

# **High energy and excellent stability asymmetric supercapacitor derived from sulphur-reduced graphene oxide/manganese dioxide composite and activated carbon from peanut shell**

Delvina Japhet Tarimo, Kabir O. Oyedotun, Abdulmajid A. Mirghni, Ndeye Fatou Sylla and Ncholu Manyala\*.

Department of Physics, Institute of Applied Materials, SARChI Chair in Carbon Technology and Materials, University of Pretoria, Pretoria 0028, South Africa.

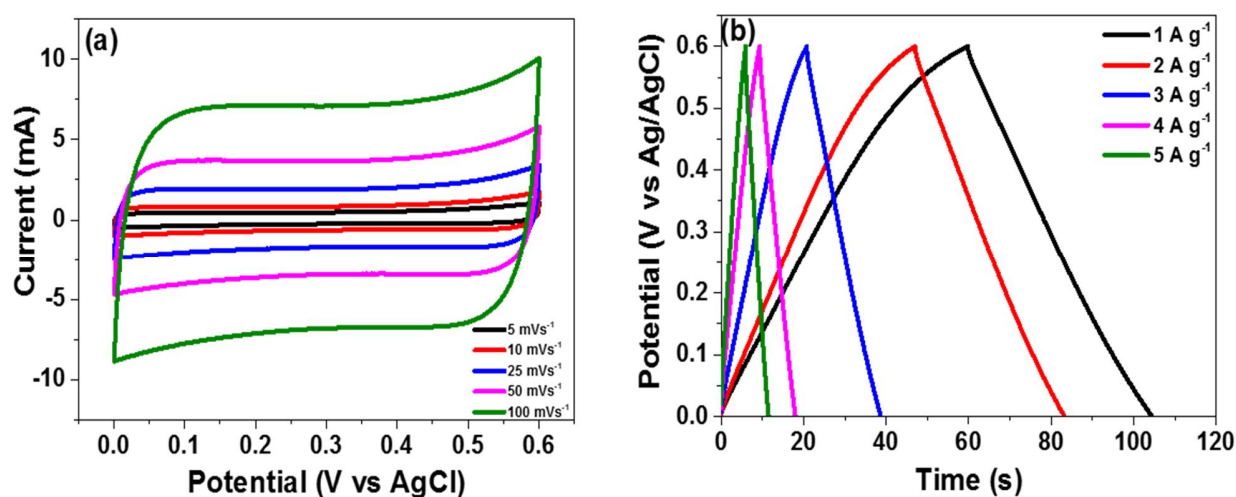
\*Corresponding author's email: [ncholu.manyala@up.ac.za](mailto:ncholu.manyala@up.ac.za), Tel.: + (27)12 420 3549.

