

Chemical synthesis of single-layer graphene by using ball milling compared with NaBH₄ and hydroquinone reductants

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Graphene materials especially single-layer graphene have been identified as a new generation of nanomaterials having various potential applications in material industries. However, the synthesis procedure of single-layer graphene to improve its quality, size and amount has been still under research for commercial applications. The graphene oxide (GO) is synthesised from graphite by Hummer's spontaneous approach which is the most suitable reaction for a large-scale production. For the single-layer graphene, in this work, GO was exfoliated by using a ball milling in an inert atmosphere. Owing to using ball milling as intermediate treatment degreased oxygen functional groups and number of layers, it facilitates to synthesise graphene. Sodium borohydride (NaBH₄) and hydroquinone were used as a reductant for the chemical conversion of the exfoliated GO to graphene. The results showed that due to the strong reduction feature, both reducing agents can be applied in the graphene production. As a preferred reductant, hydroquinone can be successfully applied for the synthesis of the single-layer graphene compared to NaBH₄. The obtained graphene particles by two different chemicals were characterised by various analytical techniques. The big difference in the structure of GO and graphene was observed in transmission electron microscope analysis.

1. Introduction: Graphene is consisting of single sheets of carbon atoms that are bonded together in a repeating pattern of hexa-graphene oxides (GOs). In the 1940s, graphene was first studied theoretically but in the opinion of scientists, it is impossible to be hapenoved two-dimensional materials as graphene. In 2004, Novoselov *et al.* [1] eventually produced a single layer of graphene in Manchester University. Then, the graphene production has improved rapidly [2–6]. Nowadays, graphene has been extensively investigated because of its special properties such as conductive, strong, flexible, and transparent. They are used in various applications in the production of solar cells, transistors, transparent screens, camera sensors, DNA sequencing, gas sensing, material strengthening, and desalination [2–5].

Chen and Yan [6] prepared 3D architectures of graphene via a one-step mild chemical reduction with reducing agents NaHSO₃, Na₂S, vitamin C, Hydrogen iodide (HI), and hydroquinone. The synthesis of graphene was performed at 95°C under atmospheric pressure. Prepared 3D architectures of graphene have demonstrated excellent properties and applications such as super capacitors, hydrogen storage, and supporting material for the catalysts.

In general, graphene can be prepared by four different methods: micromechanical exfoliation (Scotch tape), chemical vapour deposition, epitaxial growth on SiC, and solution exfoliation of GO [7–9]. For latest methods, generally strong oxidising agents (e.g. HNO₃, KMnO₄, and/or H₂SO₄) were used [9].

Hummers [10] reported a useful method for the synthesis of GO. In this method, the oxidation of graphite to graphitic oxide was accomplished by treating with sodium nitrate and potassium permanganate in concentrated sulphuric acid [3, 10]. Nowadays, this method was used to prepare a large graphitic film as shown in many papers [4–17]. The produced GO was generally performed by modified Hummers method. GO production is also used in large-scale production by this method [14]. In this Letter, they prepared GO by oxidising purified natural flake graphite in distilled water with ultrasonic waves. The properties of the products were determined by UV–vis spectrophotometer, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscope (SEM). The UV–vis spectra of GO

results showed maximum absorption peak at 237 nm. XRD results demonstrated 2 θ of 12.02° and SEM analysis results showed a thin homogeneous graphene film [6]. 2D structure GO films were prepared by the modified Hummer method. The results of transmission electron microscope (TEM) and dynamic force microscope (DFM) analyses showed the successful preparation of GO films on microscopic morphology. Elemental analysis showed the component of O in GO films was about 51% and C, H, and S were also observed. Oxygen-containing groups and characteristic peaks in FTIR and XRD analysis approved the successful preparation of GO sheets [7].

