

Morphology control and thermal stability of binderless-graphene aerogels from graphite for energy storage applications

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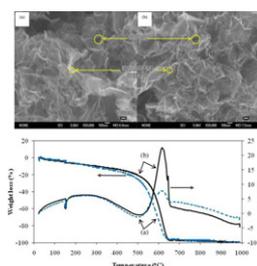
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HIGHLIGHTS

- ▶ Graphene aerogel (GA) nanostructures synthesized from commercial graphite were controlled successfully.
- ▶ A hydrothermal method was used to synthesize GAs. No binders were used.
- ▶ Effects of fabrication conditions and graphene oxide concentration on the GA nanostructures were quantified.
- ▶ A maximum BET surface area of 394 m²/g and the lightest density of 0.042 g/cm³ were achieved.
- ▶ The GAs could be stable up to 500 °C in air.

GRAPHICAL ABSTRACT



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ABSTRACT

Of all the challenges facing human beings in the near future, energy related issues are likely to be the grandest. To achieve a more sustainable society with adequate renewable energy and less environmental pollution, more versatile, robust and efficient approaches in electric energy storage and conversion are needed. To achieve these goals, the development of new electrode materials with high electrical conductivity, corrosion-resistance, high specific surface area, high porosity and low cost is highly desirable. Graphene aerogels (GAs) have been focused recently due to novel properties of graphene (extremely low electrical and thermal resistivity, large carrier mobility, high surface area and mechanical elasticity) and the low cost and easy preparation of graphene from graphite. The performance of GA-based electrodes strongly depends on the morphology and structure of the GAs. However, there has been little study on the optimization of the GA nanostructures in terms of surface area, pore size, pore volume and density for energy storage devices. In this work, the GA nanostructures synthesized from commercial graphite were controlled successfully. The graphene oxide (GO) was prepared from commercial graphite powder using a modified Hummers method. A hydrothermal method was used to synthesize GAs due to its simplicity, environmental friendliness and low cost. No binders were used to prevent their negative effects to the electrical conductivity of the aerogels. Effects of fabrication conditions and the GO concentration on the GA nanostructures were also quantified. A maximum Brunauer–Emmett–Teller (BET) surface area of 394 m²/g and the lightest density of 0.042 g/cm³ were achieved when the GA with 3 mg GO/mL was hydrothermally treated at 180 °C for 1.5 h. The thermal durability analysis showed that the GAs could

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be stable up to 500 °C in air, with 24 h of hydrothermal treatment time. Preliminarily the GA hydrothermally treated for 6 h had an electrical conductivity of 0.004 S/cm. The experimental results of the study are useful for optimizing GA structures for energy storage applications.

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1. Introduction

Human society and industrial development have been increasing their energy consumption. Most of the energy needs have been supplied by combustion of fossil fuels. However, fossil fuel resources are limited and not renewable. Therefore, there is a high demand for more efficient utilization of energy and exploration of new energy sources to substitute fossil fuels [1,2]. Energy storage and energy conversion devices, such as batteries, supercapacitors and fuel cells, play a key role in the effective use of energy. Moreover, new generations of portable electronic devices, electric vehicles and hybrid electric vehicles require high-performance energy storage systems [1–6]. Porous carbon materials, especially activated carbons, have been often used as electrode materials for energy storage devices due to their high surface areas and porous structures. However, the complicated and disordered porous structure of activated carbon affects the electron transfer and thus, limits the performance of the devices [5,7]. Therefore there has been more and more interest in developing new nanostructured materials for energy storage with a high surface area, controllable morphology and porosity, high electrical conductivity and good mechanical properties.

Aerogels are ultralight and highly porous solid nanomaterials with large pore volumes, high surface areas and tunable porosity. These properties are derived from their microstructures, which are typically composed of three-dimensional networks of interconnected nanoparticles. Aerogels are usually prepared using sol–gel techniques involving a transformation of molecular precursors into highly cross-linked gels, which then will be dried with special drying methods, i.e. supercritical or freeze drying, to preserve their tenuous network [8]. Due to their high surface areas and tunable porous structures, there have been several attempts to exploit aerogels for energy storage purpose. Carbon aerogels have been investigated as electrode materials for supercapacitors. However, boundaries between the interconnected nanoparticles and voids create a high internal resistance within the aerogels. This largely affects their applications in energy storage devices [9].

