



Morphology effects on electrical and thermal properties of binderless graphene aerogels

Zeng Fan, Daniel Zhi Yong Tng, Son Truong Nguyen, Jingduo Feng, Chunfu Lin, Pengfei Xiao, Li Lu, Hai M. Duong*

Department of Mechanical Engineering, National University of Singapore, 9 Engineering Drive, Singapore 117576, Singapore

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ABSTRACT

Three-dimensional self-assembled graphene aerogels (GAs) are successfully developed by a simple chemical reduction with L-ascorbic acid at low temperature. And for the first time, the relationship among morphologies, electrical and thermal properties of GAs is studied comprehensively by controlling reaction conditions. The electrical conductivities of the GAs are also improved by four times after an annealing at 400 °C for 5 h under Ar environment. The results are very useful to optimize the best morphology, electrical and thermal properties of GAs for the best performance of GA-based electrodes of energy storage devices such as supercapacitors and batteries.

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1. Introduction

Graphene, a two-dimensional honeycomb lattice structure of carbon atoms has attracted much attention due to its excellent electrical, thermal and mechanical properties [1–4]. Recently, a great deal of research has been done to develop graphene or graphene-based materials into various applications such as energy storage devices [5–7], sensors [8,9] and composites [9–11]. To date, the realization of a three-dimensional graphene nanostructure is believed to be one step closer to more extensive applications. However, reported methods for the fabrication of 3D graphene nanostructures are still very limited, and a binder was usually required to achieve the assembly [12–18]. Worsley et al. [12,13] reported the synthesis of ultra-low-density GAs with rather high electrical conductivity (87 S/m) and large surface area (584 m²/g) by using resorcinol (R) and formaldehyde (F) as an organic binder to produce carbon cross-links in the graphene network. Tang et al. [14] and Jiang et al. [15] developed an ion linkages method for the preparation of 3D architectures of graphene. However, it is still a great challenge to fabricate GAs with no binder in a simple and efficient way. Xu et al. [16] presented a one-stop hydrothermal technique to prepare electrical conductive and binderless GAs, but the requirements for high temperature and pressure during the process strongly limit its fabrication on a large scale. Zhang et al. [17,18] reported an easy and environmentally friendly method to synthesize GAs by a simple reduction of GO with L-ascorbic acid (LAA). The self-assembled aerogel had a large surface area

approximately 512 m²/g and a high electrical conductivity measured by a four-probe method approximately 10² S/m. Nevertheless, the morphologies, electrical and thermal properties of the GAs prepared by the simple reduction method depend strongly on the reaction conditions, such as initial GO concentration, reduction temperature and reduction time. Up to now, there were few studies on the synthetic parameters' effects on the morphologies and properties of GAs [19].

Here, we report a systematic research to effectively control the GA morphologies and their effects on electrical conductivities and thermal stability of GAs through a simple LAA reduction self-assembly method under ambient pressure. Reduction of GO was confirmed by X-ray diffraction and the thermal stability of the GAs was investigated by thermal gravimetric analysis (TGA). Excess L-ascorbic acid can easily be removed during the solvent exchange process. The developed fabrication method reported here is environmentally friendly and effective for the fabrication of GAs, while the nanostructure, electrical and thermal properties of GAs can be easily controlled by adjusting the synthesis conditions.

2. Materials and methods

2.1. Materials

Graphite powder, sodium nitrate (NaNO₃), potassium permanganate (KMnO₄), concentrated sulfuric acid (H₂SO₄), hydrogen peroxide (30% H₂O₂), hydrochloric acid (HCl) and L-ascorbic acid were purchased from Sigma–Aldrich Company Ltd. Ethanol was purchased from Fluka. All the chemicals were used without further purification.

* Corresponding author.

E-mail address: mpedhm@nus.edu.sg (H.M. Duong).

2.2. Synthesis of graphene oxide

Graphene oxide (GO) was prepared by a modified Hummers' method [20–22]. Briefly, 2 g NaNO_3 and 4 g graphite powder were added into 100 ml concentrated H_2SO_4 in an ice bath. After stirring the above mixture for 30 min, 14.6 g KMnO_4 was then slowly added into the mixture with stirring and cooling to keep the temperature lower than 20°C for another 2 h. After which, the temperature of the mixture was increased to 35°C with stirring for 12 h for the oxidization of graphite. Then, 180 ml deionized (DI) water was added into the mixture and stirred for 15 min. 14 ml 30% H_2O_2 and 110 ml DI water were added gradually into the reaction mixture with a color change from brown to yellow. The graphene oxide was separated from the mixture by centrifugation and washed with 1 M HCl and DI water to remove any impurities. The solid was dried at 60°C for several days.

