Supporting Information for

### Mechanically Robust Glucose Strutted Graphene Aerogel Paper as Flexible Electrode

Wee Siang Vincent Lee<sup>a</sup>, Erwin Peng<sup>a</sup>, Dian Chun Choy<sup>a</sup>, and Jun Min Xue<sup>\*a</sup>

\*Corresponding author at: National University of Singapore, Department of Materials Science and Engineering, Singapore 117573. Tel./fax +65 65164655

E-mail: msexuejm@nus.edu.sg (J.M. Xue)

#### Materials and methods

#### Synthesis of Sulphur-functionalized Glucose Struts

In a typical synthesis of glucose struts, 4ml of D.I water was added to 1g of glucose and 0.5g of thiourea. The mixture was vortexed till a clear solution was obtained. Meanwhile, the oil bath was preheated to 180°C. The clear solution containing glucose, thiourea, and D.I water was placed in the oil bath for 2 hours with constant magnetic stirring. After the reaction is completed, the clear solution should turn clear brown. The clear brown solution was cooled down to room temperature.

## Synthesis of Acid-treated Glucose strutted Graphene Aerogel

In a typical synthesis of the graphene aerogel, 0.2 ml of the glucose struts solution was added to 10 ml of graphene oxide colloidal solution (about 5 mg ml<sup>-1</sup>). The mixture was well vortexed and was then placed in an oven at 80°C for 1 hour. The graphene hydrogel was then freeze in the freezer for 2 hours. The frozen hydrogel was later placed in the oven at 80°C for 2 hours. The hydrogel then underwent solvent exchange with D.I water repeatedly overnight. The obtained glucose strutted graphene hydrogel was later bathed inside 5M H<sub>2</sub>SO<sub>4</sub> solution under reflux for 2 hours to remove the unwanted glucose struts by-product. The acid treated graphene hydrogel was then solvent exchanged with D.I water until pH returned to 7. The washed acid treated graphene hydrogel was then lyophilized for 1 day to finally obtain acidtreated glucose strutted graphene aerogel.

### Synthesis of Acid treated Glucose strutted Graphene Aerogel Paper

The acid treated glucose strutted graphene aerogel was mechanically compressed with 4.7 MPa for less than 30 seconds to obtain acid treated glucose strutted graphene aerogel paper (A-GSGA-P).

# Density measurement of Acid treated Glucose strutted Graphene aerogel and Graphene aerogel Paper

The density of the GSGA in the aerogel form before being mechanically compressed is 0.005g cm<sup>-3</sup>. The reason for the ultra-low density for the graphene aerogel is due to the incorporation of the additional zero-shrinkage step in the aerogel preparation process as shown in **Fig. S1**. This additional step is so-called the pre-freezing step that was utilized in our previous work [1].



**Fig. S1** Comparison between glucose strutted graphene aerogel without and with additional pre-freezing step (glucose strutted graphene oxide solution before gelation as control)

Thus, the as-synthesized graphene aerogel in this manuscript can retain its ultra-low density of about 0.005g cm<sup>-3</sup>. The density measurement of the graphene aerogel and graphene aerogel paper is as follows:



Fig. S2 Measurement of the glucose strutted graphene aerogel diameter, thickness, and mass

The diameter and the thickness of the aerogel was measured with ruler (reading error of 1 mm) and Vernier callipers (reading error of 0.02 mm) respectively. The mass of the aerogel was measured with a weighting balance (accuracy of 0.0001 g). The density of both the aerogel and aerogel paper was calculated based on the density formula  $\rho = M/r^2\pi h$ . Where M is the mass of the graphene aerogel in grams, r is the radius of the graphene aerogel in centimetre, and h is the thickness of the graphene aerogel in centimetre.

The measured dimension of the graphene aerogel and graphene aerogel paper is shown in **Fig. S2**. The measured mass of the aerogel was 49.4 mg (due to minute loss of graphene oxide that was stuck on the side of the petri dish during preparation). The thickness of the aerogel is about 0.5 cm, and the diameter is about 4.9 cm. Based on the calculation using the above formula, the calculated density of the graphene aerogel is about 5.2 mg cm<sup>-3</sup>. The same graphene aerogel was later mechanically compressed under 4.7 MPa to obtain the graphene aerogel paper. The thickness of the graphene aerogel paper was reduced to 0.4 mm. The calculated density of the graphene aerogel paper was determined to be about 65 mg cm<sup>-3</sup>.







In the capacitive characterization, the graphene aerogel paper was cut into 1 cm x 1 cm electrode as shown in the **Fig. S3**. The free-standing graphene aerogel paper was later clamped on a current collector with platinum as the collector. The mechanically strong graphene aerogel paper was then tested in a 3 electrodes setup, with platinum plate as the counter electrode, saturated calomel electrode as the reference electrode, and 1M KOH as the aqueous electrolyte. The mass of each of the 1 cm x 1 cm graphene aerogel paper was about 2 mg.