With high electrical conductivity and outstanding multi-properties, carbon nanotubes (CNTs)/graphene have been combined with the structure of aerogel to form CNT/graphene aerogels [9–14]. These CNT aerogels showed high BET surface areas as well as good electrical conductivities. However, due to the high cost of CNTs, and the non-uniform dispersion of the CNTs in surfactants, it is necessary to find cheaper substitutes with excellent electrical, mechanical properties and high surface areas, well dispersion in surfactants for energy storage applications. Recently, graphene has been found to be an ideal candidate due to its unique properties like the CNTs. Graphene sheet which is composed of a monolayer of conjugated sp^2 carbon atoms, arranged in a hexagonal lattice, has been known as the thinnest and strongest material in the world. It has been found that graphene possesses impressive properties including very high electron mobility at room temperature ($250,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), excellent thermal conductivity ($5000 \text{ W m}^{-1} \text{ K}^{-1}$) and superior mechanical properties with Young's modulus of 1 TPa [15–17]. It can be produced in bulk quantities from graphite using simple mechanical and chemical processes [15,17]. The combination of excellent properties of graphene and an aerogel can form a new class of materials with large surface areas, high porosity, high electrical conductivities,

good thermal conductivities and high mechanical strength, which is promising for applications in electrochemical energy devices like supercapacitors, fuel cells or lithium batteries.

However, there is a lack of comprehensive studies of the GAs with well-morphology control for energy applications. Worsley et al. [18] synthesized graphene oxide (GO) using Hummers' method and combined GO with resorcinol-formaldehyde (RF) gel. The GO–RF gel was dried with supercritical CO_2 and calcined at 1050 °C in nitrogen to form a GA. The pore volume and the surface area of the GA is $2.96 \text{ cm}^3/\text{g}$ and $584 \text{ m}^2/\text{g}$ respectively. The GA had a high electrical conductivity of 87 S/m. Wang et al. [19] synthesized GA from a mixture of GO and polyvinyl alcohol in water. The mixture was then flash frozen with liquid nitrogen and thermally treated at 300 °C to form the GA. The GA had a high mechanical strength with compressive modulus of 0.8–2 MPa at 2% strain and largest specific capacitance of 120 F/g [19]. By heating aqueous mixtures of GO and L-ascorbic acid, Zhang et al. [20] successfully prepared GAs with large BET surface area ($512 \text{ m}^2/\text{g}$) and high electrical conductivity (approaching to 10^2 S/m). These GAs exhibited a specific capacitance of 128 F/g and could support more than 14,000 times their own weight. Xu et al. [21] have recently used a hydrothermal method to produce graphene hydrogels. The self-assembled three-dimensional networks of graphene sheets were formed by heating GO solutions in Teflon-lined autoclaves at 180 °C for 1–12 h. The materials showed a maximum electrical conductivity of about $5 \times 10^{-3} \text{ S/cm}$, elastic modulus and yield stress of 0.29 MPa and 24 kPa, respectively. Zhang et al. [22] prepared graphene hydrogels by using a hydrothermal technique and then further reduced by hydrazine or hydroiodic acid. High electrical conductivities of 1.3–3.2 S/m were found for the materials and electrochemical tests revealed that supercapacitors based on these graphene hydrogels had a high specific capacitance of 220 F/g at 1 A/g and 92% capacitance still remained after 2000 cycle tests.