To convert graphite oxide into GO, the as-prepared graphite oxide was dissolved into DI water to form a 0.1–0.5 wt.% graphite oxide suspension, and sonicated for 12 h. GO powder was finally collected by centrifugation and dried at 60°C for several days.

2.3. Synthesis of graphene aerogels (GAs)

GO aqueous suspensions with different concentrations of 1, 2, 6 and 12 mg/ml were prepared and added into 20 ml vials. L-Ascorbic acid (LAA) was added to GO suspension with magnetic stirring for several minutes until completely dissolving. After that, the reaction mixture was heated for a number of hours (5, 10, 20, 40 h) at different temperatures of 45, 70 and 95°C . The as-prepared graphene hydrogels were immersed in DI water for 3 days to remove excessive LAA before being placed into ethanol for solvent exchange for another 3 days. Then wet gels were subsequently dried with supercritical CO_2 to obtain the GAs.

2.4. Characterization

To characterize the morphologies of the GAs, SEM was conducted on a scanning electron microscope (Model S-4300, Hitachi, Japan) with field-emission-gun operating at 10 V and the samples for SEM were directly loaded on the holder without any pre-coating. Nitrogen adsorption/desorption measurements were carried out with a Nova 2200e (Quantachrome) to obtain the pore properties of the resulting GAs, such as BET specific surface area, BJH pore size distribution and total pore volume. The samples were degassed under vacuum at 120°C for 2 h before measurements. Bulk density was calculated by measuring weight and volume of the GA samples. X-ray diffraction was used with a diffractometer (Model XRD-6000, Shimadzu, Japan) to investigate the structures of graphite, GO and GA. The bulk electrical conductivity measurements were conducted on a Solartron 1260+1287 electrochemical system with two copper plate electrodes attached to the two flat

surfaces of the coin-shape sample. TGA was performed using a DTG60H thermo gravimetric analyzer from room temperature to 1000°C in air with a heating rate of $5^\circ\text{C}/\text{min}$.

3. Results and discussion

After sonication for several minutes, GO can be dissolved into water to form a uniform aqueous mixture. The reduction of GO by reducing agents, such as L-ascorbic acid, NaHSO_3 , Na_2S and sodium ascorbate, in aqueous suspensions under mild conditions could result in the formation of hydrophobic graphene structures [17,23,24]. In this Letter, LAA was selected as the reducing agent, since it was found to be efficient and environmentally friendly for the reduction of the GO into graphene and excessive LAA can be easily removed during the solvent exchange. Also, according to estimated balanced chemical reaction reported elsewhere, the amount of LAA needed was 3.3 times of GO content by mass [17,25]. The amount of LAA used in our work was four times of GO content by mass to ensure a sufficient reduction. Figure 1 shows (a) aqueous suspension of GO and a graphene hydrogel and (b) a graphene aerogel.

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

The oxidization of graphite into GO (or GO after exfoliation) and the reduction of a GO into a GA were investigated by X-ray diffraction (XRD) technique, as shown in Figure 2. From XRD spectrum, a strong characteristic peak of 26.4° is observed for the raw graphite powder, while a peak of 11° is found for the graphene oxide obtained from the oxidization and exfoliation of graphite, which is consistent with the results reported elsewhere and indicated the conversion of graphite to GO [16,18,26,27]. For the XRD pattern of GA, a broad peak is shown at 23.5° , indicating the effective removal of oxygen groups during the LAA reduction process and a π - π interaction between graphene layers [19,23].

3.2. Nanostructured control of graphene aerogels

The effects of synthesis conditions, such as initial GO concentrations, reduction temperatures and reduction times, on the morphologies of the GAs were investigated. The GAs were synthesized with various initial GO concentrations of 1, 2, 6 and 12 mg/ml, reduction temperatures of 45, 70 and 95°C and reduction times of 5, 10, 20 and 40 h, respectively, as shown in Table 1. The mechanism of graphene self-assembly by chemical reduction was proposed by Chen et al. [23]. It is well known that GO can be well dispersed in DI water due to its hydrophilicity. When GO is reduced by reducing agents such as LAA, the reduced GO sheets will become hydrophobic and the π - π stacking of them will increase, leading to the formation of a 3D structure of graphene.

