Short Communication

Facile, Cost Effective and Green Synthesis of Graphene in Alkaline Aqueous Solution

Siti Nur Akmar Mohd Yazid[1], Illyas Md Isa[1,2,], Suriani Abu Bakar[2], Norhayati Hashim[1,2]*

[1]Department of Chemistry, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia.
[2]Nanotechnology Research Centre, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia.
[*]E-mail: illyas@fsmt.upsi.edu.my

We report a simple, green and cost effective synthesis of graphene via chemical reduction of graphene oxide in alkaline aqueous solution. Extensive characterizations have been studied to confirm the formation of graphene in sodium carbonate solution. Cyclic voltammetry was used to study the electrochemical properties of the prepared graphene-modified glassy carbon electrode using potassium ferricyanide as a redox probe. Based on the result, with the addition of graphene to the glassy carbon electrode the current flow increases and the peak also broadens as compared to graphite and graphene oxide. This method is fast, cost effectively, and green as nontoxic solvents are used which will not result in contamination of the products. Thus, this method can serve for the preparation of graphene which can be effectively used in sensors, electronic devices and supercapacitors.

1. INTRODUCTION

Graphene is a two-dimensional sp^2 bonded carbon materials which is arranged in honeycomb lattice structure. Its large surface area (2630 m^2g^{-1}), which is ~260 times greater than graphite and twice that of carbon nanotubes, provides a benefit of enhancing the electrochemical catalytic activity of materials by greatly increasing the surface area [1,2]. The other properties of graphene such as fast electron transportation, high thermal conductivity, excellent mechanical flexibility and good biocompatibility have also make it a potential candidate in the fabrication of polymer nanocomposites, supercapacitors, drug delivery and tissue engineering [3-6].

There are several reported methods for the synthesis of graphene including mechanical cleavage [7], exfoliation of graphite [8], epitaxial growth [9], unzipping of carbon nanotubes [10], electric arc discharge [11], chemical vapour deposition [12], and subsequent reduction of GO [13]. Chemical reduction of graphene oxide (GO) has been considered as an effective route because of the similarities between reduced GO and pristine graphene, its simplicity, reliability, ability for large scale and low cost production [14]. A number of reducing agents such as anhydrous hydrazine [15], hydrazine monohydrate [16], substituted borohydride [17], and hydroquinone [18] have been experimented for the reduction of GO to form graphene. Unfortunately, these reducing agents involved are very hazardous, dangerously unstable, and difficult to remove in the final product. Previous studies also reported that nitrogen from these reducing agents tend to remain covalently bound to the surface of GO likely in the form of hydrazones, amines, aziridines or other similar structures during reduction process [19, 20].

Recently, reduction process of GO in alkaline solution has been reported to substitute these toxic reducing agents. Herein, we report a simpler route to synthesis graphene via chemical reduction of GO suspended in alkaline aqueous solution. We observed that graphene could be quickly prepared by simply heating the GO suspension under sodium carbonate (Na_2CO_3) solution condition at moderate temperature. Cyclic voltammetry was used to evaluate the properties of as-prepared graphene for electrochemical sensor electrodes. This method is fast, cost effectively, and green as nontoxic solvents are used which will not result in contamination of the products.

2. EXPERIMENTAL

2.1. Reagents and materials

All chemicals were of reagent grade and were used without further purification. Graphite powder, sodium nitrate ($NaNO_3$), N,N-dimethylformamide (DMF), potassium permanganate ($KMnO_4$), and hydrogen peroxide (H_2O_2) were purchased from Merck Sdn.Bhd (Malaysia). Sodium carbonate (Na_2CO_3) was purchased from Sigma Aldrich (Malaysia), and sulfuric acid (H_2SO_4) was purchased from Scharlau (Spain).

2.2. Apparatus

Surface morphology was observed by transmission electron microscopy (TEM: JEOL-2000EX) and field emission scanning electron microscopy (FESEM: Hitachi SU 8020 UHR). Fourier transform infrared (FTIR) spectroscopy was carried out on FTIR (Thermo Nicolet Nexus) using the KBr disc method. Raman spectra were obtained on a Renishaw InVia Raman spectroscopy using a 514 nm argon ion laser. Powder X-ray diffraction (XRD) patterns were collected from a diffractometer of Bruker AXS (XRD: D8 Advance) with Сuкα radiation (λ = 1.54 Å). Electrochemical analysis was performed on a Gamry Potentiostat Series-G750 (USA) which a three electrode cell was used at room temperature, consisting of bare or modified glassy carbon electrode, GCE (diameter = 0.3 cm) as the

working electrode, an Ag/AgCl as reference electrode, and a platinum wire as the counter electrode, respectively.