Hydrazine and NaBH₄ were used as reductant materials for producing GO from natural graphite by using modified Hummers method. Obtained GO powder was put to a flask and pure water was added. After addition of hydrazine monohydrate to the flask, it was immersed in an oil bath at 80°C. In this process, the chemically reduced graphite oxide (RGO) was obtained and the structure and elemental analysis were identified by using X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), XRD, and SEM [13, 15]. In another study, the reducing character of borohydride (NaBH₄) and hydrazine (N₂H₄) was compared [11, 18]. The results showed that the sheet resistance of NaBH₄-reduced films was much lower than that of N₂H₄-reduced films exhibiting similar C–O composition.

The facile synthesis and application of Ag-chemically converted graphene (CCG) nanocomposites were produced by using Hummers method. By generation of Ag nanoparticles, the reduction of GO sheets was accompanied. The antibacterial activity of free Ag nanoparticles is retained, which suggests the materials may be used as graphene-based biomaterials [11]. In produced graphene nanosheets in large quantity via graphite oxidation, ultrasonic exfoliation, and chemical reduction, GO powders were prepared by a modification of Hummers and Offerman's method. The obtained samples were analysed using analytical methods, especially TGA analysis found that graphene nanosheets have much lower stability than pristine natural graphite powders [13]. The modified Hummers method has been used for the synthesis of hydrophilic and organophilic graphene nanosheets with poly(sodium 4-styrene sulfonate)

and simultaneously reducing by hydrazine hydrate under hydro-thermal conditions [9].

Currently, many methods have been applied to prepare graphene. Ball-milling is the most common process for graphene synthesis. In several studies, the mill was run in different features [2, 5, 8]. Edge-carboxylate graphite (ECG) was produced by ball milling and analysed by using a finite-element method. The ball-mill machine runs 48 times at 500 rpm, each time with 50 min of ball-milling and 10 min of rest. After the ball milling, the elemental analysis of ECG samples was completed. After ball milling process, elemental analyses showed that the oxygen of ECG samples increased from 0.13 to 15.6%, 19.67, and 26.46%, but the carbon content of ECG samples decreased from 99.64 to 86.89%, 72.09 and 72.04% [2]. In another study, GO was prepared using a modified Hummers method. The GO powder was ball-milled for different durations with zirconium oxide balls of diameter 5 mm and the ball to mass ratio was kept constant at 20:1 with 800 rpm speed in an inert (Ar) atmosphere. The analysis showed that the material of interest was considerably different from GO and very much close to that of CCG [5]. The other research group developed the synthesis ECG nanosheets via ball milling. In the experiment, the pristine graphite and dry ice were placed into a stainless steel capsule containing stainless steel balls of 5 mm in diameter with 500 rpm for 48 h. The final product was freeze dried at -120°C under a reduced pressure (0.05 mmHg) for 48 h to yield of dark black powder [8]. A feasible way is to produce graphene from graphite flakes using wet ball milling exfoliation with the help of carefully selected solvents [19]. Pei and Cheng [12] reviewed the reduction of GO to prepare RGO. They reported that the reduction of GO by chemical reactions has advantage of maintaining the structure of the carbon plane, and thermal annealing at high temperature can facilitate the desorption of various functional groups. A combination of chemical reactions and thermal annealing is more efficient for deoxygenation compared with one-step processes realised by thermal or chemical reduction.

The aim of this Letter is to examine the effect of NaBH_4 and hydroquinone on the reduction of GO to single-layer graphene. For this purpose, GO was first obtained from graphite particles by means of Hummer's method. Subsequently, these GO particles produced were separated into their layers by ball-milling method. Following these operations, the exfoliated GO particles were separately reduced by using NaBH_4 and hydroquinone reductants. As a result, chemical bond characterisation and crystal structure analysis of the produced GO and graphene particles were evaluated by FTIR, XRD, Raman spectroscopy (RS) and microstructure analysis by SEM and TEM images.

2. Experimental

2.1. Synthesis of GO: GO was synthesised from graphite powder, which was purchased from Alfa EASER (99.995%). The experiment was carried according to the modified Hummer's method. First, 5 g of natural graphite and 15 g of KMnO_4 (99.35%, KIMETSAN) were mixed and then, 115 ml of sulphuric acid and nitric acid (1:3) were carefully added to the mixture. This process was performed with continuous stirring at 0°C temperature in an ice-water bath to prevent overheating and explosion.

