



Synthesis procedure and type of graphite oxide strongly influence resulting graphene properties

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ABSTRACT

Graphene is the one of the most intensively studied materials for its unique mechanical, electrical and thermal properties. The aim of this study is to compare the significant differences between individual graphenes prepared using different graphite oxides as starting materials. Graphene was prepared by chemical and thermal reduction of five different graphite oxides, which were prepared according to Brodie, Hofmann, Hummers, Staudenmaier and Tour method. Due to the significant differences in the composition of graphite oxide used for synthesis significant differences can be also observed in graphene prepared by chemical and thermal reduction of starting material. The synthesized graphene materials were characterized in detail using different chemical and structural analytical methods. Significant level of unintentional nitrogen doping was observed on chemically reduced graphite oxide synthesized by permanganate methods. Also the degree of exfoliation and the corresponding structural properties were strongly dependant on the degree of oxidation of the starting graphite oxide. Finding the best synthesis procedure of graphene with desirable properties is essential to optimize technologies in large scale production of graphene for its utilization in industrial applications.

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1. Introduction

Due to its unique electrical, optical and mechanical properties graphene has been intensively studied since its isolation in 2004 [1–3]. These unique properties make graphene a highly promising material for a wide range of applications in modern electronics and electrochemical power sources such as supercapacitors, fuel cells or batteries which are of extreme importance for the green energy production and storage [4–9]. Thanks to extremely high surface area, graphene also seems to be useful for removal of toxic contaminants from environment [10–12]. A number of various methods for the synthesis of graphene have been reported. One possibility how to obtain graphene directly is the mechanical exfoliation of graphite [13], other common methods are CVD techniques [14]. CVD-based graphene layers are of large size, high-quality and they are important for optoelectronic or microelectronic devices. However, for applications in the field of electrochemical power sources and composites, graphene should be produced in larger amounts [15–17]. For this purpose, the reduction of graphite oxide seems to be the most suitable method. In this method graphite precursor is oxidized

in acidic environment using chlorate or permanganate methods to graphite oxide. Subsequently, the formed graphite oxide is reduced by different routes yielding graphene. Graphite oxide can be reduced using microwaves [18], by ion bombardment [19], or by chemical or thermal reduction [20,21]. Various reducing agents for the chemical reduction have been reported from which the most common are hydrazine and its derivatives [20], hydroquinone [22], complex hydrides [23] or nascent hydrogen [24–26]. Graphite oxide can be also reduced thermally in inert (nitrogen) or reducing atmosphere (hydrogen). The thermal reduction of graphite oxide produces graphene with the highest degree of exfoliation and also largest surface area [27,28]. The thermal reduction is usually performed by rapid heating in suitable non-oxidizing atmosphere. The mechanism of the thermal reduction has been described as a process of decomposition of oxygen containing functional groups forming carbon dioxide, carbon monoxide and water during the heating. The evolved gaseous products increase interlayer pressure, which eventually leads to the exfoliation. However, a few papers described that the process is much more complex accompanied by a release of more complex species during exfoliation [29,30].

In this study, we investigated in detail the influence of starting graphite oxide preparation method on the composition, structure and properties of thermally and chemically reduced graphene. For these syntheses we selected the methods which can be easily scaled

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up for industrial production using rapid thermal exfoliation in nitrogen atmosphere and chemical reduction using hydrazine in alkaline environment. For the synthesis of graphite oxides the chlorate based methods (Brodie, Staudenmaier and Hofmann method) and permanganate methods (Hummers and Tour method) were applied. Chemical composition of the obtained products was investigated in detail using X-ray photoelectron spectroscopy (XPS) and elemental combustion analysis. The structural properties were investigated by scanning electron microscopy (SEM), Raman spectroscopy, X-ray diffraction (XRD), surface area measurement (BET method) and the thermal stability towards oxidation was probed by simultaneous thermal analysis (STA). In addition basic electrochemical properties were investigated using cyclic voltammetry and various redox probes.

2. Experimental

We prepared five different graphite oxides from pure graphite microparticles (2–15 μm , 99.9995%) from Alfa Aesar, Germany. Sulphuric acid (98%), nitric acid (68%), fuming nitric acid (>98%), potassium chlorate (99%), potassium permanganate (99.5%), sodium nitrate (99.5%), hydrogen peroxide (30%), hydrochloric acid (37%), silver nitrate (99.5%), phosphoric acid (85%), barium nitrate (99.5%), potassium hydroxide (>99.9%), hydrazine hydrate (99%), methanol (>99.9%) and N,N-dimethylformamide (DMF) were obtained from Penta, Czech Republic. Nitrogen (99.9999%) was obtained from SIAD, Czech Republic.

Graphite oxide prepared by the Brodie method was termed BR-GO [31]. Fuming nitric acid (>98%, 62.5 mL) was added to a reaction flask containing a magnetic stir bar. The mixture was then subsequently cooled to 0 °C and graphite (5 g) was added. The mixture was stirred to obtain a homogeneous dispersion. While keeping the reaction flask at 0 °C, potassium chlorate (25 g) was slowly added to the mixture. Upon the complete dissolution of potassium chlorate, the reaction flask was loosely capped to allow the escape of the gas evolved and the mixture was stirred for 20 h at 40 °C. Upon completion of the reaction, the mixture was poured into 3 L of deionized water and decanted. Graphite oxide was then redispersed in HCl solution (5%, 3 L) to remove sulphate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction on chloride ions was achieved. Graphite oxide slurry was then dried in a vacuum oven. The composition obtained by elemental combustion analysis was 59.99 at.% C, 23.06 at.% O, 16.82 at.% H and 0.13 at.% N. More details are given in [Supporting Information](#).