## **Supporting document**

### **S1: Preparation of reduced graphene oxide (RGO) Samples**

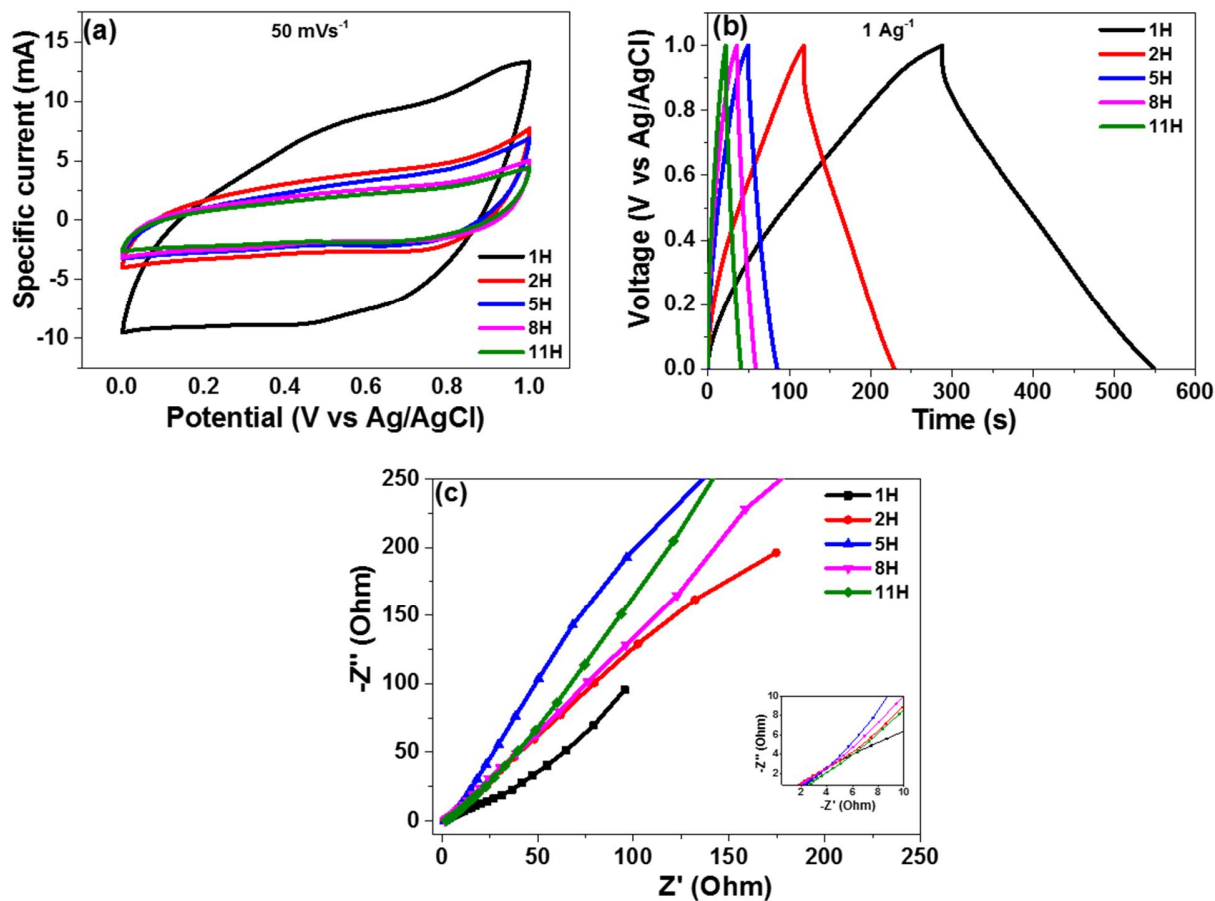
A modified hummer's method was used to synthesize graphene oxide using graphite powder as detailed below. Briefly, 5 g of graphite powder was added slowly to 100 mL of sulphuric acid ( $\text{H}_2\text{SO}_4$ ) followed by 2.5 g each of potassium hydrogen sulphate ( $\text{KHSO}_4$ ) and calcium chloride ( $\text{CaCl}_2$ ) subsequently upon stirring for pre-oxidation of the bulk graphite. The solution was stirred (400 rev/min) for 40 min. at 60 °C, followed by a further addition of 10 g of potassium permanganate ( $\text{KMnO}_4$ ) as an oxidizing agent. The solution was further stirred (250 rev/min) for 2 hours at 60 °C for homogeneity. The dark-grey resulting mixture was left to cool down to room temperature. Thereafter, 20 mL of hydrogen peroxide ( $\text{H}_2\text{O}_2$  - 30 %) alongside 120 mL of deionized water (DI water) were added to stop the reaction which caused a vigorous rise in temperature of the mixture and beard great potential hazard. Therefore, great cautions must be taken during the synthesis of the material. The mixture was left to cool naturally to room temperature. The resulting mixture was called graphene oxide (GO). The recovered mixture was re-dispersed into a 100 mL of DI water and sonicated for 2 hours for further reduction of GO. The mixture was left to settle down for 12 hours, washed several times with DI water and then centrifuge and dried in a vacuum oven at 80 °C for 6 hours to obtain the final sample named as reduced graphene oxide (RGO).

Fig. S2 display the CV curves at different scan rates and GCD curves at different specific currents for RGO-S (Pristine) sample conducted in three electrode measurements in a positive potential window range 0.0 – 0.6 V in 2.5 M KNO<sub>3</sub> electrolyte.