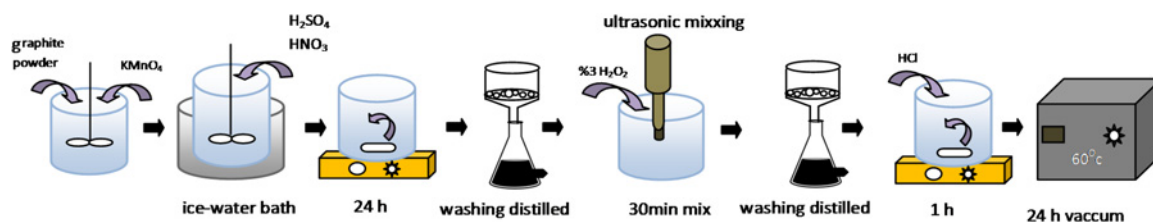


Fig. 1 Schematic diagram of the synthesis GO by using Hummer method

The resultant mixture was stirred for 24 h in a magnetic stirrer at room temperature and washed with deionised water. Then 700 ml of 3 vol.% H_2O_2 was added to the mixture, turning the colour of the solution from dark brown to yellow. The resulting solution was scattered with a prop for 30 min (Bandelin Sonopuls) in an ultrasonic bath. The washing process was repeated and the sample was stirred for 1 h in 30 ml of concentrated HCl with a magnetic stirrer. Then, the mixture was washed again with distilled water. Finally, GO was obtained as slurry. The colloidal solution was dried at 60°C for 24 h under vacuum (Fig. 1).

2.2. Separation of GO layers: GO is transformed to exfoliated GO by high-energy ball milling in inert atmosphere using a Tetsch PM 100 ball-mill machine. GO and ethyl alcohol were placed into the milling machine. The GO powder was ball-milled for 40 h at 500 rpm in atmospheric condition with seven balls (made from zirconium oxide) of diameter 5 mm (Fig. 2). GO separated layers by ball milling was converted to graphene with two reductants.

2.3. Synthesis of single-layer graphene: There are two chemicals for graphene synthesis from the GO. In the former, 100 mg of GO was refluxed in 80 ml of NaBH_4 solution at 100°C for 3 h. Then the reaction mixture was filtered and washed with distilled water and then dried at 60°C under vacuum (Fig. 2).

In the second, 100 mg of dried GO was refluxed in 350 ml of hydroquinone at 100°C for 12 h. Then, the solution was washed with pure water and was dried under the same conditions like in the first procedure (Fig. 2).

2.4. Centrifugal process: To separate single and monolayer of graphene and remove the unexfoliated graphite, samples were exposed to the centrifugal process [9, 19]. The process was carried about 15 min at 6000 rpm (Fig. 3). After centrifuge, the single-layer graphene accumulated as supernatant on the top of the liquid, while a multi-layer graphene and unexfoliated graphite collapsed to the wall. Then graphene products were obtained and dried at 60°C for 24 h under vacuum.

3. Results and discussion: According to the modified-Hummers method, GO was produced by the oxidation of bulk graphite powder in the acidic oxidising medium. The oxidation can be occurred by the oxidising agent attacking the graphene layers. The obtaining GO was subjected to ball milling process to separate the layers into the few layers. During this process, the functional oxygen groups in the structure of GO were removed by ball-milling method, thus creating the new sp^2 band gap of all intermediate stages of the structural evolution [2, 5, 8, 19]. The GO particles were then reduced in graphene using NaBH_4 and hydroquinone solutions. The produced GO and graphene were characterised using FTIR, XRD, SEM, TEM, and RS.

