Holst in 1939. According to this model oxygen atoms were bound to carbon atoms of hexagon layer by epoxide linkages with ideal formula C_2O [35]. In 1947, Ruess et al. proposed a model taking into consideration the hydrogen atoms of GO and indicated the sp^3 hybridization form of basal plane structure [36]. Lerf et al. suggested a structural model of GO having random distribution of aromatic and wrinkled regions on the basis of H NMR and solid state NMR spectra [37]. Nakajima and co-worker represented a poly like model $(C_2F)_n$ by fluorination of GO through the XRD information [38]. Szabo et al. model was based on a ribbon like arrangement of flat carbon hexagons connected by C=C double bonds. These functional groups serve as the basis for the reactive sites that used for chemical modification by using selective organic moieties thus making GO organophillic [39].

The tunability of the ratio of the sp^2 and sp^3 fractions with the aid of reducing agent is a powerful way to tune its band gap and thus controllable transformation of GO from an insulator to a semi-conductor and to a graphene like semi-metal [40–43]. Thus GO has been considered as a prominent precursor and a starting material for the synthesis of graphene like materials [44–46]. Various chemical routes for the reduction of GO has been reported, Agharkar et al. summarized all the salient features of green method for the natural reduction of GO, which are based on the use of biomolecules, microorganisms and plant extract as reducing agents [47].

GO is widely applicable in the fields of biotechnology, bioengineering, drug delivery, imaging of cells and biosensors as it is biocompatible [48–51]. The biocompatibility of graphene oxide is examined in bacterial cellulose/GO composite that exhibited good antibacterial activity against *E. coli* due to the formation of a strong hydrogen bond between carboxyl group of graphene oxide and hydroxyl group of bacterial cellulose [52,53]. GO properties have been exploited for the sensing of wide range of inorganic and organic molecules. Because of the monolayer configuration of GO, all its carbon atoms are exposed to the environment and the charge carriers are confined to the surface of the sheets. Thus the electrical conductivity of flake becomes very sensitive to local electrostatic perturbations [10]. This property makes the GO a rising material for sensing applications [54,55].

The fluorescence quenching ability of GO has been exploited for the detection of multiple DNA [56]. So GO can be developed as an excellent fluorescence quencher to lower the background signal and help strengthen the detection sensitivity further [57]. Such flo-