

Electronic Supplementary Information

Controlling Uniform Deposition of Discharge Products in Nanoscale for Rechargeable Na-O₂ Batteries

Sanpei Zhang^a, Zhaoyin Wen^{a}, Jun Jin,^a Tao Zhang,^a Jianhua Yang^a and Chunhua
Chen^b*

^aCAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of
Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China.

**E-mail: zywen@mail.sic.ac.cn*

^bCAS Key Laboratory of Materials for Energy Conversion, University of Science and
Technology of China, Hefei 230026, Anhui, P. R. China

Table S1. Comparison of various metal–air battery

Anode	Discharge products	Working potential (V)	Energy Density (Wh/kg)	Reversibility
Li ¹	Li ₂ O ₂	2.96	3505	√
Na ²	Na ₂ O ₂	2.33	1602	√
	NaO ₂	2.27	1105	√
K ³	KO ₂	2.48	935	√
	K ₂ O ₂	2.20	1070	√
Fe ⁴	Fe(OH) ₂	1-1.28	764	√
Al ⁵	Al(OH) ₃	1.20~1.60	2800	×
Zn ⁶	ZnO	1.65	1086	×
Mg ⁷	Mg(OH) ₂	3.10	3910	×

Energy densities are given per weight of the total discharge product.

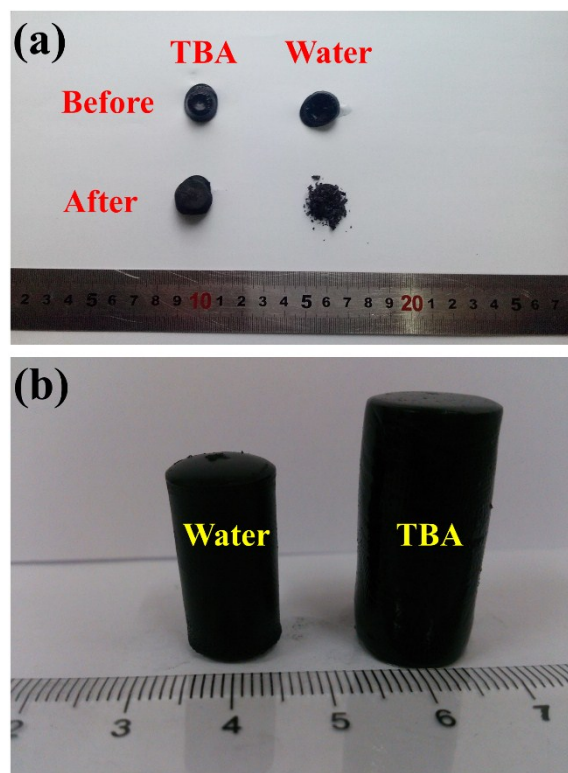


Figure S1. (a) 3D N-GA@Ni before and after freeze-drying with water and TBA as solvent, (b) the obtained nitrogen graphene aerogels after freeze-drying with water and TBA as solvent.



Figure S2. The sodium anode after 100 cycles at the current density of 100 mA g^{-1} with a cut-off capacity of 500 mA h g^{-1} .

Owing to the volatility of the DEGDME after 100 cycles at the current density of 100 mA g^{-1} with a cut-off capacity of 500 mA h g^{-1} , the Na anode was found to be oxidized and destroyed, which resulted in performance degradation for the Na-O₂ batteries. In order to confirm the excellent reversibility of 3D N-GA@Ni, we reassemble the cycled air electrode in a new cell with fresh Na foil and electrolyte.