The obtained FTIR spectra for the bond characterisations of the produced GO and reduced graphene particles with hydroquinone solution are given in Fig. 4. According to results, both spectra have characteristic small peaks due to aromatics $\text{C}=\text{C}$ (1618 cm^{-1}), carbonyl/carboxyl $\text{C}=\text{O}$ ($\sim 1750\text{ cm}^{-1}$) and alkoxy

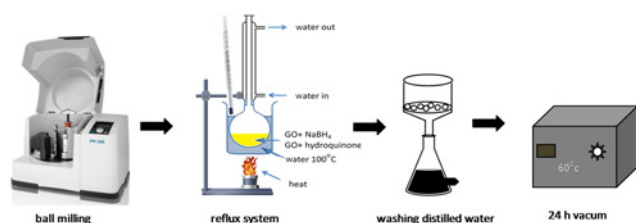


Fig. 2 Schematic diagram of the synthesis graphene from GO



Fig. 3 Centrifugation of graphene samples

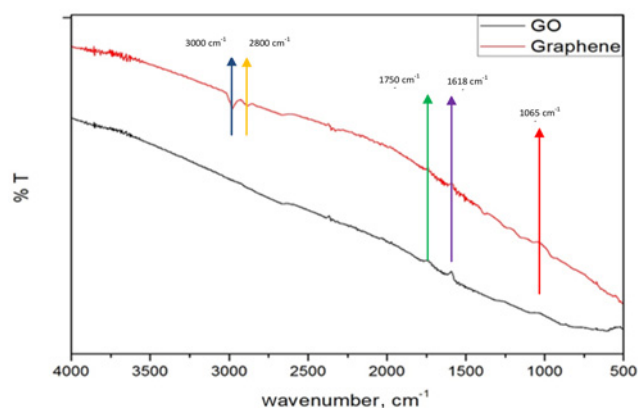


Fig. 4 FTIR spectra of GO and graphene

C–O groups ($\sim 1065 \text{ cm}^{-1}$) [3, 5, 14]. After reduction of GO, the intensities of FTIR peaks corresponding to the oxygen functionalities, such as C=O stretching vibration peak at 1750 cm^{-1} decreased and the C–C vibration peaks weakened at 1618 cm^{-1} [20, 21]. It can be said that there are abundant oxygen-containing groups on the surface due to the C=O peak in the GO spectrum. Peaks at 2800 and 3000 cm^{-1} in the spectrum of graphene are very different than GO peak which corresponding to the bending and stretching modes of OH groups. This hydroxyl group belongs to the formation of hydrogen bonds between graphite and water molecules [3].

The crystal structure and particle size distribution of graphene were characterised by Bruker D8 Advance X-Ray diffraction (Fig. 5). According to the obtained results, it is seen that there is a significant difference between the GO and the graphene spectra. However, there was no significant difference in the crystal structure between the graphene particles obtained with different solutions. The XRD results of GO and graphene show that the crystal structures were not changed by the modification. While the synthesise of graphene from GO with both reductants, the significant characteristic strong diffraction peak around 27° and weak peaks about

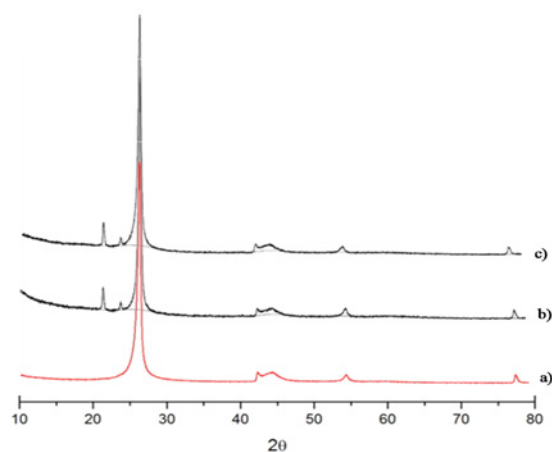


Fig. 5 X-ray pattern
a GO, synthesised graphene using
b Hydroquinone
c NaBH_4

23° , 43° , 54.5° , and 78° were belong to graphite structure [4, 11, 14, 22–27]. In graphene images, appearing a peak about 25.5° is thought to be caused by the pollution during the experiment.

Microstructure images of graphene particles produced with two different reductants are shown in Fig. 6. Based on the figure, it seems to have been separated into layers of graphene sheets. When examined in more detail, it is understood that the size of the graphene sheets is very large and overlapping. It is also seen that the width of these layers varies considerably. However, it is difficult to determine the thickness of each layer by examining these images. Thus, RS and TEM images were examined to investigating the number of layers of the graphene plates [2–4, 7, 11, 27].

