

# **An Enhanced Electrochemical Performance of Sodium-air Battery with Graphene Nanosheets as Air Electrode Catalysts**

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**Electronic Supplementary Information (ESI)**

## Materials Synthesis

The details of the preparation of GNS film electrode have been described in our recent work<sup>1-2</sup>. Firstly, the aqueous graphene dispersions with the concentration of 250 µg/ml were prepared according to Li's method<sup>3</sup>. Then one high-porosity nickel foam (420 g/m<sup>2</sup> in areal density and 1.1 mm in thickness) was submerged into the graphene colloids and sonicated for several minutes followed by drying in a vacuum oven at 80 °C for 24 h. As a comparison, carbon film electrodes deposited onto nickel foam were prepared by r.f. sputtering method and their preparations have been described in our previous work<sup>4</sup>.

## Electrochemical measurements

For electrochemical measurement, a conventional two-electrode cell was constructed in the dried air filled in glove box with the deposited film as the cathode and one sheet of high-purity sodium foil as the anode, respectively. The model cell consisted of an H shape glass tube to separate positive and negative electrodes as well as two rubber plugs for sealing. The electrolyte was 0.25M NaPF<sub>6</sub> (Alfa-Aesar) non-aqueous solution in 1,2-dimethoxyethane(DME) (Alfa-Aesar). Weight of thin film was directly obtained by subtracting the original substrate weight from total weight of the substrate and deposited film onto its surface, which were examined by electrobalance (BP 211D, Sartorius). The precision of the weight was ± 0.01 mg. Charge-discharge measurements were performed at room temperature with a Land BT 1-40 battery test system. The cyclic voltammograms (CV) measurements were performed with a scanning rate of 0.1 mV/s on a CHI660A electrochemical working station(CHI Instruments, TN). The current densities and capacities of electrodes were calculated based on the total mass of electrode materials.

## Physical characterization

High resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED) measurements were carried out on a JEOL 2010 TEM at 160 kV accelerating voltage. N<sub>2</sub> adsorption-desorption data were measured using a Micromeritics Tristar ASAP 3000 analyzer at 77 K, and the isotherms were evaluated with the Barrett-Joyner-Halenda(BJH) theory to give the pore size and its distribution.

## References

1. Y. Yang, M. Shi, Q. F. Zhou, Y.S. Li, and Z.W. Fu, *Electrochem. Comm.*, 2012, **20**, 11.
2. Y. Yang, M. Shi, Y.S. Li, and Z.W. Fu, *J. Electrochem. Soc.*, 2012, **159**, A1917.
3. D. Li, M. B. Muller, S. Gilje, R. B. Kaner, G. G. Wallace, *Nat. Nanotechnol.*, 2008, **3**, 101
4. Y. Yang, Q. Sun, Y. S. Li, H. Li, Z. W. Fu. *J. Electrochem. Soc.*, 2011, **158**, B1211.

**Table S1 Electrochemical Properties of Na-air/O<sub>2</sub> batteries produced by this work and from literatures.**

Cathode	Electrolyte	Air	Specific capacity	Refs
GNS	0.25M NaPF <sub>6</sub> /DME	Dried air	9268mAh/g(200mA/g) 6208mAh/g(300mA/g)	This work
GNS	0.25M NaClO <sub>4</sub> /DME	Dried air	1402mAh/g(200mA/g)	This work
Thin film carbon	0.25M NaPF <sub>6</sub> /DME	Dried air	2030mAh/g(300mA/g)	This work
Carbon-fibre	0.25M NaPF <sub>6</sub> /DME	Dried air	180 mAh/g(300mA/g)	This work
Diamond-like carbon(DLC)	1M NaPF <sub>6</sub> /(EC:DMC=1:1)	Dried air	1884mAh/g(0.1C)	[1]
90% Super P (TIMCAL) carbon and 10% PVDF binder	0.75M NaCF <sub>3</sub> SO <sub>3</sub> /1-ethyl-3-methylimidazolium trifluoromethanesulfonate (IL)	Pure O <sub>2</sub>	1315mAh/g(70mA/g)	[2]
90% Super P (TIMCAL) carbon and 10% PVDF binder	1M NaClO <sub>4</sub> /tetraethylene glycol dimethylether	Pure O <sub>2</sub>	1390mAh/g(70mA/g)	[2]
carbon-fibre gas diffusion layer (GDL)	0.5M NaSO <sub>3</sub> CF <sub>3</sub> /DEGDME	Pure O <sub>2</sub>	700mAh/g(45.2mA/g)	[3]

