



A rapid low-temperature synthetic method leading to large-scale carboxyl graphene



Ning Pan^{a,b}, Debin Guan^b, Yuntao Yang^b, Zhenling Huang^a, Ruibing Wang^{c,*}, Yongdong Jin^{a,*}, Chuanqin Xia^{a,d,*}

^a College of Chemistry, Sichuan University, Chengdu 610064, China

^b New Materials R&D Center, Institute of Chemical Materials, Chinese Academy of Engineering Physics, Mianyang 621900, China

^c Targeted Therapies, BTG International, 447 March Road, Ottawa, Ontario K2K 1X8, Canada

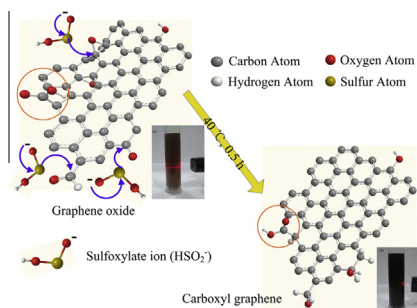
^d MOE Key Laboratory of Radiation Physics and Technology, Institute of Nuclear Science and Technology, Sichuan University, Chengdu 610064, China

HIGHLIGHTS

- A facile, low-temperature, and environmental friendly synthetic method leading to carboxyl graphene.
- A highly selective reducing agent.
- A functional graphene product, carboxyl graphene, with relatively high surface area.
- Feasibility for large-scale production.
- A proposed mechanism for the novel synthesis of carboxyl graphene.

GRAPHICAL ABSTRACT

Carboxyl graphene was prepared by selective reduction of the epoxy and carbonyl groups on graphene oxide using thiourea dioxide, while carboxyl groups were left behind. The carboxyl graphene possessing relatively high surface area still contains approximately 6.9 ± 1.6 mmol of carboxyl groups per gram of material. The method is feasible for scale-up.



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ABSTRACT

We report a rapid, environmentally-friendly and cost-effective route for the preparation of a graphene-based nanomaterial, carboxyl graphene (aka. reduced graphene oxide, RGO) from graphene oxide (GO). Carboxyl graphene was prepared on the scale of several grams through the reduction of GO by thiourea dioxide (TUD) at a relatively low temperature ($40\text{ }^\circ\text{C}$) in an alkaline medium ($\text{pH} = 10$). The reduction of GO was confirmed by FT-IR, UV-vis, X-ray photoelectron, and Raman spectroscopy. In addition, this reduction was also confirmed by thermal gravimetric analysis, X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Characterizations of these materials demonstrated that selective reduction of the epoxy and carbonyl groups occurred on the surface of GO, while carboxyl groups were left behind. In addition, the conjugation of the carbons in the structure was restored through this reduction and a single-layer of carboxyl graphene (with a thickness of 0.80 nm , as observed by AFM) was obtained under these conditions. Carboxyl graphene had a high surface area (of $454.52\text{ m}^2\text{ g}^{-1}$) and contained approximately 6.9 ± 1.6 mmol of carboxyl groups per gram of material, as determined via Boehm titration. The mechanism for selective reduction of the epoxy and carbonyl groups on GO to form carboxyl graphene by TUD is proposed and discussed in detail.

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* Corresponding authors. Tel.: +1 613 801 1840 (R. Wang), +86 28 85412343 (Y. Jin, C. Xia).

E-mail addresses: ruibing.wang@btgplc.com (R. Wang), jinyongdong@scu.edu.cn (Y. Jin), xiachqin@163.com (C. Xia).

1. Introduction

Graphene [1], a new allotrope of elemental carbon, possesses a structural unit that is similar to benzene rings that are connected to each other forming a two-dimensional planar honeycomb structure. Graphene has remarkable thermal, electronic, optical and mechanical properties [2–5] owing to its unique planar structure and extended conjugation. These properties make graphene very suitable for applications in sensors [6,7], supercapacitors [8], field effect transistors (FET) [9], and various other devices. Graphene has a high specific surface area (with a calculated value of $2630 \text{ m}^2 \text{ g}^{-1}$) [10], and thus has potential applications as a catalyst or as a catalyst support material for methanol oxidation [11].

However, the parent graphene has poor solubility and processability, which thus restrict its applications. Therefore, the covalent modification of graphene has recently stimulated a vast amount of research to improve the properties of graphene. This research has demonstrated that graphene can be covalently functionalized by various direct functionalization methods, such as diazotization [12–15], 1,3-dipolar cycloadditions [16] and nitrene addition [17]. An additional indirect method involves functionalizing the intermediate product, graphene oxide (GO), which typically bears hydroxyl, epoxy, carbonyl, and carboxyl groups [18]. Alternatively, residual oxygen-containing groups (such as epoxy groups) on the surface of reduced graphene oxide (RGO) can be reacted with the functional groups of various molecules to introduce new functional groups [19]. At present, various functional groups have been grafted onto GO or graphene, including poly-L-lysine [18], aryl addends [13,14], amines [15], polyamidoamine [16], sulfonic acid [12], porphyrin [20], C_{60} [21], and poly(vinyl alcohol) [22]. All of the above functional groups could also further extend the application of graphene into various areas, such as for biosensors [18], graphene/polymer composites [19], dye-sensitized solar cells [15], and water desalination [12].