The aerogel-based performance strongly depends on the morphology and structure of the GAs. Therefore, the best designs of the developed GA nanostructures in terms of surface area, pore size, pore volume and density is very important for energy storage devices [1,4,23]. However, to date there have been few studies on the effect of synthesis conditions to the morphology and structure of GA. Therefore, in this work, a systematic research was performed to investigate the influence of synthesis parameters on the morphology and nanostructure of GA. A hydrothermal synthesis method was used for the preparation of GAs from GO due to its advantages, i.e. simple equipment, relatively low process temperature, low environmental impact and low cost. No binders were used in the syntheses of GAs to prevent their negative effects to the electrical conductivities of the materials. GO was prepared from commercial graphite powder by a modified Hummers' method due to its effectiveness and simplicity. Since high thermal stability of electrode materials is very essential for practical applications, thermogravimetric analysis (TGA) was also performed to investigate the thermal durability of the GAs.

2. Experimental

2.1. Chemicals

Chemicals used in this work were deionized water, graphite powder (Sigma–Aldrich), sodium nitrate (NaNO_3 , Sigma–Aldrich),

potassium permanganate (KMnO_4 , Sigma–Aldrich), concentrated sulfuric acid (H_2SO_4 , Sigma–Aldrich), hydrogen peroxide (30 wt% H_2O_2 , Sigma–Aldrich), hydrochloric acid (HCl , Sigma–Aldrich), ethanol ($\text{C}_2\text{H}_5\text{OH}$, Fluka) and L-ascorbic acid (Sigma–Aldrich). All the chemicals were used as received without further purifications.

2.2. Synthesis of graphene oxide (GO)

Graphene oxide (GO) was prepared via a modified Hummers' method [24–26]. In a typical synthesis, 2 g of graphite powder and 1 g of NaNO_3 were mixed with 50 mL of concentrated H_2SO_4 at 0°C in an ice bath. The mixture was stirred for 30 min. Then 7.3 g of KMnO_4 was slowly added into the mixture with stirring and cooling to keep the temperature lower than 20°C . The stirring was continued for 2 h. The temperature of the mixture was then increased to 35°C and stirred for 12 h for the conversion of graphite into graphite oxide. The mixture would become pasty with a brown color. 90 mL of deionized (DI) water was then gradually added into the reaction mixture. To reduce the residual KMnO_4 and MnO_2 to soluble MnSO_4 , 7 mL of 30% H_2O_2 and 55 mL of DI water were added into the suspension. The color of the mixture would change to yellow. Graphite oxide was isolated from the mixture by centrifugation and washed with a solution of 5% HCl to remove metal ions in the graphite oxide and then washed with DI water to remove the unwanted HCl . The solid was dried at 60°C for 2 days. For the exfoliation of graphite oxide, the graphite oxide powder was dispersed into DI water to form 0.1–0.5 wt% graphite oxide solution. The solution was sonicated for 12 h to convert graphite oxide into GO. Finally GO powder was collected by centrifugation and dried at 60°C for 2 days.

2.3. Synthesis of graphene aerogels (GAs)

A hydrothermal method was used for the synthesis of the GA. Briefly, GO solutions with different concentrations of 2, 3, 5 and 10 mg GO/mL were prepared, added into Teflon-lined autoclaves and kept at 180°C for different time periods (1.5, 3, 6, 12 and 24 h). GO would form a hydrogel under this hydrothermal condition. After that, L-ascorbic acid (LAA) was added to reduce GO hydrogel to graphene hydrogel at 95°C for 4 h. The graphene hydrogel was immersed in DI water for 2 days to remove excessive LAA before being placed into ethanol for solvent exchange for 2 days. The alcogel was dried with supercritical CO_2 (Tousimis Autosamdri-815) to form graphene aerogel (GA). In our work, LAA was chosen as the reducing agent due to the fact that, unlike when using sodium borohydride or hydrazine, no gas is formed as a by-product of the reduction reaction, which could otherwise damage the porous structure of GA [20]. Moreover, LAA is environmental friendly and has recently been found to be effective in reducing graphene oxide into graphene [27].