2.3. Synthesis of alkaline reduced graphene

GO flakes were prepared by a modified Hummer's method [21]. In a typical experiment, 100 mg of GO flakes were dispersed in 50 mL ultrapure water to form yellow-brown GO dispersion. This was then sonicated for 30 min, transformed to a flake and stirred with Na_2CO_3 solution (1 mol/L) for 3 h at the desired temperature (100 ^{o}C). The resulting black mixture was centrifuged to collect the products and washed with distilled water. Finally, the products were dried at 60 ^{o}C in the oven for 24 h.

2.4. Preparation of graphene modified electrode

For the preparation of graphene-modified glassy carbon electrode (GCE), the bare GCE was polished with alumina powder, rinsed ultrasonically with deionized water and dried at room temperature before use. Approximately 1 mg of graphene was dispersed in 1 mL of dimethylformamide/water (DMF/H_2O) (9:1) and ultrasonicated for 30 min. About 7 µL of the suspension was casted on the surface of GCE and dried in air.

3. RESULTS AND DISCUSSION

3.1. Characterizations

The synthesis of GO was achieved by placing flakes graphite in concentrated acid in the presence of oxidizing agent using a modified Hummer's method. This method demonstrated a less hazardous and more efficient method for graphite oxidation [22]. GO is cannot be used without further processing as a conductive nanomaterial due to its electrically insulating properties. In addition, the presence of oxygen-containing groups makes GO thermally unstable, as it undergoes pyrolysis at high temperature [23]. However, the electrical conductivity of GO can be restored close to the level of graphite by chemical reduction of GO under alkaline condition [24-26]. Although the mechanism is remaining unclear, the mechanism may be supported by the pH dependency of deoxygenation reaction in which the higher pH of the GO suspension, the faster the reaction.

The changes in the color of solution are a good indicator of GO reduction in alkaline aqueous solution. The yellow-brown GO solution before reaction (Fig. 1a) turned to a black dispersion after it had been heated for 3 h at the desired temperature (100 ^{o}C), which indicates the successful conversion of GO to graphene (Fig. 1b). The FESEM image (Fig. 1c) and TEM image (Fig. 1d) reveal that the graphene consists of randomly aggregated, thin and crumpled sheets closely associated with each other and forming a disordered solid. The absence of charging during the imaging process indicates that the graphene sheet is electrically conductive.
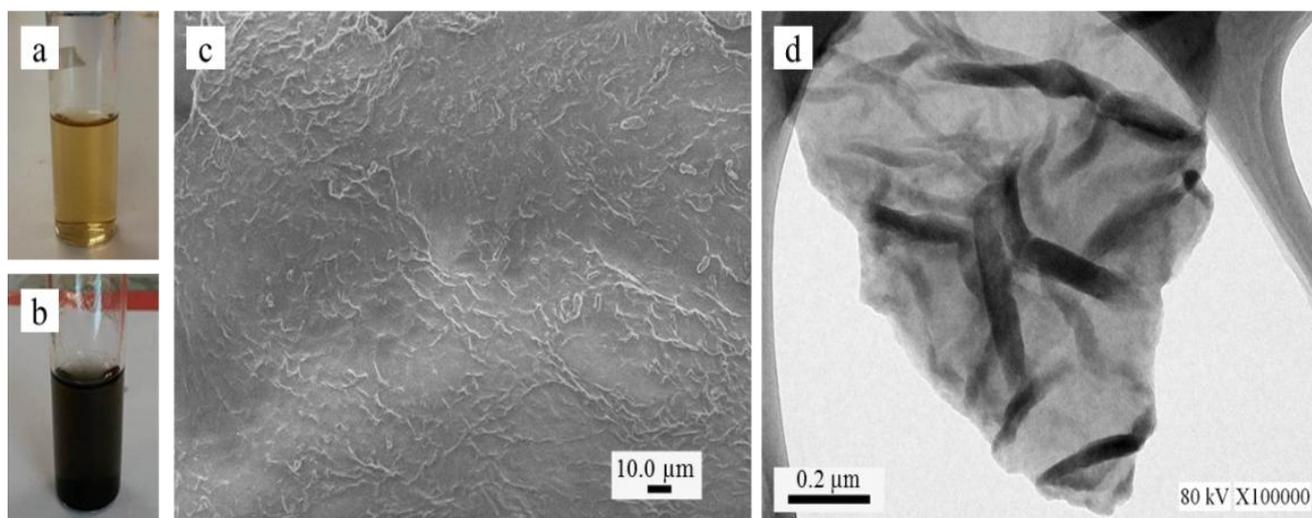
Figure 1. Photographs of (a) GO and (b) graphene, (c) FESEM image of graphene, and (d) TEM image of graphene.