It is well known that carboxyl groups play an important role in organic synthesis, and are precursors to various compounds via ammonification, acylation and esterification reactions [16,20–22]. Yuge et al. reported that the carboxyl groups should mainly be localized at the edge of graphene plane [23], which are easily modified and provide excellent precursors for various graphene derivatives and/or composites without damaging or distorting the graphene plane. However, there are currently only a few reports in the literature describing the synthesis of carboxyl graphene [24,25].

Herein, we describe a rapid (requiring 30 min or less) and low temperature (40°C) method for the chemical reduction of GO. This method employs an environmentally-friendly reducing agent, thiourea dioxide (TUD), and is performed under nitrogen protection in an alkaline solution. The epoxy and carbonyl groups on the surface of GO can be selectively reduced by TUD, leaving functional carboxyl groups behind so that a significant degree of the conjugation of graphene can be restored. The selective reduction allows formation of carboxyl graphene (RGO), which will be further processed or incorporated into devices or other composite materials through the functionalization of the carboxyl groups. A tentative reaction mechanism for this process is proposed and discussed. To the best of our knowledge, the method described in this report represents the first time that TUD has been used as a reducing agent for the preparation of carboxyl graphene under extremely mild conditions and through a facile method. This study further advances the oxidation/reduction method and presents an extremely simple, environmentally-friendly, and cost-effective method to both selectively reduce GO and to prepare carboxyl graphene, which has a high specific surface area of $454.52 \text{ m}^2 \text{ g}^{-1}$. Meanwhile, $6.9 \pm 1.6 \text{ mmol}$ of the surface carboxyl groups were retained per gram of graphene.

2. Materials and methods

2.1. Materials

Graphite powder (purity $\geq 99.95\%$) with particle diameters of no more than $1.3 \mu\text{m}$ was obtained from the Aladdin Chemistry Co., Ltd. (Shanghai, China). Other chemicals, including KMnO_4 , concentrated sulfuric acid (95–98%), H_2O_2 (30%), thiourea, methanol, ethanol, NH_4HCO_3 , aqueous ammonia and concentrated hydrochloric acid (36–38%) were supplied by Chengdu Forest Science and Technology Development Co., Ltd. (Chengdu, China). All of the chemicals were of analytical reagent grade and used as received without further purification. TUD was prepared in the laboratory by the oxidation of thiourea with H_2O_2 (as shown in the Supporting Information).

2.2. Synthesis of graphite oxide

Graphite oxide was synthesized from graphite powder according to a modified Hummers method [26]. Initially, 10 g of graphite powder and 240 mL of 98% sulfuric acid were placed in a 2 L beaker. This mixture was then mechanically stirred for 30 min while being cooled in an ice bath, and 60 g of KMnO_4 was slowly added into the mixture as it was stirred and kept at 0°C . The mixture was then stirred at 0°C for another 2 h and in a water bath at 35°C for 30 min, before 200 mL of deionized (DI) water was added to the mixture as it was kept in an ice bath. Next, the mixture was placed in an oil bath and kept at a temperature of 95°C for 15 min. The mixture was subsequently cooled to 60°C before 1 L of DI water and 120 mL of hydrogen peroxide (30%) were added into the mixture in sequence, and the mixture turned bright yellow. After the mixture was allowed to settle for one day, the clear supernatant was decanted. Subsequently, 1 L of DI water and several drops of concentrated hydrochloric acid were added into the remaining mixture under stirring and the mixture was allowed to settle for one day before the clear supernatant was decanted. This process was repeated at least five times until no SO_4^{2-} remained in the supernatant. Graphite oxide powder (18 g) was obtained by filtering the supernatant with a $0.22 \mu\text{m}$ Millipore membrane and drying under vacuum at 45°C .

For the traditional centrifugation dialysis method in purifying graphite oxide, the bright yellow mixture was filtered, and the obtained filter cake was washed repeatedly with 5% HCl solution under centrifugation at 4000 rpm in order to remove residual salts. The sediment in the mixture was collected by centrifugation, and subsequently dialyzed for 1 week in DI water until the dialysate was neutral. Finally, the wet graphite oxide was dried under vacuum at 45°C .

2.3. Synthesis of carboxyl graphene

Initially, 200 mg of graphite oxide powder was dispersed into 200 mL of DI water under ultrasonication (360 W) with a FS-1200 ultrasonic processor for 1 h to yield a homogenous brownish yellow aqueous GO dispersion with no visible precipitation. After the pH of the aqueous dispersion was adjusted to 10 by addition of aqueous ammonia, 0.2 g of TUD was added into the aqueous GO dispersion and the dispersion was stirred for 0.5 h at 40°C under nitrogen protection. Until the reduction was completed, several drops of dilute hydrochloric acid (5%, w/v) were added into the as-prepared carboxyl graphene dispersion to cause the aqueous ammonia to form a salt that was washed away with DI water as it was filtered. Finally, the black carboxyl graphene product was obtained after the filtered residue was freeze-dried for one day (yield: $\sim 54\%$).

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