3. Results and discussion

3.1. Structure characterization of graphite, graphene oxide and graphene aerogel

To investigate structures of graphite, graphene oxide (GO) and graphene aerogel (GA), X-ray diffraction (XRD) technique was used with a D8 Bruker AXS X-ray diffractometer ($\text{CuK}\alpha$ radiation, 40 kV, 20 mA, 2θ range of $5\text{--}30^\circ$, scan rate $0.025^\circ/\text{s}$). Fig. 1 presents XRD patterns of the raw graphite powder, GO obtained from the oxidation and exfoliation processes of graphite and GA. The XRD spectrum of graphite exhibits a strong characteristic (002) peak at 26.4° . After the oxidation and exfoliation process, this peak disappears in the XRD pattern of the product and a new peak is observed at 11° , corresponding to the lattice of GO, which indicates

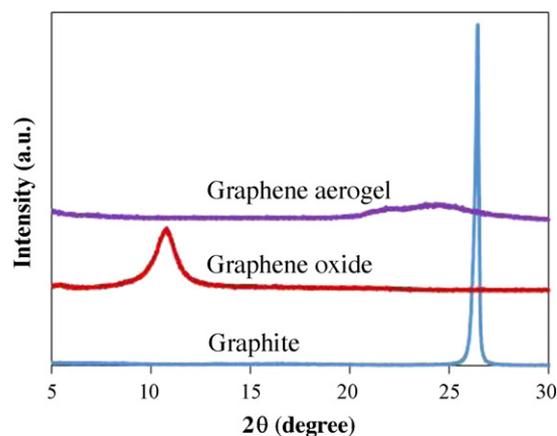


Fig. 1. XRD patterns of graphite, graphene oxide and graphene aerogel.

that graphite was converted into GO [20–22,28,29]. The calculated interlayer spacing of GO is 8.2 \AA , which is much larger than that of graphite (3.4 \AA) due to oxygen-containing groups formed on the layers. The XRD pattern of GA shows a broad peak at 23.5° with an interlayer spacing of 3.7 \AA . This interlayer spacing value is smaller than that of GO, but slightly larger than that of graphite, suggesting that the hydrothermal treatment and reduction with L-ascorbic acid (LAA) mostly removed the oxygenated groups on graphene sheets and the $\pi\text{--}\pi$ stacking between graphene sheets in the GA structure was recovered [20–22,27,29,30].

3.2. Morphology control of the graphene aerogels through GO concentrations

To synthesize GA, GO was dissolved in DI water by sonication (Fig. 2a). Then the mixture was sealed and heated in a Teflon-lined autoclave at 180°C for a certain time to form a hydrogel (Fig. 2b). After the solvent exchange, the alcogel was dried with supercritical CO_2 to form a GA (Fig. 2c). The morphologies of the GAs with 2 and 5 mg GO/mL were imaged by FE-SEM (Hitachi S4300 microscope) and are shown in Fig. 3a and b, respectively. It can be seen that the GAs have interconnected three-dimensional porous structures with a denser network observed for the GA formed from 5 mg GO/mL. It concluded that GO sheets are well dispersed in DI water due to their strong hydrophilicity and electrostatic repulsion effect. Under the hydrothermal conditions, GO sheets are partially reduced and form hydrophobic domains due to the removal of oxygenated groups and the recovery of $\pi\text{--}\pi$ -conjugated system. The combination of hydrophobic domains and $\pi\text{--}\pi$ interactions creates a rigid three-dimensional structure between partial overlapping graphene sheets with pore sizes ranging from submicrometer to several micrometers [21,22].

3.3. Morphology control of the graphene aerogels through synthesis conditions

The effect of synthesis conditions on the morphology of GA was studied in this research. Several GAs were synthesized with different initial GO concentrations (2, 3, 5 and 10 mg GO/mL) and hydrothermal treatment times (1.5, 3, 6, 12 and 24 h). To characterize the specific surface areas and porous properties of the GAs, nitrogen adsorption/desorption measurements were performed at -196°C with a Nova 3200e (Quantachrome). Initially the samples were degassed at 125°C in vacuum for 2 h. Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods were used to calculate the specific surface area and pore size of the GA samples. Fig. 4 displays a typical nitrogen sorption

