

The novel synthesis of highly water-soluble few-layer graphene nanosheets by a simple one-pot chemical route and without any modification



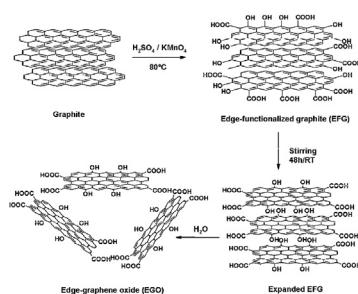
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HIGHLIGHTS

- Water-soluble graphene was synthesized by a simple one-pot and scalable process.
- This process did not utilize any reduction agents, stabilizer and ultrasonication.
- The effects of oxidant amount and reaction time on process were explored.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a simple one-pot and scalable process including mild oxidation of graphite in mixture of $H_2SO_4/KMnO_4$ at $60^\circ C$ was developed to synthesize water-soluble graphene. In this process, effects of the oxidant amount and reaction time on oxidation and exfoliation degree of graphite were explored. At this temperature, most oxygen-containing functional groups were introduced at the edges of graphite by preserving the pristine sp^2 carbon-bonded structure. These functional groups were responsible for exfoliation of edge-functionalized graphite (EFG) sheets to edge-graphene oxide (EGO). Various techniques including atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman and Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction pattern (XRD) and direct-current measurements proved that resulting EGO was formed from few-layer graphene nanosheets (GNS) with sub-2 nm thickness, low-defect sites in basal plane owing good solubility in water from pH 6 to 11 through electrostatic stabilization, as determined by zeta-potentiometry. This low-cost and high-efficiency solution processing techniques has enabled to produce aqueous graphene dispersions without need to use polymeric or surfactant stabilizers for many technological applications.

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1. Introduction

Since discovery of graphene in 2004, graphene has attracted global attention as new building block for carbonaceous-based materials due to high electrical [1] and thermal conductivity [2], excellent mechanical strength [3], large specific surface area [4] and

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low-cost large-scale production process rather than carbon nanotubes (CNTs) [5]. These properties provide many applications of graphene in composites of various fields such as catalysis [6], energy storage devices as electrode for batteries [7] or super capacitors [8], sensors [9], electromagnetic interference shielding [10], etc.

The developed techniques for preparing graphene can be classified into two main categories, which are bottom-up and top-down approaches [11]. The bottom-up approach is commonly substrate-based method such as chemical vapor deposition (CVD) [12], epitaxial growth [13] and growth of graphene from metal-carbon molten [14]. These methods have a high-cost and a low-production rate [15]. Organic synthesis of graphene from molecular building blocks [16,17] also suffers from the size limitation of obtained graphene and occurrence of side reactions [18]. In top-down approach, graphene can be produced by the exfoliation of graphite using, for example, mechanical cleavage, liquid-phase exfoliation, chemical and electrochemical exfoliation and so on [19]. Graphene was first exfoliated mechanically from graphite using a scotch tape in 2004 [20]. Although this method produces graphene of the highest quality and least defects, it is limited due to low-productivity [21]. Liquid-phase exfoliation can produce high-quality graphene without defects and functional groups [22–24], but in this process, the surfactants and toxic solvents have been applied which hardly removed and affected graphene properties [19]. Of these methods, the chemical exfoliation method is thought to be an efficient route for high-yield production of graphene with low-cost. This approach that is well-known as Hummers method [25] includes chemical oxidation of graphite in strong oxidizers mixture for preparation of graphite oxide. Graphite oxide is then delaminated into graphene oxide (GO) via ultrasonication. During oxidation of graphite, a large number of pendent polar groups, such as hydroxyl and epoxide would be introduced on the surface and carboxylic acid at edges by partial breakage of sp^2 - sp^2 bonds into sp^3 - sp^3 bonds which makes GO hydrophilic and water-dispersible, but insulator [26,27]. To restore π -conjugated structure, GO is subsequently reduced into reduced graphene oxide (rGO) with toxic and expensive reductants ($NaBH_4$ or hydrazine). The pristine sp^2 carbon-bonded structure has been repaired by reduction incompletely. So, there are many structural defects in resulting graphene [28]. Contrary to GO, graphene is intrinsic hydrophobic which would not be dispersed in water, so its high tendency to restacking through van der Waals interactions results formation of graphite [29].