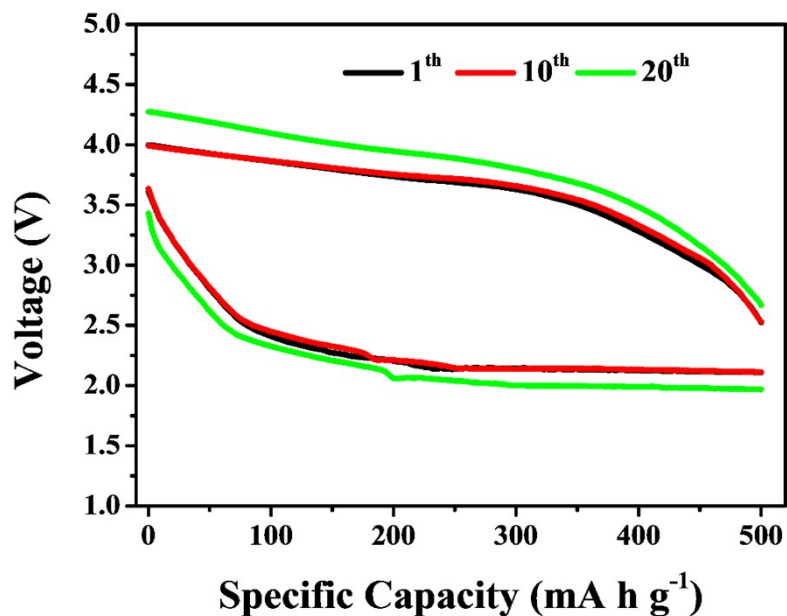


Figure S3. Cycling performance of the cycled 3D N-GA@Ni cathode in a new cell with fresh Na foil and electrolyte at the current density of 100 mA g^{-1} with a cut-off capacity of 500 mA h g^{-1} .

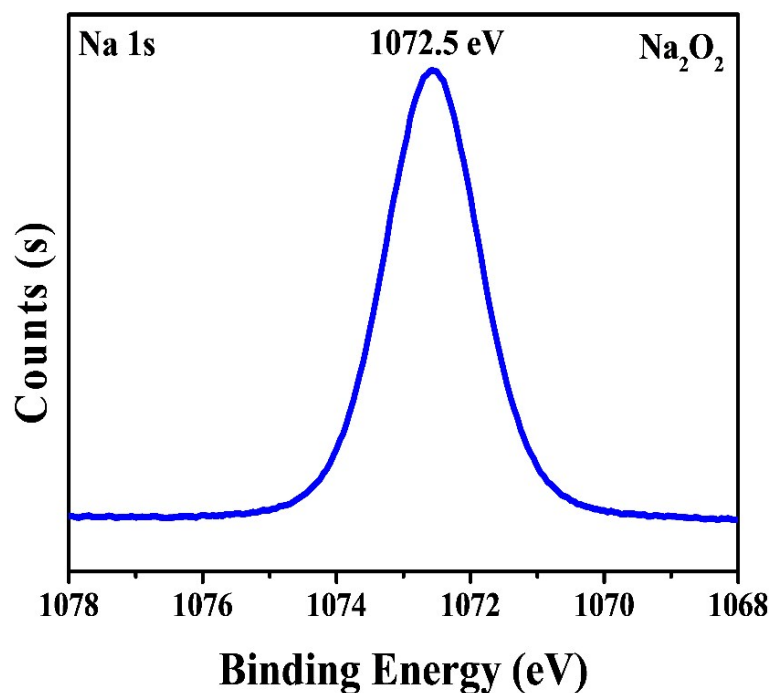


Figure S4. Na 1s XPS spectra of the 3D N-GA@Ni after discharge to 1.8 V.