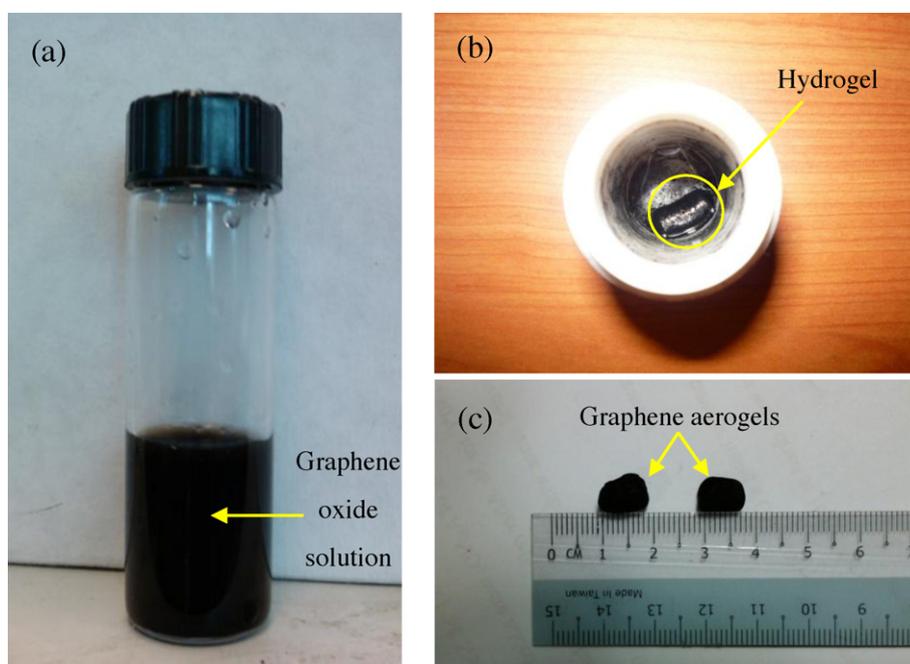


Fig. 2. Images of (a) initial graphene oxide solution, (b) graphene oxide hydrogel and (c) graphene aerogel.

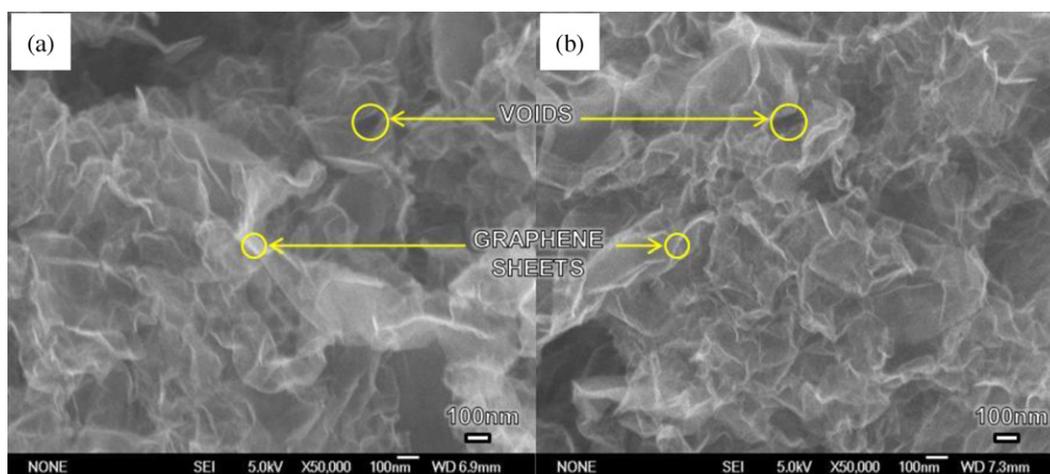


Fig. 3. FE-SEM images of graphene aerogels with (a) 2 and (b) 5 mg GO/mL.

isotherm and BJH pore size distribution of the synthesized GAs. It can be seen that the GAs possess a type IV isotherm with an adsorption hysteresis, indicating that the GAs contain many mesopores in their structures. All the porous characteristics of the GAs are summarized in Table 1 and Fig. 5. Table 1 and Fig. 5a show the effects of GO concentrations on the GA morphology with a hydrothermal

treatment time of 24 h (samples 5–8 in Table 1). The lowest BET surface area of 121 m²/g and pore volume of 0.36 cm³/g is obtained for the GA with 2 mg GO/mL while the highest values (156 m²/g and 0.93 cm³/g, respectively) are for the GA with 10 mg GO/mL. The BET area and total pore volume values increase when increasing the initial GO concentration from 2 to 10 mg/mL. It can be explained

Table 1
Effect of initial GO concentrations and hydrothermal treatment times on the morphology of GA.