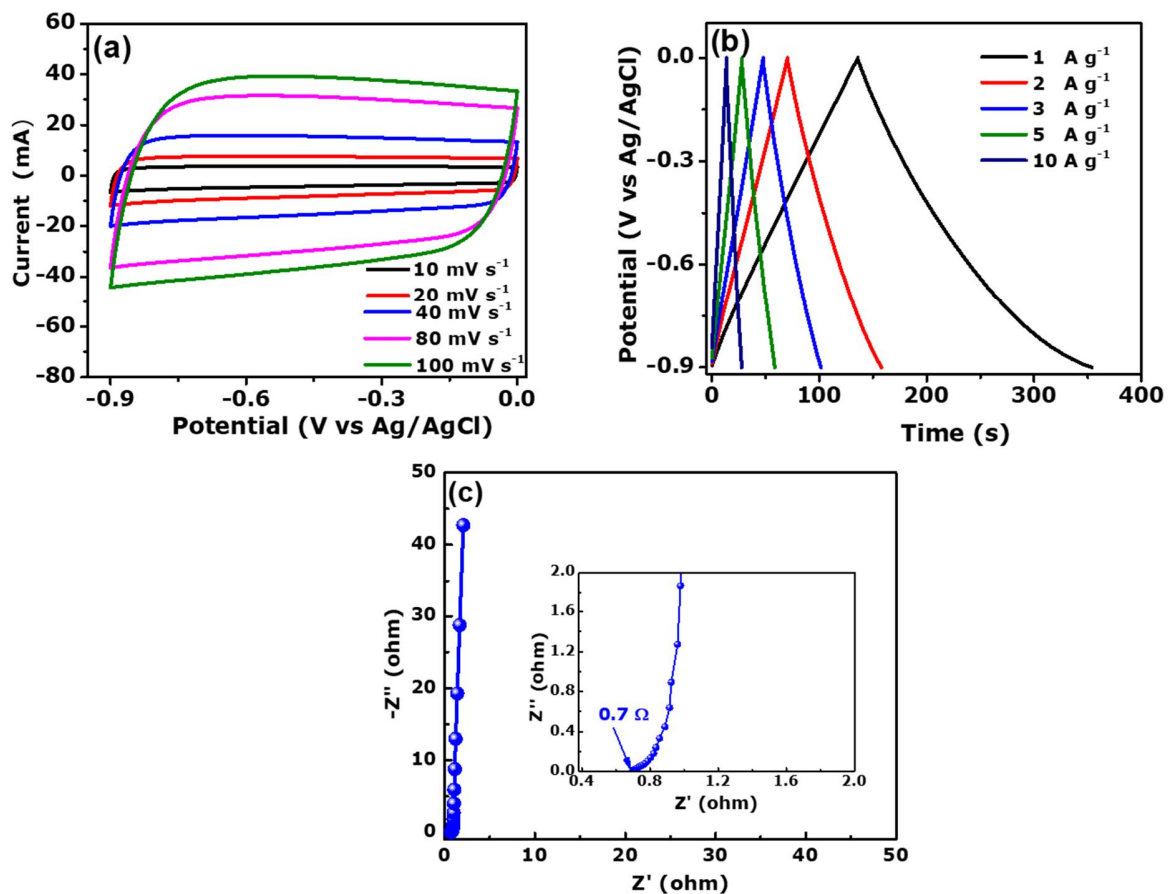
**Fig. S2:** (a) CV curves at different scan rates and (b) GCD curves at different specific currents in a positive potential window for RGO-S sample in 2.5 M KNO<sub>3</sub>, respectively.

Fig. S3 (a, b and c) shows the CV curves at 50 mV s<sup>-1</sup>, GCD curves at 1 A g<sup>-1</sup> and EIS Nyquist plot for MnO<sub>2</sub> sample at different hydrothermal times (1 H, 2 H, 5 H, 8 H and 11 H), respectively. The measurements were done in three electrode set-up using 2.5 M KNO<sub>3</sub> electrolyte in a positive potential window range 0.0 – 1.0 V. From the figure, 1 H hydrothermal time displayed better performance in terms of high current response in the CV curve, long discharge time in the GCD curve and short diffusion length in the EIS Nyquist plot, hence it was selected as an additive sample to make a composite with RGO-S in the revised manuscript.