#### **Results and Discussion**



**Fig. S4** Mechanical compression test on a) GSGA for 30 compressions, and b) control without glucose struts for 5 compressions. Further mechanical compression test on c) GSGA for 1000 compressions

The synthesized GSGA was firstly studied for its compressive strength. As a preliminary testing GSGA underwent 30 compression as shown in **Fig. S4a**, and the compressed sample was able to exhibit a 100% recoverability after the test. To study the effect of the glucose struts in enhancing the mechanical properties of the aerogel, a control sample (GA) with the equivalent amount of thiourea was used in the synthesis process. The control sample exhibited poor mechanical robustness as the structural breakdown can be observed after a mere 5 compression shown in **Fig. S4b**. This set of results show a glaring contrast in the mechanical robustness between the samples with and without glucose struts. The feather-like property of GSGA, with a density of about 5 mg cm<sup>-3</sup>, was demonstrated by resting the aerogel on top of a small dandelion (**Fig. S1c** inset). To further demonstrate the robustness of the synthesised GSGA sample, 1000 compression cycles were conducted. Even after the vigorous 1000 compression cycles, the glucose strutted aerogel was able to exhibit 100% recoverability in its height, which suggests excellent mechanical robustness of GSGA.



**Fig. S5** a) Setup of the tensile test on the graphene paper, and b) cyclic tensile stress performance on A-GSGA-P with a stress of 0.13 MPa

A schematic illustration of the mechanical testing setup is shown in **Fig. S5a**. The A-GSGA-P strip was clamped at each end with paper clip. One end was connected to a retort stand while the other end was connected to a measuring beaker. To test for the mechanical tensile strength of the sample, the width and the thickness of the strip was pre-determined. Water was used as the weight with the assumption of a density of 1 g ml<sup>-1</sup>. Water was added into the measuring beaker until the material snaps into half. The amount of water after the failure was noted down. GA-P, without the glucose struts, was also tested in the similar method. GA-P was prepared without the glucose struts and was prepared from the mechanical compression of GA (control).



Fig. S6 SEM image of a) GSGA (aerogel form), and b) GSGA-P (paper form)

**Fig. S6** shows the SEM images of glucose-strutted graphene aerogel before and after mechanical compression to obtain the flexible graphene aerogel paper. As it can be observed

from the SEM images, the porous structure of the aerogel was squeezed into alignment to a relatively arranged layer by layer structure.



**Fig. S7** BET result for A-GSGA-P. a) Nitrogen adsorption isotherm, and b) pore size distribution The analysis of the nitrogen adsorption/desorption of A-GSGA-P gives a specific surface area of about 340 m<sup>2</sup> g<sup>-1</sup>, with a pore volume of 0.81 cm<sup>3</sup> g<sup>-1</sup>. The isotherm curve exhibits a Type IV isotherm shape as filling of the void with nitrogen occurs only at high relative pressure  $p/p^{o}$ , which is a characteristic of mesoporous absorbent. Also, the almost lack of hysteresis loop in the nitrogen sorption isotherm curve hints the existence of macropores. The pore size distribution curves (**Fig. S7**) shows that A-GSGA-P possesses pores which are in mesoporous range (25-35nm) and in microporous range (< 2nm).



**Fig. S8** a) Low magnification SEM of the graphene aerogel, and the measured pore size distribution As the graphene aerogel has many wide pores which are larger than  $50\mu m$ , N<sub>2</sub> sorption experiment may not be able to fully characterize the surface area of the aerogel form. Thus as an alternative method to estimate the pore size distribution for the graphene aerogel, low

magnification SEM image of the graphene aerogel (**Fig. S8a**) was used. Assuming in a 2 D situation, 40 pores were randomly measured (longest length of the pores were taken as the pore size) for 3 different SEM images of aerogel (in total, approximately 120 pores were randomly measured). Based on the sample group, the estimated pore size distribution was tabulated in **Fig. S8b**. The estimated pore size distribution revealed a relatively wide range of pore size between 30 to 200 µm, where greater proportion of the pores was measured to be around 80 µm. The graphene aerogel paper also has large pore sizes available as seen in the SEM image (**Fig. S5b**). However due to the mechanical compression process, the graphene oxide sheets were brought closer to the adjacent sheets, creating mesopores averaging 25-35nm in size which was previously almost non-existence in the aerogel form.



Fig. S9 C1s high resolution XPS spectrum of pristine graphene oxide



**Fig. S10** The CV curves of graphene aerogel paper between potential window -0.8 to 0V and 0 to 0.5V The potential window, 0 to 0.5V, was used due to the existence of redox peaks due to pseudocapactive reaction of the sulphur functional groups. Electric double layer capacitance contribution can be observed, as shown in **Fig. S10**, when the potential window is in the negative region, between -0.8 to 0V. The graphene aerogel paper was able exhibit an EDLClike contribution with a potential window of 0.8V. A smaller potential window between 0 to 0.5V was used due to the additional contribution from the pseudocapactive reaction from the thioester to sulphone, as proposed in the manuscript. 0.5V was chosen as the upper limit due to the oxygen evolution reaction (OER) starts to occur beyond this limit.



**Fig. S11** S2p high resolution XPS spectrum of a) charged A-GSGA-P and b) discharged A-GSGA-P **Fig. S11** shows the S2p high resolution XPS spectrum for A-GSGA-P fully charged, and after it experienced discharged. The proportion of C-S doublet for the A-GSGA-P charged

decreased significantly from the uncharged state (**Fig. 3b**). At the same time, sulphone doublet became much more dominant as compared to the other sulphur doublets. This XPS observation suggests that during the charging process, proportion of C-S in the form of R-S-R decreased relative to sulphone as thioester is oxidised to sulphone. After being discharged, the sample showed lower proportion of sulphone doublet and a higher proportion of C-S doublet as compared to the charged sample. This suggests that R-SO<sub>2</sub>-R species were reduced to R-S-R species under discharging which agreed with our previous work [1]

#### Reference

Wee Siang Vincent Lee, Mei Leng, Meng Li, Xiao Lei Huang, Jun Min Xue, Nano Energy, 2015, 12, 250–257