Sample	GO concentration, mg/mL	Hydrothermal treatment time, h	BET surface area, m ² /g	BJH mean pore size, nm	Total pore volume, cm ³ /g	Bulk density, g/cm ³
1	3	1.5	394	3.7	1.46	0.042
2	3	3	189	3.7	1.05	0.048
3	3	6	148	3.7	0.60	0.061
4	3	12	136	3.7	0.48	0.079
5	3	24	133	3.6	0.42	0.085
6	2	24	121	3.7	0.36	0.098
7	5	24	150	3.7	0.72	0.099
8	10	24	156	3.7	0.93	0.067

Shadings are used to show the changes of GO concentration and hydrothermal treatment time.

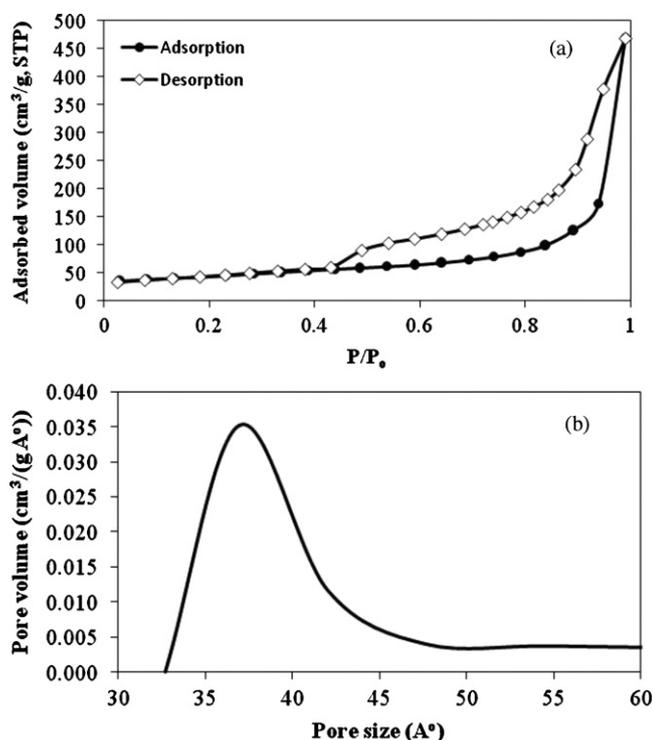


Fig. 4. Typical (a) N₂ adsorption/desorption isotherm and (b) BJH pore size distribution of graphene aerogel.

that higher GO concentrations in the initial solution will create more graphene nanosheets in the aerogel structure and thus, more pores are produced in the network. As a result, larger BET areas and higher pore volumes are obtained. The effect of the hydrothermal treatment time to the morphology of the aerogel is also displayed in Table 1 and Fig. 5b (samples 1–5 in Table 1). The results show that with the same initial GO concentration of 3 mg/mL, samples with longer hydrothermal treatment time have a higher BET surface area and total pore volume. The sample with the longest treatment time (24 h) has the lowest BET area (133 m²/g) and pore volume (0.42 cm³/g) while the one with the shortest hydrothermal treatment time (1.5 h) has the highest values (394 m²/g and 1.46 cm³/g, respectively). As a result, the former has the highest density of 0.085 g/cm³ and the latter possesses the lightest density of 0.042 g/cm³. The reason is that when reducing hydrothermal treatment time, less cross-linking sites are formed between