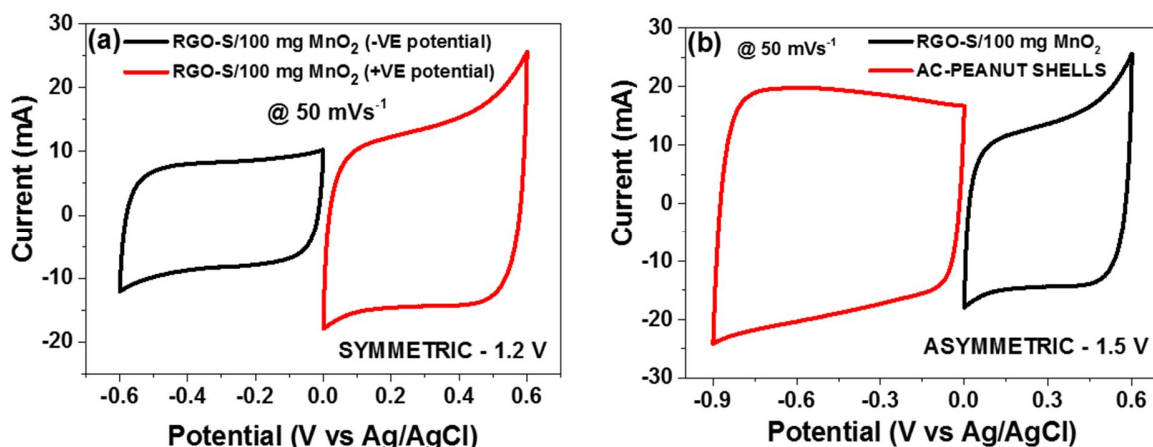
**Fig. S3:** (a) CV curves at 50 mV s<sup>-1</sup> in a positive potential window, (b) GCD curves at 1 A g<sup>-1</sup> in a positive potential window and (c) EIS Nyquist plot for MnO<sub>2</sub> sample at different hydrothermal times (1 H, 2 H, 5 H, 8 H and 11 H) in 2.5 M KNO<sub>3</sub>, respectively.

Fig. S4 (a, b and c) shows the CV, GCD curves and EIS Nyquist plot of peanut shells-based activated carbon (AC-PS) used as negative electrode, and measured as three-electrode in 2.5 M KNO<sub>3</sub> in a potential window range of -0.9 – 0.0 V. The negative electrode showed no noticeable peaks in its curves, with an ideal rectangular and triangular CV and GCD curves, respectively, indicating the electrode's double-layer capacitive signatures with good reversibility. The Nyquist plot in Fig. S4 (c) reveals a low equivalent series resistance,  $R_s$  value of 0.7  $\Omega$ , hinting the material's good conductivity.



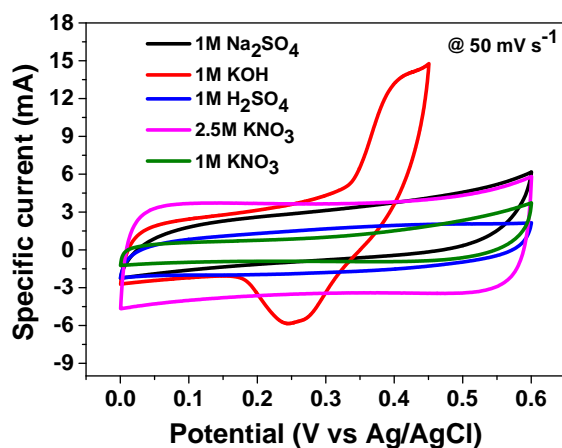
**Fig. S4:** Electrochemical measurement of the AC-PS: (a) CV curves at different scan rates, (b) GCD curves at different specific currents and (c) EIS Nyquist plot, respectively.

Fig. S5 (a) displays the CV curves at  $50 \text{ mV s}^{-1}$  in a positive potential range  $0.0 - 0.6 \text{ V}$  and negative potential range  $-0.6 - 0.0 \text{ V}$  for RGO-S/100 mg  $\text{MnO}_2$  sample. The sample displays better performance in a positive potential window than negative potential window hence it was selected as a positive electrode to make up the device. Fig. S5 (b) displays the CV curves at  $50 \text{ mV s}^{-1}$  for RGO-S/100 mg  $\text{MnO}_2$  in a positive potential range  $0.0 - 0.6 \text{ V}$  and AC-PS sample used as a negative electrode in a negative potential range  $-0.9 - 0.0 \text{ V}$ . Furthermore, Fig. S5 (a) shows that the combined symmetric has a voltage of  $1.2 \text{ V}$  while combined asymmetric has  $1.5 \text{ V}$  (Fig. S5 (b)) hence the combined asymmetric was selected to make up the device. All samples were tested in three electrode measurements in  $2.5 \text{ M KNO}_3$  electrolyte before making up the device.