The number of carbon layers and separation of the ordered and disordered crystal structures of samples were identified by Raman spectra [3, 4, 11] and the results are in Fig. 7. Owing to its non-destructive properties, RS is widely used for carbon-based materials. The typical Raman spectrum of GO was characterised by a G band at 1590 cm^{-1} and a D band around 1345 cm^{-1} in Fig. 7. These lines appropriated E_{2g} phonon of C sp^2 atoms and breathing mode of k-point phonons of A_{1g} symmetry, respectively [11, 20, 28]. D peak represents the defects or disorders in the carbon structure [3–5, 11]. The ratio of the bands (I_d/I_g) shows the quality of the products. In comparison with GO, I_d/I_g ratio of graphene

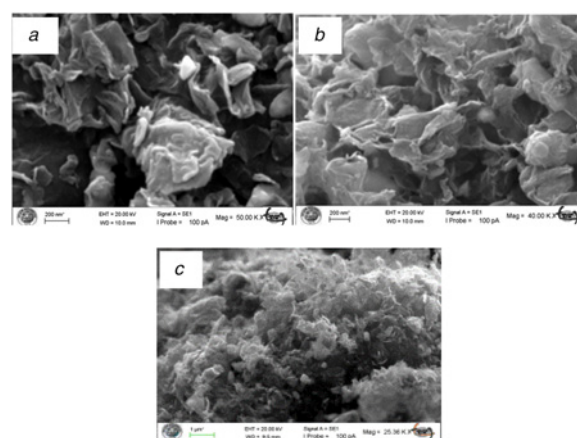


Fig. 6 SEM images
a GO, synthesised graphene using
b NaBH_4
c Hydroquinone

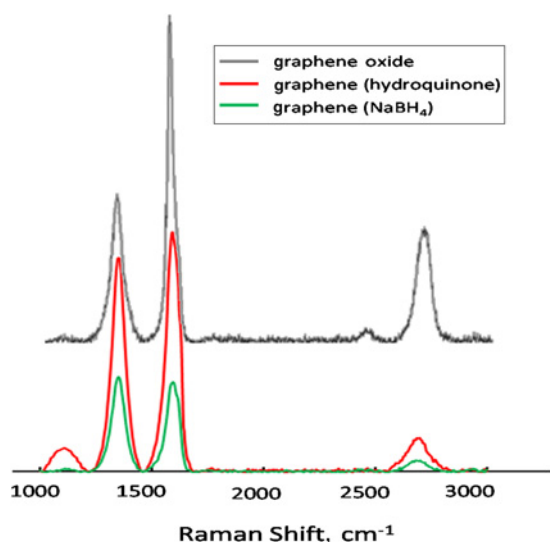


Fig. 7 Raman spectra of GO, synthesised graphene by hydroquinone and NaBH_4

decreased from 0.45 to 0.2. This reduction indicated the decrease of defects of the aromatic structures. 2D is a function of the number of graphene layers (N) which observed at 2700 cm^{-1} [1, 3, 29]. The same characteristic peaks are exhibited by the Raman spectra of the graphene synthesised with NaBH_4 and hydroquinone around 1347 , 1590 , and 2684 cm^{-1} for D, G, and 2D peaks, respectively, in Fig. 7.

The morphology and structure of GO and synthesised graphene particles were observed using JEM-2100 TEM. TEM samples were prepared by pipetting a few millilitres of ethanol onto holey carbon coated Au grids. Typical TEM images and selected area diffraction (SAED) pattern of GO are given in Fig. 8.

Based on the images, it is clearly seen that GO flakes are formed in the production made by the Hummer's method (Fig. 8a). The images are displayed that the larger proportion of flakes are of a multi-layer of GO. Fig. 8b shows an SAED of GO. The images of before and after the centrifugal process of graphene synthesised by using NaBH_4 are shown in Figs. 9a and b. It is clearly shown that the structure of graphene synthesised by using NaBH_4 was produced single- and multi-layer flakes. The individual sheets, including kinked areas, are clearly seen in Fig. 9. Based on TEM analysis in Fig. 9a, monolayer graphene can be seen, and these samples were separated into the layers with a centrifuge and analysed with TEM. Before the centrifugal process, TEM images are shown that NaBH_4 -synthesised graphene was in the single layer and after the centrifugation; a few multi-layers appeared on the structure of graphene.