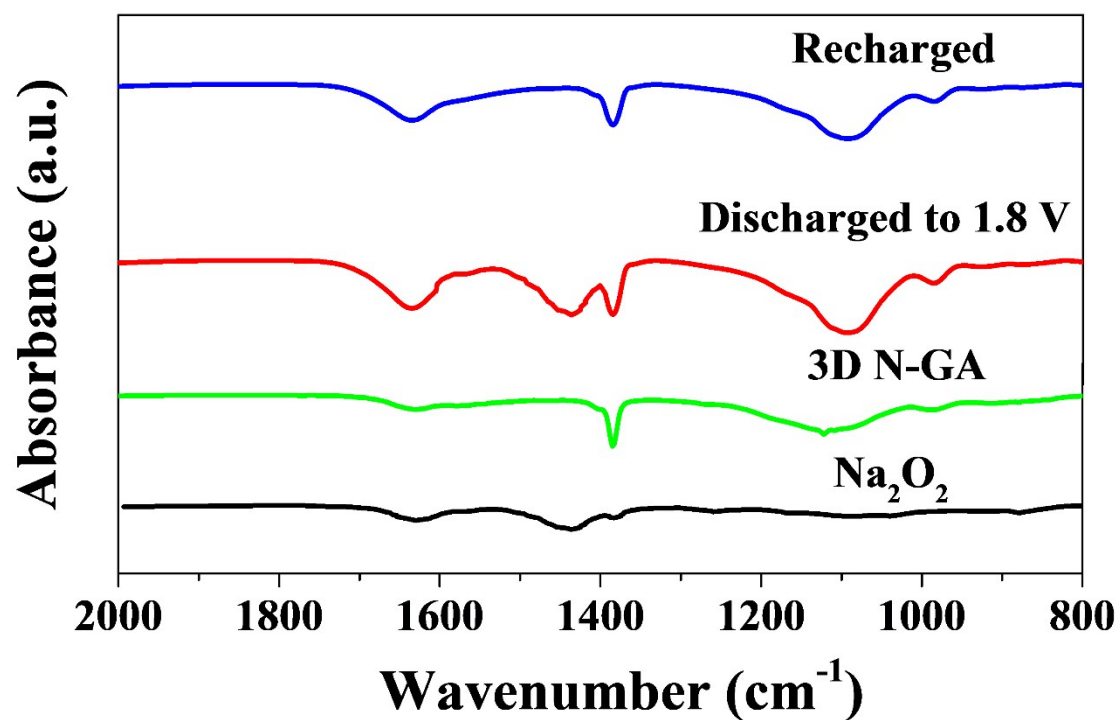


Figure S5. FTIR spectra of 3D N-GA@Ni electrode after discharge and charge.

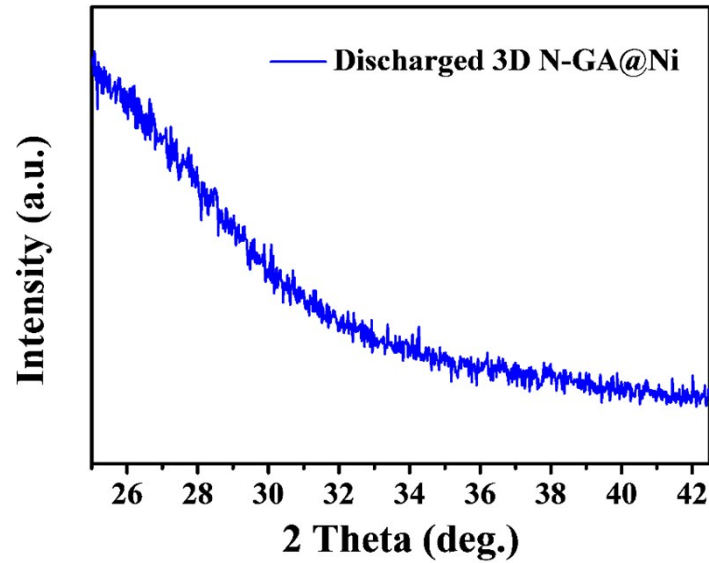


Figure S6. XRD pattern of the 3D N-GA@Ni after discharge to 1.8 V.

When characterized the discharge products on 3D N-GA@Ni by XRD, we could not observe the discharge products and significant structural changes in the air electrode after deep discharging, which is mainly attributed to insufficient amounts of the discharge products on the surface of the air electrode. During discharge, the discharge products tend to deposit uniformly in the 3D N-GA@Ni, while only a small proportion was deposited on the surface of air electrode. Owing to that the X-ray can only detect the surface of the air electrode, it is difficult to verify the discharge products by XRD. Therefore the XRD pattern of the discharged 3D N-GA@Ni didn't show obvious change.