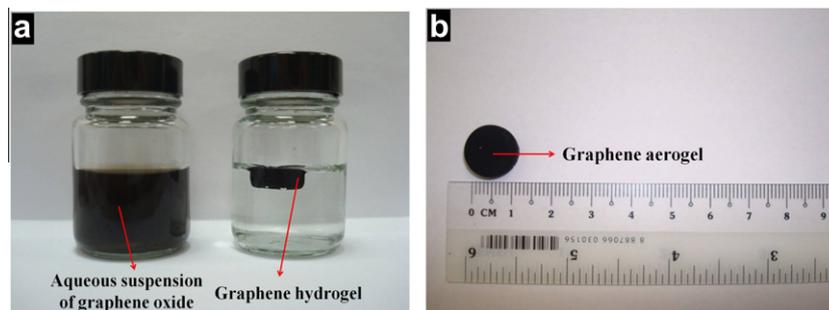


Figure 1. (a) Aqueous suspension of GO and a graphene hydrogel and (b) a graphene aerogel.

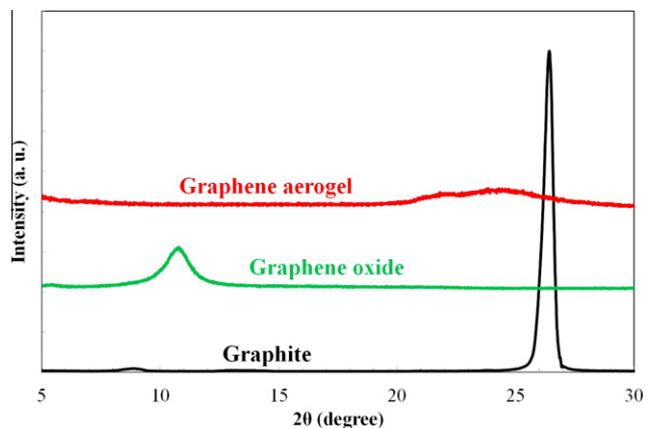


Figure 2. XRD patterns of graphite, graphene oxide and graphene aerogel.

The nanostructures of the GAs obtained under different concentrations, different reduction temperatures and different treatment times are compared in Figure 3. All of them present interconnected three-dimensional network structures. It can be seen that the 3D network formed from 12 mg/ml GO suspension is denser than that from the concentration of 2 mg/ml, while the GA synthesized at 95 °C has a more packed structure than those at 70 and 45 °C. Otherwise, the GA sample reduced for 40 h is also more overlapped than that for 5 h.

The characterization of the specific surface areas and porous properties of the GAs obtained under different conditions were conducted by nitrogen adsorption/ desorption measurements with a Nova 2200e (Quantachrome). Before measurements, samples were degassed at 120 °C in vacuum for 2 h to remove moistures, and the calculations of the specific surface area and pore size of the GA samples were conducted by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. A typical

Table 1
Nanostructure control and morphology effects on electrical properties of the graphene aerogels.

| No. | Synthesis conditions | Surface area (m ² /g) | Average pore size (nm) | Pore volume (cm ³ /g) | Density (g/cm ³) | Conductivity (S/m) |
|--|----------------------|----------------------------------|------------------------|----------------------------------|------------------------------|--------------------|
| <i>Different GO concentrations (Temperature: 70 °C, time: 40 h)</i> | | | | | | |
| 1 | 1 mg/ml | 284 | 3.6 | 0.51 | 18.24 | 0.7 |
| 2 | 2 mg/ml | 302 | 4.1 | 0.63 | 26.53 | 0.8 |
| 3 | 6 mg/ml | 365 | 3.9 | 0.72 | 56.44 | 1.1 |
| 4 | 12 mg/ml | 473 | 4.0 | 0.95 | 67.97 | 2.1 |
| <i>Different reduction times (GO concentration: 2 mg/ml, temperature: 70 °C)</i> | | | | | | |
| 5 | 5 h | 560 | 3.9 | 1.09 | 18.47 | 0.5 |
| 6 | 10 h | 438 | 4.0 | 0.88 | 20.81 | 0.6 |
| 7 | 20 h | 381 | 3.9 | 0.74 | 22.84 | 0.7 |
| 2 | 40 h | 302 | 4.1 | 0.63 | 26.53 | 0.8 |
| <i>Different reduction temperatures (GO concentration: 2 mg/ml, time: 40 h)</i> | | | | | | |
| 8 | 45 °C | 577 | 4.0 | 1.17 | 25.61 | 0.5 |
| 2 | 70 °C | 302 | 4.1 | 0.63 | 26.53 | 0.8 |
| 9 | 95 °C | 245 | 3.8 | 0.46 | 35.78 | 1.0 |