partially overlapping graphene sheets and therefore higher BET areas and pore volumes are achieved. It is interesting that the highest BET surface area of GAs obtained in this work is 394 m²/g, which is more than two-fold those values (215, 202 m²/g) [22,31] reported in previous works using the same hydrothermal methods. However, this value is smaller than the theoretical value (2600 m²/g) [20] of a single graphene sheet due to the overlapping of graphene sheets in the GAs. It can be seen that hydrothermal treatment time has greater impact on the BET areas of GAs than GO concentration. This confirms that the formation of hydrophobic sites and π - π interactions between graphene sheets under hydrothermal condition is the main factor deciding the porous structure of the GAs. It is also remarkable that in our investigation, the changes of initial GO concentration and hydrothermal treatment time have little effect on the BJH mean pore size of the aerogels (3.6–3.7 Å).

3.4. Thermal durability of graphene aerogels

Thermal durability of electrode materials is very important for the performance of electrochemical power devices at high temperatures. In this work, thermal stability analysis was performed for samples having the longest hydrothermal treatment time (24 h, sample 2) and shortest hydrothermal treatment time (1.5 h, sample 8) using thermogravimetric analysis (TGA) technique on a Shimadzu DTG60H. The samples were heated from 25 °C to 150 °C and held for 30 min to remove adsorbed water and then heated to 1000 °C in air and cooled down to room temperature. As can be seen in Fig. 6, both TGA curves of the GAs have similar trends, but different burning temperatures. TGA curve of sample 2 (24 h) shows a sharp weight decrease in the range of 500–640 °C while that of sample 8 (1.5 h) has a sharp decrease in the range of 460–640 °C. The differential thermal analysis (DTA) curve of sample 2 (24 h) displayed a peak at 611 °C while that of sample 8 showed a peak at 604 °C (Fig. 6). The TGA and DTA data confirm that sample 2 is more stable than sample 8. It can be explained that longer hydrothermal treatment time results in a more rigid 3D structure of overlapping graphene sheets due to more π - π bonds formed between them. It can be seen that there is a secondary peak around 650 °C in the DTA curve of sample 2. As discussed above, GA structure was formed by hydrophobic and π - π interactions between overlapping graphene sheets under hydrothermal conditions. It is possible that some parts of the structure have more interactions than others due to larger overlapping area of graphene sheets and thus, is more stable. As a result, the degradation of these parts occurs at higher temperature and forms the secondary peak.

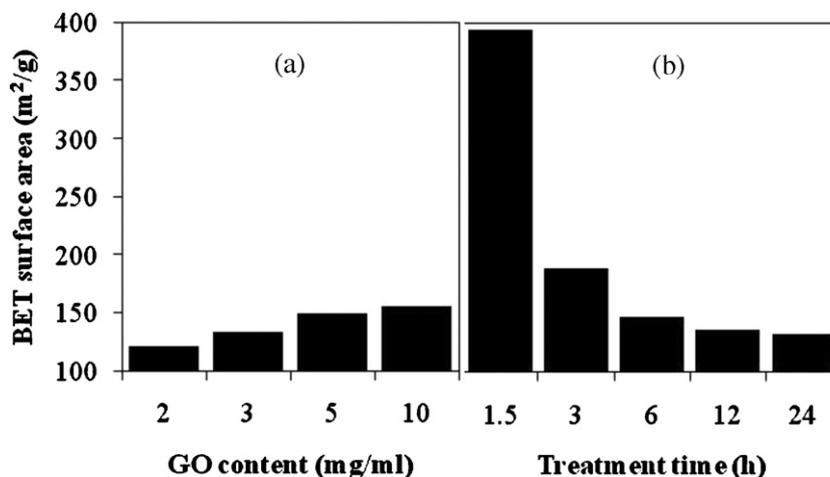


Fig. 5. (a) Effect of GO concentrations on BET surface area and (b) Effect of hydrothermal treatment times on BET surface area.

