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Review article

Chemical reduction of graphene oxide using green reductants

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ABSTRACT

Graphene has exceptional physical, chemical, mechanical, thermal and optical properties which offer huge potential for applications in various sectors. Chemical oxidation of graphite to graphene oxide followed by the reduction process is the commonly used method for mass scale production of graphene or reduced graphene oxide (RGO). Among the large number of chemical reducing agents used to prepare RGO or graphene, the most efficient reductant is hydrazine. It is toxic in nature and harmful to the environment, thus it is in high demand to use green reductants for RGO synthesis. We understand that due to high demand of graphene/graphene oxide/reduced graphene oxide recently and which is expected to be more in future, green synthesis methods are extremely important. In this article, we have studied the synthesis methods, characterization and the possible mechanism for green reduction, especially by ascorbic acid. This article could possibly motivate the researcher worldwide to innovate new green methods for mass scale production of graphene based materials.

Contents

1. Introduction

Graphene, as the first two-dimensional material to know, has become the celebrity in the nanomaterial world with the revolutionary discovery of graphene by Geim and co-workers [1]. Ever since the gold rush for graphene has enhanced. The reason being

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that graphene has proven to have many outstanding properties applicable in diverse areas including electronic, light processing, energy related, sensors, and various biomedical applications [2]. Until now, many techniques have been introduced to synthesize graphene. Among all, the chemical reduction of graphene oxide (GO) is believed to be the most promising method with respect to large-scale productivity at a low cost in a short time. Why GO and its reduced product (here onwards referred to as RGO) are becoming popular among researchers? The answer being that both materials have confirmed to be applicable in many areas that pristine graphene cannot be directly applied in, such as water purification [3–6].

GO is not a naturally occurring compound. The mechanism of oxidation and the chemical structure of GO are still ambiguous due to its non-stoichiometric nature and strong hygroscopic property as it is rich in oxygen functionalities [7], [8]. The removal of these oxygen moieties is a vital topic that determines the properties of the ultimate product and to which extent RGO will resemble pristine graphene [9]. Therefore, finding a suitable reducing agent for this task is very important. The first known reducing agent, H_2S was introduced in 1934 [10] and there onwards, a large number of reductants have been used to reduce GO. Among these, hydrazine ($N_2H_4 \cdot H_2O$) is the best-known reductant in terms of giving RGO with improved electrical and structural properties resembling pristine graphene to a large extent [11]. However, hydrazine suffers from some problems which have encouraged researchers to find alternative reducing agents with qualities comparable to hydrazine. One such problem which has led to the introduction of the "green reduction" approach in this field is the toxic nature of hydrazine to the environment as well as to the living organisms [12]. The first known environmentally friendly reducing agent is ascorbic acid (2010), and it has verified to be the best alternative to toxic hydrazine and is being studied currently [13]. This review is mainly focused on the chemical reduction of GO by ascorbic acid which is a non-toxic, inexpensive organic acid Fig. 1.

2. Need of green reducing agents

When it comes to the term "green reduction", it includes both chemical and non-chemical approaches. Chemical reduction of GO involves a reducing agent and sometimes a stabilizer. On the other hand, non-chemical reduction of GO, such as hydrothermal and solvothermal reduction [14], electrochemical reduction [15], UV and solar irradiation [16], supercritical fluids-based reduction [17] and photothermal reduction [18] is also being studied for years [12]. Nevertheless, chemical reduction has taken the priority over non-chemical reduction methods because of the high quality and productivity of acquired RGO and the ability to make stable dispersions essential for many applications [19,20].

Though hydrazine is an effective and efficient reductant for RGO synthesis, it suffers from a number of limitations. Hydrazine and its by-products are toxic to both the living organisms and the environment [21]. It is also unstable and could have detrimental effects and hence, care should be taken in handling such chemicals. Moreover, remediation of hazardous wastes generated may significantly increase the cost on industrial scale [22,23]. Also, if the final product contains residues of these hazardous chemicals, it may not be suitable for many applications particularly in biomedical applications and water remediation. To counteract above-mentioned problems, scientists have focused more on finding environmentally friendly reducing agents with the reducing power similar to or higher than hydrazine.