1. Q. Sun, Y. Yang, Z.W. Fu, *Electrochem. Comm.*, 2012, **16**, 22.

2. S. K. Das, S.Xu, L.A. Archer, *Electrochem. Comm.*, 2013,**27**, 59.

3. P. Hartmann, C.L. bender, M. Vracar, A. K. Durr, A. Garsuch, J. Janek, P. Adelhelm, *Nature Mater.*, DOI:10.1038/NMAT3486

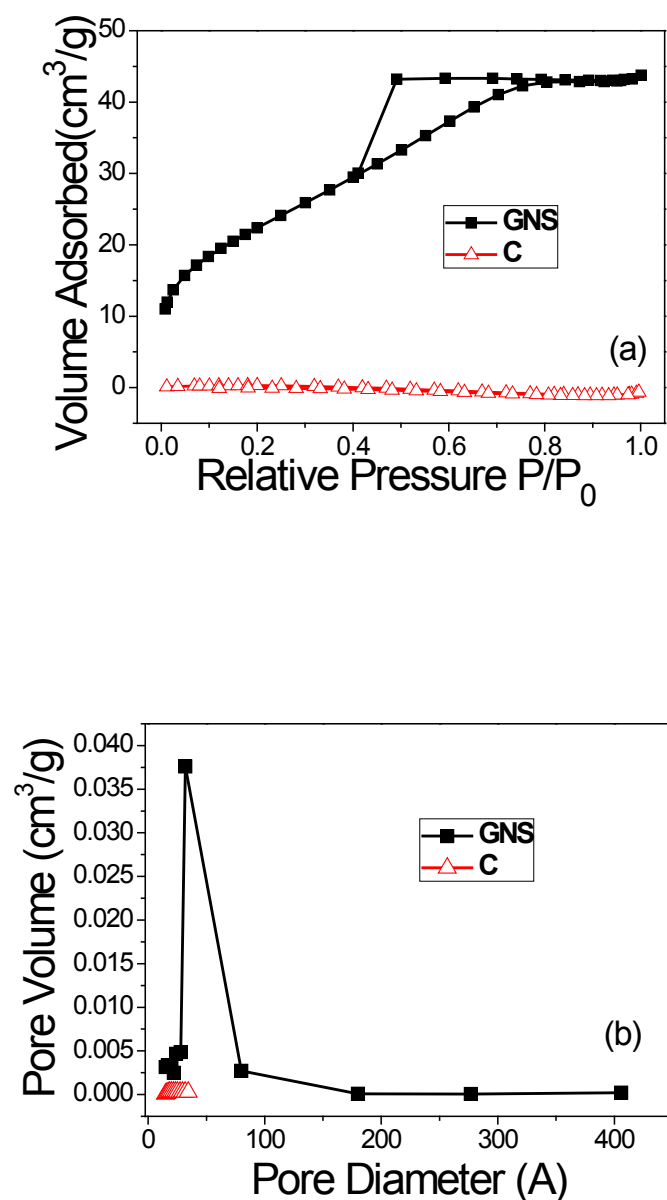


Figure 1S (a) Nitrogen adsorption-desorption isotherm plots for GNS and carbon film and (b) their pore size distribution

N<sub>2</sub> adsorption-desorption isotherm (Figure S1(a)) for the GNS exhibits a type IV curve, which indicate the presence of micropores at P/P<sub>0</sub> lower than 0.4 and mesoporosity in the P/P<sub>0</sub> range of 0.4~1.0. The BJH analysis show that GNS have a wide distribution of pore size at the pore size range from 3-100 Å (Figure S1(b)). The BET surface area of GNS is found to be 83 m<sup>2</sup>/g, which is much larger than 1 m<sup>2</sup>/g of carbon film. IV curve is different from the data of GNS reported by Li and Sun et al. (Y. Li, J. Wang, X. Li, D. Geng, R. Li, X. Sun, *Chem. Commun.*, 2011, **47**, 9438) due to different preparation process.