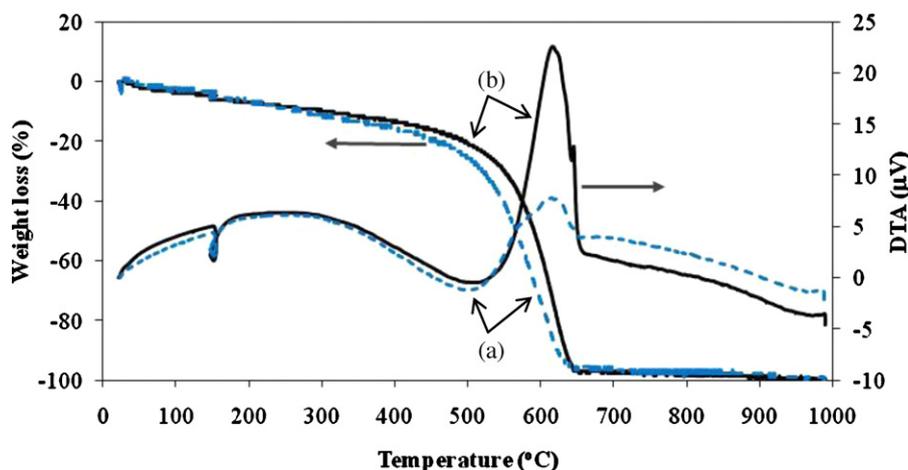


Fig. 6. TGA and DTA curves of graphene aerogels with different hydrothermal treatment times: (a) 1.5 h and (b) 24 h.

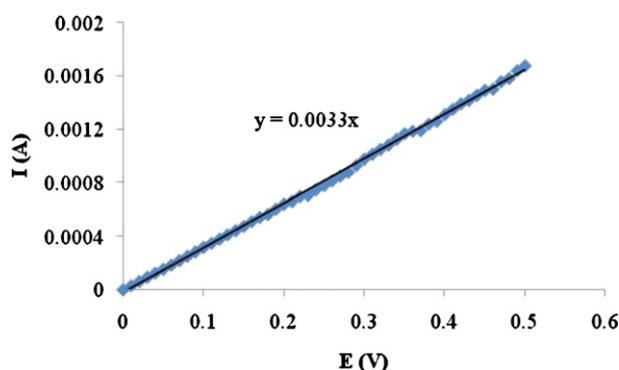


Fig. 7. I - V plot of sample 3.

The TGA data indicate that our tested GA samples are much more stable until 500 and 460 °C in air, respectively, while GA samples in Zhang et al.'s work [20] can only stand up to 250 °C in N_2 .

3.5. Electrical properties of graphene aerogels

Some preliminary electrical conductivity measurements were performed for sample 3 using a two-probe method on a Solatron analytical 1470E system. Two platinum plate electrodes were connected with two ends of the cylindrical sample and a conductive paint was used to eliminate the contact resistance between the sample and the electrodes. An I - V plot was obtained (Fig. 7) and used to calculate the electronic conductivity of the sample. The result shows that it possesses an electronic conductivity of about 0.004 S/cm, which is comparable to what Xu et al. obtained in their research [21]. More investigations will be carried out to study the effect of synthesis conditions to thermal conductivity, electrical conductivity and mechanical property of the aerogels.

4. Conclusions

In this research, a comprehensive study on morphology control of the GAs and the effects of hydrothermal conditions on their nanostructures was carried out. Several rigid GA samples with well-controlled morphologies were successfully developed with various GO concentrations and hydrothermal treatment times. The experimental results showed that the aerogels having mesoporous structures were formed from overlapping graphene nanosheets. A higher GO concentration resulted in a higher BET surface area and pore volume of the GAs. Longer hydrothermal treatment time

reduced their BET surface area, pore volume and increased the bulk density. A maximum BET area value of 394 m^2/g was found when the GA with 3 mg GO/mL was hydrothermally treated at 180 °C for 1.5 h. TGA tests showed that GA samples hydrothermally treated for 24 and 1.5 h were stable up to 500 and 460 °C in air, respectively. Preliminarily, the GA hydrothermally treated for 6 h had an electrical conductivity of 0.004 S/cm. The results of this work are very useful for experimentalists deciding the best GA nanostructures for their needs.

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