FTIR analysis is a good tool to identify functional groups present on the graphite, GO and as-prepared graphene (Fig. 2a). The graphite spectrum shows O–H broad peak at 3453 cm^{-1} resulting from intercalated water and C=C at 1637 cm^{-1} which assigned to the skeletal; vibrations of graphitic domains [27]. The spectrum of GO illustrates several characteristic peaks corresponding to O–H vibration at 3434 cm^{-1}, absorption bands at 1735 cm^{-1} (C=O stretching in carboxylic and/or carbonyl moiety), 1628 cm^{-1} (O–H bending and aromatic C=C, skeletal ring vibrations from the graphitic domain), at 1384 cm^{-1} (O–H deformation in carboxylic moiety), and 1065 cm^{-1} (C–OH stretching in alcoholic moiety). After reduction process in alkaline aqueous solution, the bands associated with the oxygen-containing group were dramatically reduced and finally the peak at 1735 cm^{-1} for carboxyl C=O entirely vanishes.
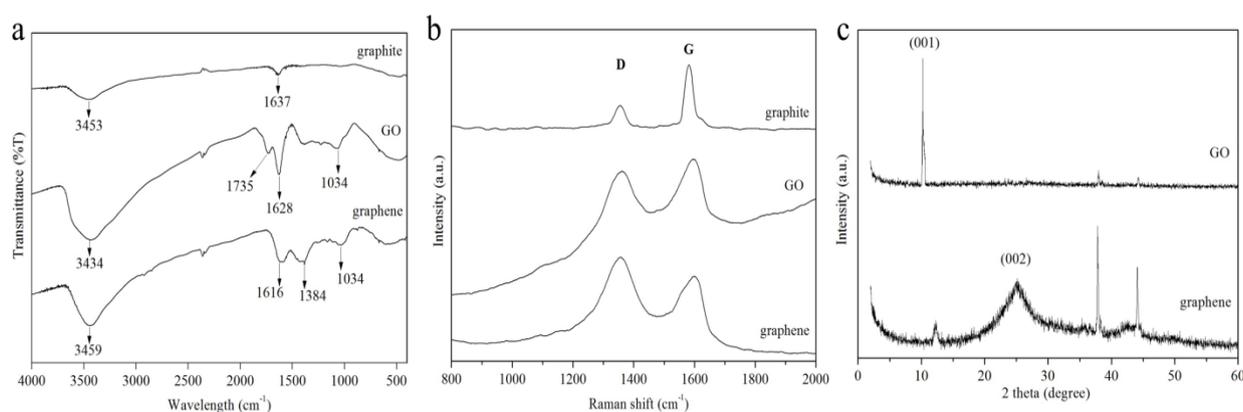

Figure 2. (a) FTIR spectra of graphite, GO and graphene, (b) Raman spectra of graphite, GO, and graphene, (c) XRD patterns of GO and graphene.

The formation of graphene was further confirmed by Raman spectroscopy (Fig. 2b). The spectrum of graphite shows typical D peak at 1351 cm^{-1} and G peak at 1582 cm^{-1} respectively. For Raman spectra of GO, the G peak is broadened and blue shifts to 1619 cm^{-1}, which attributed to the presence of isolated double bonds that resonate at higher frequencies than G peak of graphite. In addition, the D peak at 1365 cm^{-1} becomes prominent, indicating the destruction of sp^2 character and the formation of defects in the GO sheets due to extensive oxidation [28]. After GO reduction in alkaline aqueous solution process, the G peak of graphene moves to 1586 cm^{-1} and 1594 cm^{-1} respectively, which closer to graphite indicating that GO is reduced.

Fig. 2c shows XRD patterns of GO and the as-prepared graphene. A sharp diffraction peak at $2\theta = 10.2°$ with an interlayer distance of 0.867 nm corresponds to GO, and it clearly indicates the damage of the regular crystalline of pattern graphite during the oxidation [29]. After GO reduction in alkaline aqueous solution, a broad peak at $2\theta = 24.8°$, with an interlayer distance of 0.359 becomes visible. The large $d_{(002)} = 0.867$ nm of GO drastically decreases to $d_{(002)} = 0.359$ nm for the as-prepared graphene which implies that most of the oxygen-containing groups are removed.

3.2. Electrochemical studies

The study of cyclic voltammetry (CV) for the as-prepared graphene was carried out to understand the electrochemical behavior of the graphene. In this work, the electrochemical properties of the as-prepared graphene were studied by recording the CV of graphene-modified GCE using 4 mM $K_3Fe(CN)_6$ as a redox marker in 0.1 M KCl supporting electrolyte. This redox was chosen due to its sensitivity to the surface chemistry and microstructure as well as the density of electronic states near the Fermi potential [30]. Fig. 3a presents the voltammetric responses for graphite, GO and graphene at 100 mVs^{-1}. It shows that with the addition of graphene to the GCE the current flow increases from 23.53 μA of the bare GCE to 82.31 μA, and the peak also broadens as compared to graphite and GO. The shapes of CV curves show the reversible charge-discharge behavior. Both anodic and cathodic peak currents in the CVs are also linear with the square root of the scan rate, which suggest that the redox processes on graphene-based electrodes are predominantly diffusion controlled [31].