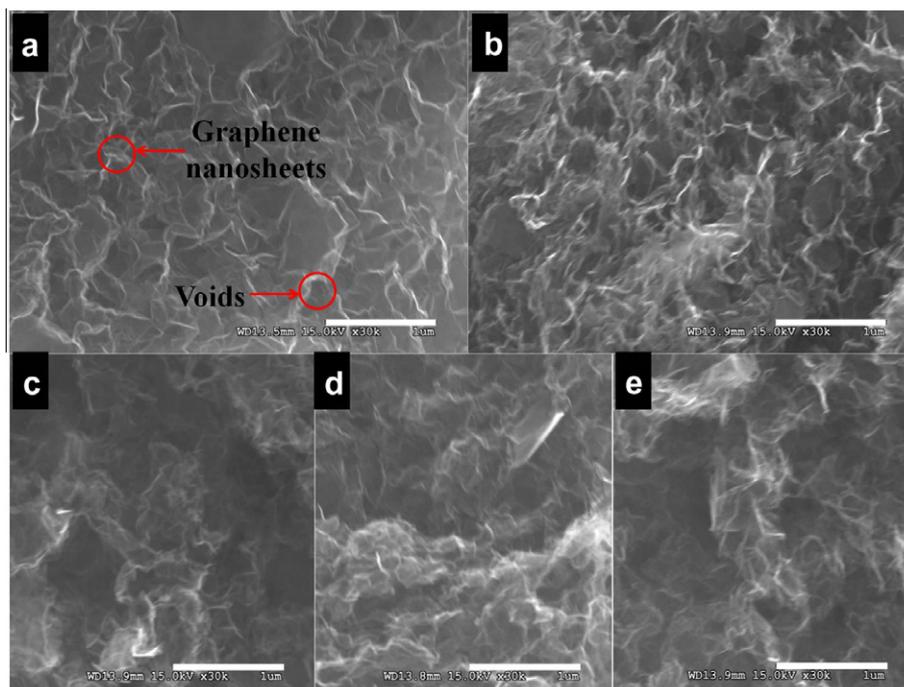


Figure 3. SEM images of graphene aerogels synthesized under different conditions: (a) 2 mg GO/ml, 70 °C, 40 h; (b) 12 mg GO/ml, 70 °C, 40 h; (c) 2 mg GO/ml, 45 °C, 40 h; (d) 2 mg GO/ml, 95 °C, 40 h; (e) 2 mg GO/ml, 70 °C, 5 h. Compared to image (a), more graphene nanosheets can be observed in image (b). The GA sample in image (c) shows a more loose structure than those in image (a) and image (d). The image (e) also shows a less dense network than that in image (a).

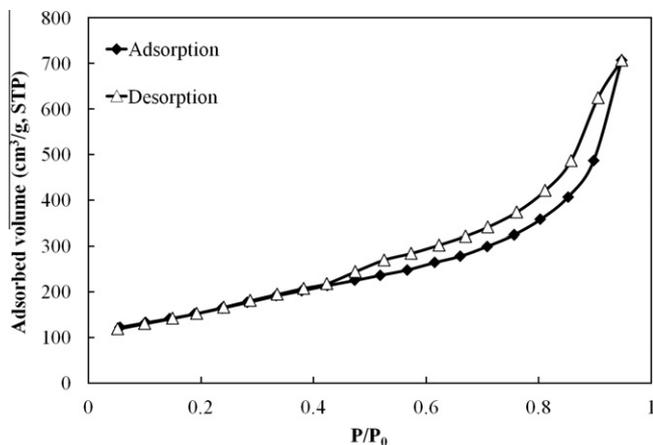


Figure 4. Typical N_2 adsorption/desorption isotherm of a GA.

nitrogen adsorption/desorption isotherm is shown in Figure 4. Type IV adsorption/desorption isotherms are displayed for all the GA samples, indicating that there are many mesopores in the GA structures. All the morphological characteristics and electrical conductivities of as-prepared GA samples are summarized in Table 1.