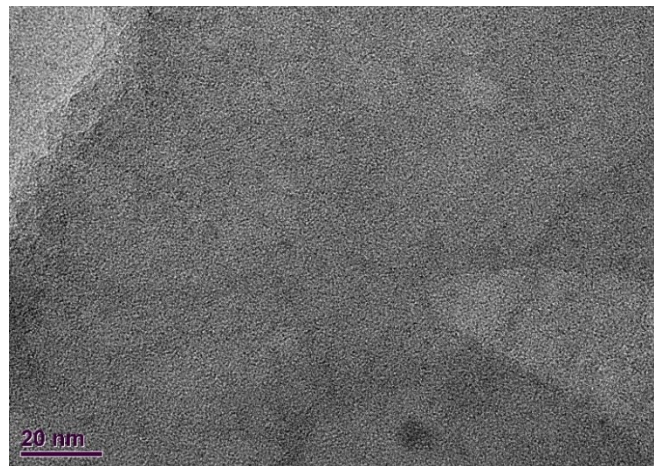


Figure S7. TEM image the 3D N-GA@Ni cathode after 20 cycles at the current density of 100 mA g^{-1} with a cut-off capacity of 500 mA h g^{-1} .

The TEM image of the 3D NGA@Ni cathode after 20 discharge-charge cycles reveals that the deposited discharge products on the surface can be reversibly reduced. This result confirm the reversible formation of the discharge products.

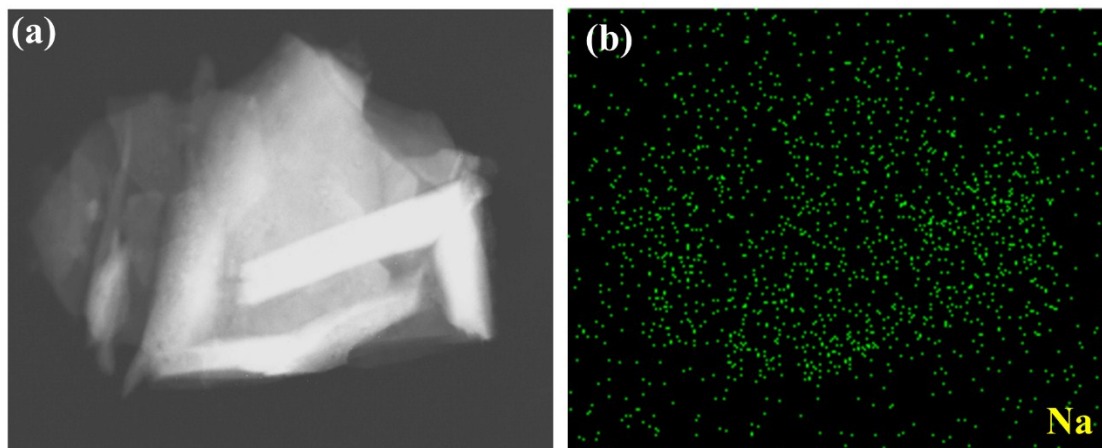


Figure S8. (a, b) The high-angle annular dark-field scanning TEM (HAADF-STEM) image and corresponding elemental mapping image of the pure N-GA after discharge.

References

1. Y. Cui, Z. Wen and Y. Liu, *Energy & Environmental Science*, 2011, **4**, 4727-4734.
2. P. Hartmann, C. L. Bender, M. Vracar, A. K. Duerr, A. Garsuch, J. Janek and P. Adelhelm, *Nat Mater*, 2013, **12**, 228-232.
3. X. Ren and Y. Wu, *J Am Chem Soc*, 2013, **135**, 2923-2926.
4. D. T. Kuo, D. W. Kirk and C. Q. Jia, *Journal of Sulfur Chemistry*, 2006, **27**, 461-530.
5. M. Nestoridi, D. Pletcher, R. J. Wood, S. Wang, R. L. Jones, K. R. Stokes and I. Wilcock, *J Power Sources*, 2008, **178**, 445-455.
6. Y. Li and H. Dai, *Chemical Society Reviews*, 2014, **43**, 5257-5275.
7. W. Li, C. Li, C. Zhou, H. Ma and J. Chen, *Angewandte Chemie*, 2006, **118**, 6155-6158.