Water-dispersible graphene have been widely applied in biosensors [30], biomedicine [31] and electronic [32]. In order to improve its water-solubility, graphene sheets have been functionalized via covalent [33–35] or non-covalent [36,37] coupling reactions. However, there are some limitations in these approaches reported so far such as long and complexity of process and need for stabilizer [38]. Although graphene dispersion could be improved by anchoring polymers and surfactants onto the graphene sheets, the presence of these substances is undesirable for most applications [39,40]. Therefore, facile and low-cost approach to prepare low-defect graphene with good dispersibility without use of stabilizers is highly desirable.

In this study, we report a simple and one-step chemical route to graphene nanosheets (GNS) by heating the mixture of H_2SO_4 /graphite at 60 °C following by gradually adding $KMnO_4$ as oxidant and stirring for 48 h at room temperature. This temperature is higher than that used in hummers method (where, $KMnO_4$ is added to the mixture at temperature below 5 °C) which would cause oxidation of graphite edges only. In this edge-functionalized graphite (EFG), hydroxyl and carboxyl groups are introduced at edges by preserving the basal plane structure, improving water-

solubility of graphene and preventing the graphitic sheets from aggregating in solution. Many researchers attempted to prepare GNS from EFG. EFGs have been obtained by grafting the carboxyl groups [41], organic [42,43], dendritic [44] and polymer [45] molecules to the edges of graphite following by strain-induced delamination of EFG to GNS for various applications.

Controlling the oxygen content in graphene-based compounds will be effective on their properties and for tailoring the functionalities appropriate to their application [46]. The oxygen content in these compounds can be changed by several factors such as oxidation time, oxidant and reductant and their dose, temperature control of the process and so on [46–55].

In our process, EFG was obtained by functionalizing graphite edges with oxygen-containing groups while controlling for amount of $KMnO_4$ and reaction time as effective factors on oxidation and exfoliation degree of graphite during the process. The most exfoliation of EFG was achieved with 2 g $KMnO_4$ at 48 h stirring time. More importantly, the resulting edge-graphene oxide (EGO) was dispersed into water without need to sonicate and use stabilizer which contained few-layer GNS with stability for 12 months and concentration of 1.6 and 0.3 mg/mL for dispersion and solution, respectively.

2. Experimental

All materials were purchased from the Merck Company without further purification.

2.1. Synthesis of EFG samples

1 g natural graphite flake ($\leq 50 \mu m$) and 0.1 g $NaNO_3$ in 23 mL H_2SO_4 were stirred. The obtained homogenous mixture was heated in a water bath of 60 °C. Then, 1, 2 and 4 g $KMnO_4$ were added very slowly in separate experiments for exploring the effect of oxidant amount. The mixture was stirred at room temperature for 48 h. The prepared samples were named EFG (1), EFG (2) and EFG (4), respectively. For studying effect of reaction time, the mixture containing 2 g $KMnO_4$ was stirred at room temperature for 12, 24, 48 h and prepared samples were named EFG (12), EFG (24) and EFG (48), respectively. Upon completion of given time for all samples, the mixture was poured onto 150 ml of a mixture of H_2O_2/H_2O (1:30 v/v) to stop the reaction. The black precipitation was washed with 0.1 M HCl to remove the impurities and rinsed several times with deionized water until pH value reached around 7. The black homogeneous suspension was vacuum-filtered through the porous cellulose filter membrane (0.45 μm pore size, Sartorius) and dried at 70 °C in vacuum oven for 12 h to obtain graphene nanosheets.

2.2. Synthesis of GO

GO was prepared according to hummers method [56]. The mixture of 0.5 g graphite, 0.5 g $NaNO_3$ and 23 mL H_2SO_4 was stirred in an ice bath (0–5 °C) for half hour. Next, 3 g $KMnO_4$ was added very slowly during 2 h. The mixture was stirred in the same bath for 1 h, followed by stirring for 2 h at 35 °C until it became pasty brownish. Next, 40 mL water was added gradually. The temperature was raised to 90 °C and the color changed to brown color. Then, 150 mL deionized (DI) water and 5 mL H_2O_2 (30%) were added to reduce residual permanganate to soluble manganese ions. The brown suspension was filtered, washed with 0.1 M HCl and then DI water several times, dried at 70 °C for 12 h to obtain brownish graphene oxide powder.

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