Fig. 10 shows TEM images of before, after centrifuge and SAED pattern of hydroquinone-synthesised graphene. When TEM images of the products compared with each other, the graphene flakes

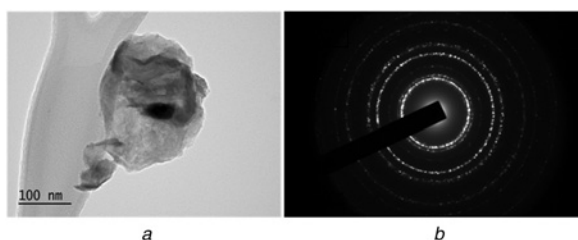


Fig. 8 Typical TEM images and (SAED) pattern of GO
a TEM image
b SAED pattern of GO

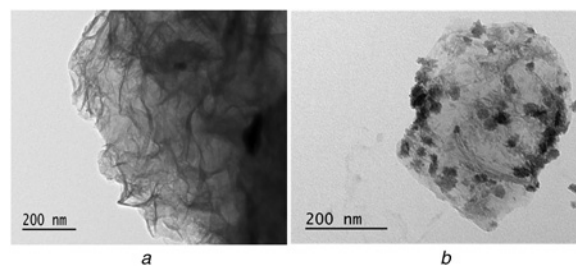


Fig. 9 TEM image
a NaBH_4 -synthesised graphene before centrifuge
b After centrifuge

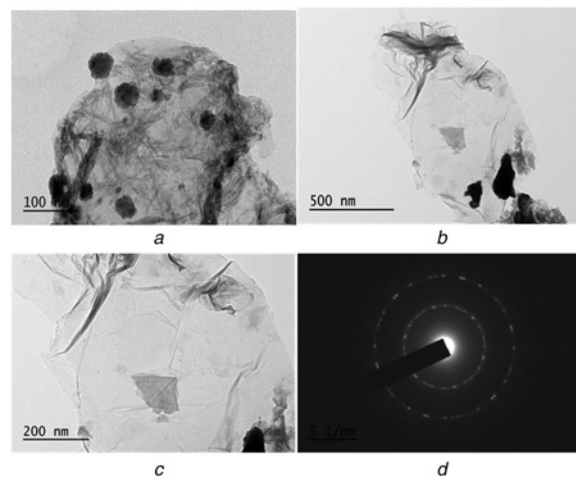


Fig. 10 TEM images of hydroquinone-synthesised graphene
a Before centrifuge
b, c After centrifuge
d SAED pattern

synthesised by hydroquinone, have single-layer, multi-layer and some nano-sized graphite on the structure before the centrifugal process (Fig. 10a).

After the centrifugation, it was determined by TEM images that graphene particles synthesised with hydroquinone were obtained as a single layer. As a result, hydroquinone has been found to be a very effective solution for destruction of a Van der Waals interaction between GO layers and the reduction of GO to graphene.

4. Conclusions: In this Letter, the graphene production with NaBH_4 and hydroquinone was realised by using high-energy ball milling. GO prepared via Hummer's method from graphite was further exfoliated by using a ball milling in an inert atmosphere of layers. GO separated into layers converted to graphene using NaBH_4 and hydroquinone. Different characterisation techniques were employed for single-layer graphene. According to these analysis results, the feature of both reductants (NaBH_4 and hydroquinone) was accepted as more strongly reducing agents due to the good reduction of GO. As a preferred reductant, hydroquinone can be successfully applied for the synthesis of the single-layer graphene compared to NaBH_4 . The big difference in the structure of GO and graphene on microscopic morphology was observed in TEM analysis. All these processes in this Letter can be applied confidentially to the industrial production of graphene.

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6 References

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