Graphite oxide prepared according to the Hofmann method was termed HO-GO [32]. Sulphuric acid (98%, 87.5 mL) and nitric acid (68%, 27 mL) were added to a reaction flask (Pyrex beaker with thermometer) containing a magnetic stir bar. The mixture was then cooled by immersion in an ice bath for 30 min. Graphite (5 g) was then added to the mixture with vigorous stirring motion. While keeping the reaction flask in the ice bath, potassium chlorate (55 g) was slowly added to the mixture. Upon the complete dissolution of potassium chlorate, the reaction flask was then loosely capped to allow the escape of the gas evolved and the mixture was continuously stirred for 96 h at room temperature. The mixture was poured into 3 L of deionized water and decanted. Graphite oxide was then redispersed in HCl solution (5%, 3 L) to remove sulphate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction on chloride and sulphate ions was achieved. Graphite oxide slurry was then dried in a vacuum oven. The composition obtained by elemental combustion analysis was 47.45 at.% C, 28.81 at.% O, 23.71 at.% H and 0.02 at.% N. More details are given in [Supporting Information](#).

The third graphite oxide was synthesized similarly to the Hummers method and was termed as HU-GO [33]. Graphite (5 g)

and sodium nitrate (2.5 g) were stirred with sulphuric acid (98%, 115 mL). The mixture was then cooled to 0 °C. Potassium permanganate (15 g) was then added over a period of 2 h. During the next 4 h, the reaction mixture was allowed to reach room temperature before being heated to 35 °C for 30 min. The reaction mixture was then poured into a flask containing deionized water (250 mL) and heated to 70 °C for 15 min. The mixture was then poured into deionized water (1 L). The unreacted potassium permanganate and manganese dioxide were removed by the addition of 3% hydrogen peroxide. The reaction mixture was then allowed to settle and decant. The obtained graphite oxide was then purified by repeated centrifugation and redispersing in deionized water until a negative reaction on sulphate ions was achieved. Graphite oxide slurry was then dried in a vacuum oven. The composition obtained by elemental combustion analysis was 41.38 at.% C, 31.80 at.% O, 26.80 at.% H and 0.02 at.% N. More details are given in [Supporting Information](#).

Graphite oxide prepared by the Staudenmaier method was termed ST-GO [34]. Sulphuric acid (98%, 87.5 mL) and fuming nitric acid (>98%, 27 mL) were added to a reaction flask containing a magnetic stir bar. Subsequently, the mixture was cooled to 0 °C and graphite (5 g) was added. The mixture was vigorously stirred to avoid agglomeration and to obtain a homogeneous dispersion. While keeping the reaction flask at 0 °C, potassium chlorate (55 g) was slowly added. Upon the complete dissolution of potassium chlorate, the reaction flask was loosely capped to allow the escape of the gas evolved. Then the mixture was continuously stirred for 96 h at room temperature. The mixture was then poured into deionized water (3 L) and decanted. Graphite oxide was redispersed in HCl solution (5%, 3 L) to remove sulphate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction on chloride and sulphate ions was achieved. Graphite oxide slurry was then dried in a vacuum oven. The composition obtained by elemental combustion analysis was 70.47 at.% C, 17.94 at.% O, 11.34 at.% H and 0.25 at.% N. More details are given in [Supporting Information](#).

The last graphite oxide prepared according to the Tour method (TO-GO) [35]. Firstly the mixture of concentrated sulphuric acid and phosphoric acid in a volume ratio 9:1 (360 mL:40 mL) was cooled under 0 °C. Next we added graphite (3.0 g) and subsequently potassium permanganate (18.0 g). The ongoing reaction heated the mixture itself to 20–25 °C due to the exothermic process. The reaction mixture was stirred and then heated to 50 °C during 12 h. Then was the mixture cooled to 20 °C and poured onto to ice with hydrogen peroxide (3.0 mL) to remove an excess of permanganate ions and manganese dioxide. After the ice dissolve 30% hydrogen peroxide was added to remove remaining unreacted potassium permanganate and manganese dioxide. The obtained graphite oxide was then purified by repeated centrifugation and redispersing in deionized water until a negative reaction on sulphate ions was achieved. Graphite oxide slurry was then dried in a vacuum oven. The composition obtained by elemental combustion analysis was 34.83 at.% C, 36.23 at.% O, 28.94 at.% H and 0.00 at.% N. More details are given in [Supporting Information](#).

Chemically reduced graphene denoted “CRG” was prepared by reduction with hydrazine hydrate. 1 g of graphite oxide was dispersed in 1 L of deionized water by ultrasonication (150 W, 60 min). The suspension was alkalized to pH 10 by 1 M KOH. 10 mL of hydrazine hydrate was added to the reaction mixture and the solution was kept under reflux for 24 h. The obtained CRG was separated from the reaction mixture by suction filtration using a nylon membrane with 0.45 μm porosity and repeatedly washed with deionized water and methanol. Prior to further use, CRG was dried in a vacuum oven at 60 °C for 48 h.

The thermal reduction–exfoliation of graphite oxide was performed at 1000 °C in quartz glass reactor in nitrogen atmosphere. Accordingly, samples were termed “TRG”. Graphite oxide (0.1 g)

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