The reduction process of GO is concerned with removing other atomic-scale lattice defects and recovering the conjugated network of the graphitic lattice in order to improve the electrical conductivity and other properties of graphene. The electronic structure and the surface physicochemistry of as-prepared graphene are beneficial for electron transfer. In this study, the removal of the oxygen-containing groups of GO due to alkaline reduction gives a dominant contribution to the increase in conductivity of graphene, in coherent with previous studies [32,33].
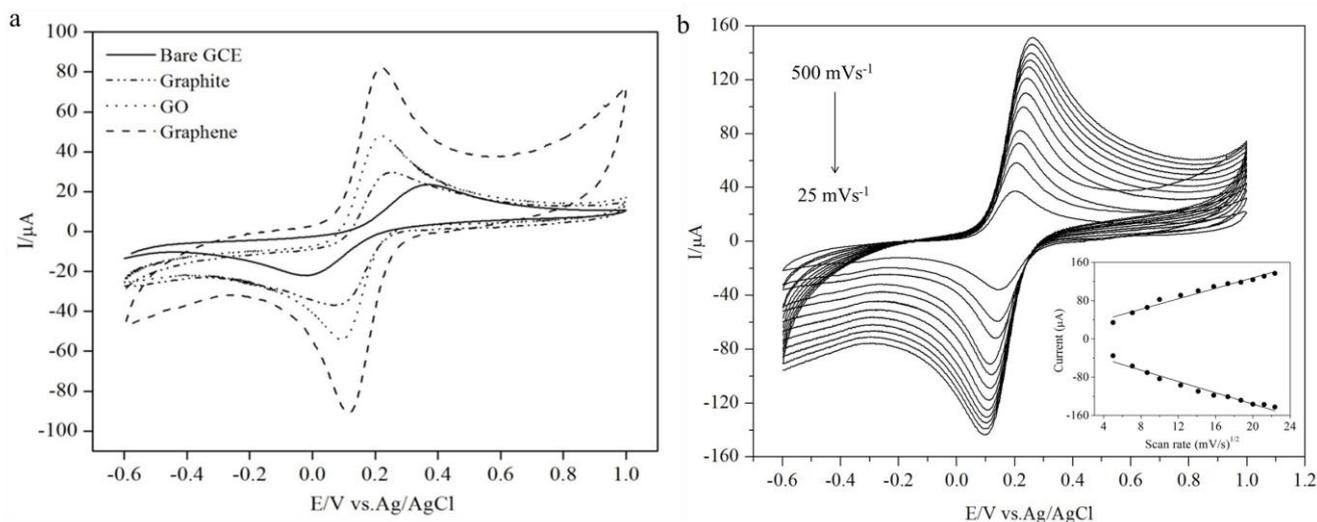
Figure 3. (a) CV curves of bare GCE, graphite-modified GCE, GO-modified GCE and graphene-modified GCE in 4mM $K_3Fe(CN)_6$ at scan rate of 100 mVs^{-1} and (b) CV curves of graphene-modified GCE at different scan rates from 25 to 500 mVs^{-1} (inset shows the calibration curve of current vs. scan rate).

The variation of peak current and peak potential with the scan rate was studied. Fig. 3b presents the CV of graphene-modified GCE in 4mM $K_3Fe(CN)_6$ in 0.1 M KCl supporting electrolyte at different scan rates from 25 to 500 mVs^{-1}, in order to investigate the mechanism on the graphene-modified GCE, whether diffusion or adsorption controlled electrode process. There is a good linear relationship between the anodic peak currents (i_{pa}) and cathodic peak currents (i_{pc}) with the square root of scan rates (inset Fig. 3b). The regression equations representing $i_{pa} = 5.616v^{1/2} - 18.37$, with $R^2 = 0.985$ and $i_{pc} = -0.595v^{1/2} - 18.36$, with $R^2 = 0.993$, indicating that graphene-modified GCE was controlled by adsorption controlled electrode process [34]. Therefore, the scan rate of 100 mVs^{-1} was used for all subsequent measurement.

4. CONCLUSIONS

A simple, green and cost effective synthesis of graphene via chemical reduction of GO in alkaline aqueous solution is achieved. The FTIR and Raman spectra confirm the removal of oxygen-containing groups from the GO. The XRD, FESEM and TEM also demonstrate the formation of graphene. The CV results indicated that the current flow of graphene-modified GCE is higher than bare GCE due to its good conductivity. Therefore, this method can serve for the large scale synthesis of graphene with low cost production which can be effectively used in the field of nanoscience and technology.

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