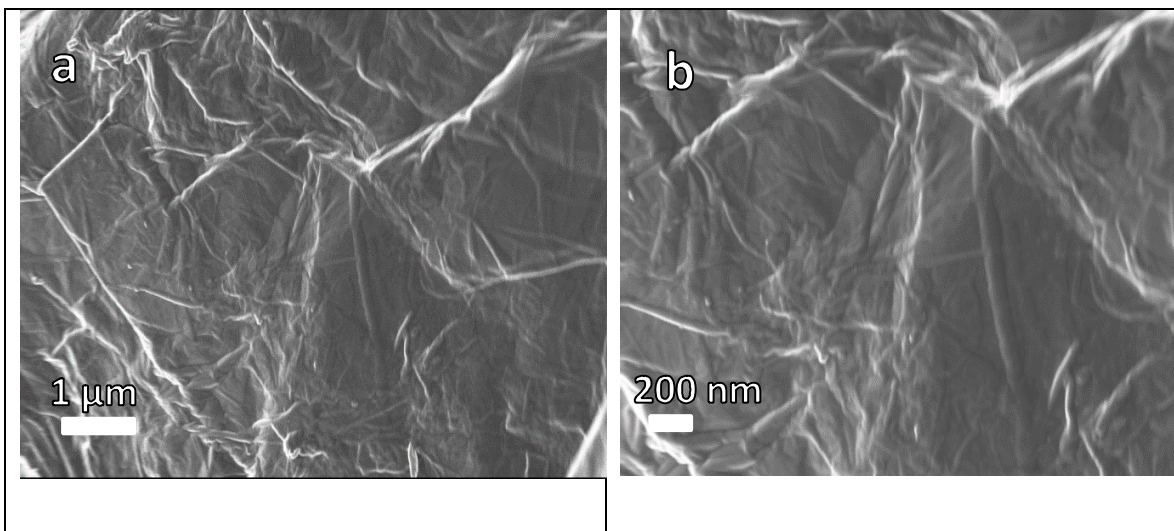


**Fig. S5:** (a, b) CV curves at  $50 \text{ mV s}^{-1}$  in a positive and negative potential window for symmetric and asymmetric respectively in  $2.5 \text{ M KNO}_3$ .

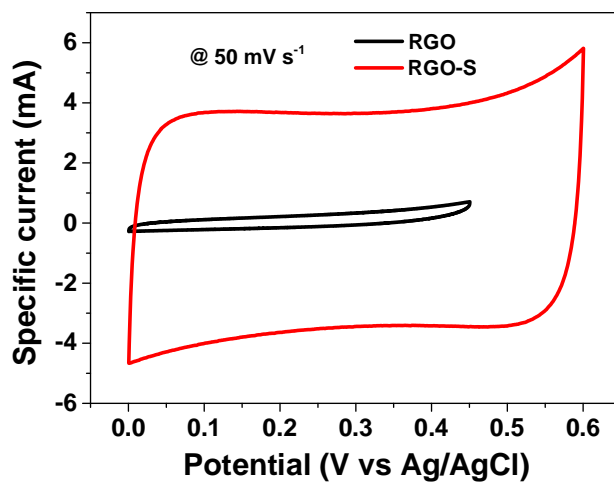
Fig. S6 shows the CV curves at  $50 \text{ mV s}^{-1}$  in a positive potential range  $0.0 - 0.6 \text{ V}$  for RGO-S/100 mg  $\text{MnO}_2$  sample tested in different electrolytes. From the figure it can be observed that  $2.5 \text{ M KNO}_3$  electrolyte displayed better performance than  $1 \text{ M Na}_2\text{SO}_4$ ,  $1 \text{ M KOH}$ ,  $1 \text{ M H}_2\text{SO}_4$  and  $1 \text{ M KNO}_3$  and hence it was selected for electrochemical measurements in three- and two-electrode system.



**Fig. S6:** CV curves at  $50 \text{ mV s}^{-1}$  in a positive potential window showing different type of electrolytes.



**Fig. S7:** (a, b) SEM images of RGO at low and high magnifications respectively.



**Fig. S8:** CV curves at a scan rate of 50 mV s<sup>-1</sup> in a positive potential window for RGO and RGO-S sample in 2.5 M KNO<sub>3</sub>, respectively.