The thirst of finding such alternatives has introduced a number of green reductants within the last decade. They include organic acids, plant extracts, microorganisms, sugars, antioxidants, amino acids and proteins, *etc.* All these reductants are known as "green reducing agents" as they are non-toxic or environmentally friendly. However, as nothing is perfect, these reductants may also come with some limitations. Sometimes one agent may need a supporting agent to perform complete reduction or a stabilizer to prevent aggregation of RGO sheets, and the need of performing repeated centrifugation or filtration to remove excess reductant or its by-products. Therefore, the applicability of these green reductants is still under study for large-scale of RGO synthesis [24]. In one such environmentally friendly reduction method, Loryuenyong *et* al. have performed reduction of exfoliated GO solution in deionized water, in the absence of a reducing agent for 4 days at 95 °C [25]. Among all the green reducing agents mentioned above, ascorbic acid (AA), also known as Vitamin C, has attained a great interest in the field of RGO synthesis due to many reasons. The chemistry and the reducing behaviour of AA towards GO compared to other agents will be discussed in here.

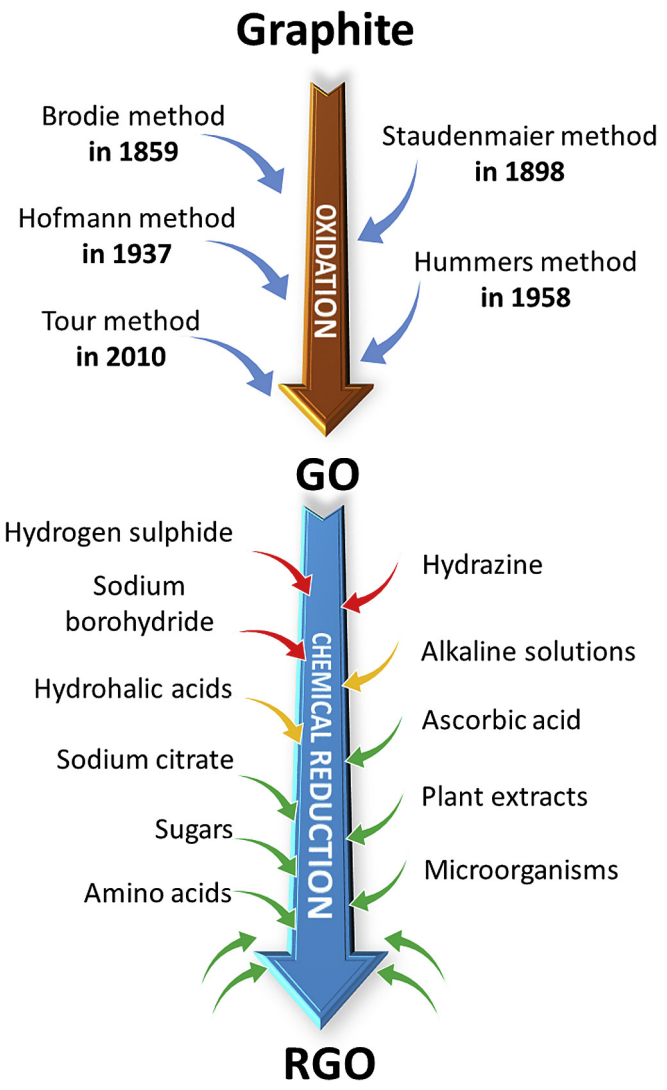

Fig. 1. Schematic representation of the major oxidation methods of graphite to graphene oxide and the chemical reduction of graphene oxide by some reductants. (A colour version of this figure can be viewed online.)

2.1. Organic acids

The use of organic acids and/or their salts as reducing agents is