For all the GAs synthesized at 70°C for 40 h, the highest surface area of $473\text{ m}^2/\text{g}$ is obtained with 12 mg/ml initial GO concentration while the lowest value of $284\text{ m}^2/\text{g}$ is found with GO concentration of 1 mg/ml . It can be seen that under the same reduction conditions, the surface area and pore volume of the GAs increase along with the increase of initial GO concentration, since more graphene nanosheets are more likely to create more pores during the reduction process. The effect of synthesis conditions on GAs was all conducted with 2 mg/ml GO. With the same reduction time of 40 h, the GA synthesized at 45°C has the largest surface area of $577\text{ m}^2/\text{g}$ and pore volume of $1.17\text{ cm}^3/\text{g}$, while that at 95°C has the least value of $245\text{ m}^2/\text{g}$ and $0.46\text{ cm}^3/\text{g}$, respectively. When the reduction temperature is kept at 70°C , the surface area and pore volume value of the GA sample with 5 h reduction treatment are much larger than those of the one treated for 40 h. As reduction temperature and reduction time increase, more overlapping sites in the structure will form due to higher pressure formed in the reaction vial. Such overlapping between the graphene nanosheets results in a reduction of the surface area and pore volume. Therefore, it can be concluded that with the same GO concentration, the surface area of the GAs reduces with the increase of reduction temperature or reduction time. Compared to the previous work [19], the surface area and pore volume of the GAs prepared by mild chemical reduction method are all higher than the samples prepared by hydrothermal method, indicating the negative effect of higher pressure on the surface area and pore volume of the GAs.

3.3. Morphology effects on electrical properties of graphene aerogels

Figure 5 shows a typical current–voltage curve of sample 4, which was obtained from 12 mg/ml GO suspension at 70°C for 40 h and achieved the highest electrical conductivity in this Letter. The electrical conductivity was calculated from this linear I – V plot. It can be seen that under the same reduction temperature and reduction time, GA synthesized from higher initial GO concentration has a higher electrical conductivity, i.e. the highest electrical conductivity 2.1 S/m is obtained when initial GO concentration is 12 mg/ml , which is comparable to the data reported elsewhere [24]. It can be explained that more graphene nanosheets in higher GO concentration can form more overlapping during the synthesis process and thus, better electron mobility will be obtained. Figure

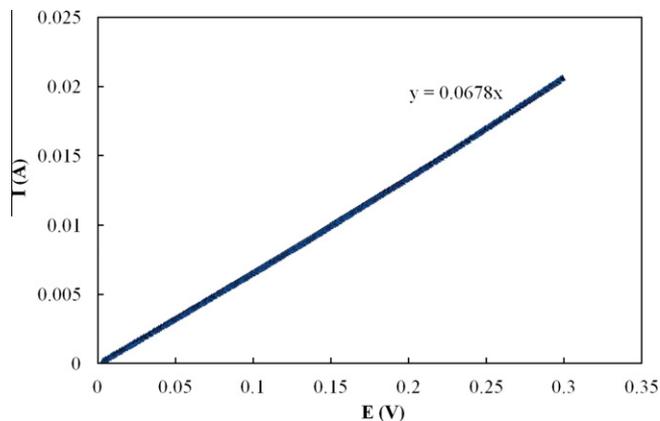


Figure 5. I – V plot of sample 4, which was obtained from 12 mg/ml GO suspension at 70°C for 40 h and achieved the highest electrical conductivity in this work.

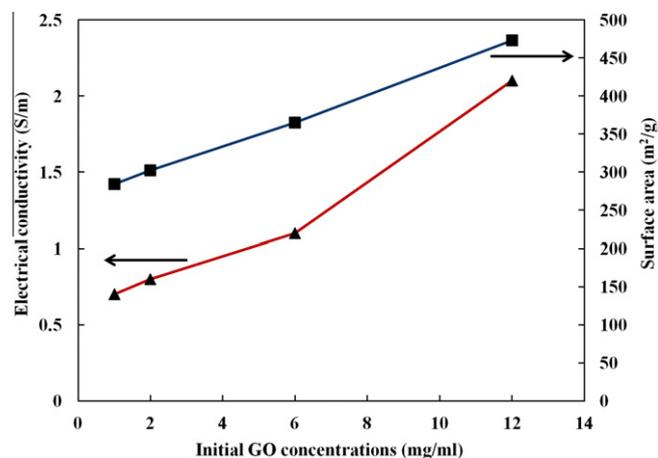


Figure 6. Effects of initial GO concentrations on electrical conductivities and surface areas of GAs.

6 shows the effect of initial GO concentrations on electrical conductivities and surface areas of GAs. It can be noted that increasing the concentration of initial GO aqueous suspension can both increase the electrical conductivity and surface area of GA. However, if the GO concentration is too high, it will be very difficult to form a uniform structure in the as-prepared GA. For GAs synthesized from the same initial concentration of GO, the electrical conductivities decrease with the increase of surface areas. It is mainly because for a denser structure of GA, more stacking of graphene nanosheets and stronger π – π interactions are formed in the network, which provide more channels for electrons to transmit, resulting in a higher electrical conductivity.

Furthermore, a thermal annealing at 400°C under Ar atmosphere was performed for 5 h on the sample with the highest surface area, which was synthesized at 45°C for 40 h. After the annealing treatment, the electrical conductivity of the sample is increased to 2.0 S/m , four times higher than the value before thermal annealing. More systematical studies will be conducted to study the effect of thermal annealing treatment on the morphology, electrical and mechanical properties of the GAs.

3.4. Morphology effects on thermal properties of graphene aerogels

The thermal durability, which is also an important factor for electrode materials working at high temperatures, was studied

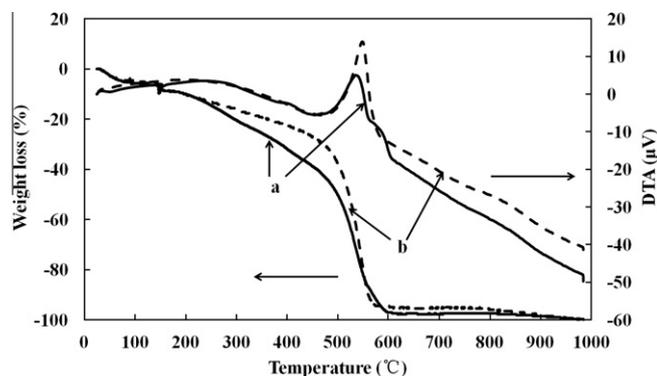


Figure 7. Thermal stability of GAs at (a) 45 °C and (b) 95 °C.

by TGA on DTG60H using sample 8 and 9, which are synthesized at 45 and 95 °C, respectively. During TGA test, the samples were heated from 25 to 1000 °C in air with a heating rate of 5 °C/min. Thermal stability of these as-prepared GAs is shown in Figure 7 which both exhibit similar trends but with different burning temperatures. As seen from the TGA curves, sample 9 shows an obvious weight loss in the range of 450–560 °C with a DTA peak at 544 °C, while the sample 8 possesses a continuous decrease in weight from 200 to 570 °C with a DTA peak at 529 °C. It can be observed that sample 9, which was synthesized at a higher temperature, creates a denser structure and higher thermal stability, which also indicated that the more overlapping of graphene nanosheets makes the GA a more rigid network. For comparison, sample 8, which was synthesized at a lower temperature, has a looser structure and appears to be less thermally stable due to the existence of some unpacked part inside.

4. Conclusions

In conclusion, the GAs were synthesized in a simple way with different conditions, various initial GO concentrations, reduction temperatures and reduction times. A morphology control of the as-prepared GAs can be achieved by changing synthesis parameters appropriately. The experimental results showed that the GA synthesized from higher GO concentration possessed higher surface area and electrical conductivity, while higher reduction temperature and reduction time made GA a packed structure with lower surface area and higher electrical conductivity as well as better thermal stability. The experimental results of this Letter are

very useful for energy storage applications as the performance of graphene aerogel-based electrodes can benefit from the high surface area of the aerogels and high electrical properties of the graphene in GAs.

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