

Note after first publication: This version of the Electronic Supporting Information replaces the version originally published on March 16, 2017.

Supporting Information

Modified chemical synthesis of MnS nanoclusters on nickel foam for high-performance all-solid-state asymmetric supercapacitors

Vijay S. Kumbhar, Yong Rok Lee,¹ Choon Sup Ra,² Dirk Tuma,³ Bong-Ki Min,⁴ and Jae-Jin Shim*

¹*School of Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk 38541, Republic of Korea*

²*Department of Chemistry, Yeungnam University, Gyeongsan, Gyeongbuk, Republic of Korea*

³*BAM Federal Institute for Materials Research and Testing, Berlin, Germany*

⁴*Central Instrumental Analysis Center, Yeungnam University, Gyeongsan, Gyeongbuk, Republic of Korea*

Equation for calculating the specific capacitance from the CV data

$$C_s = \frac{\int_{V_1}^{V_2} i dV}{(V_2 - V_1) m} \quad (S1)$$

where C_s is the specific capacitance, i is the current response to the given voltage V , V_1 is the lower potential limit, V_2 is the upper potential limit, v is the scan rate, and m is the mass of electrode (g).

Equation for calculating the specific capacitance from the charge-discharge data

$$C_s = \frac{I \cdot \Delta t}{m \Delta V}, \quad (S2)$$

Note after first publication: This version of the Electronic Supporting Information replaces the version originally published on March 16, 2017.

where C_s is the specific capacitance ($F g^{-1}$), I is the discharge current (A), m is the mass of electrode (g), and ΔV is the potential window (V).

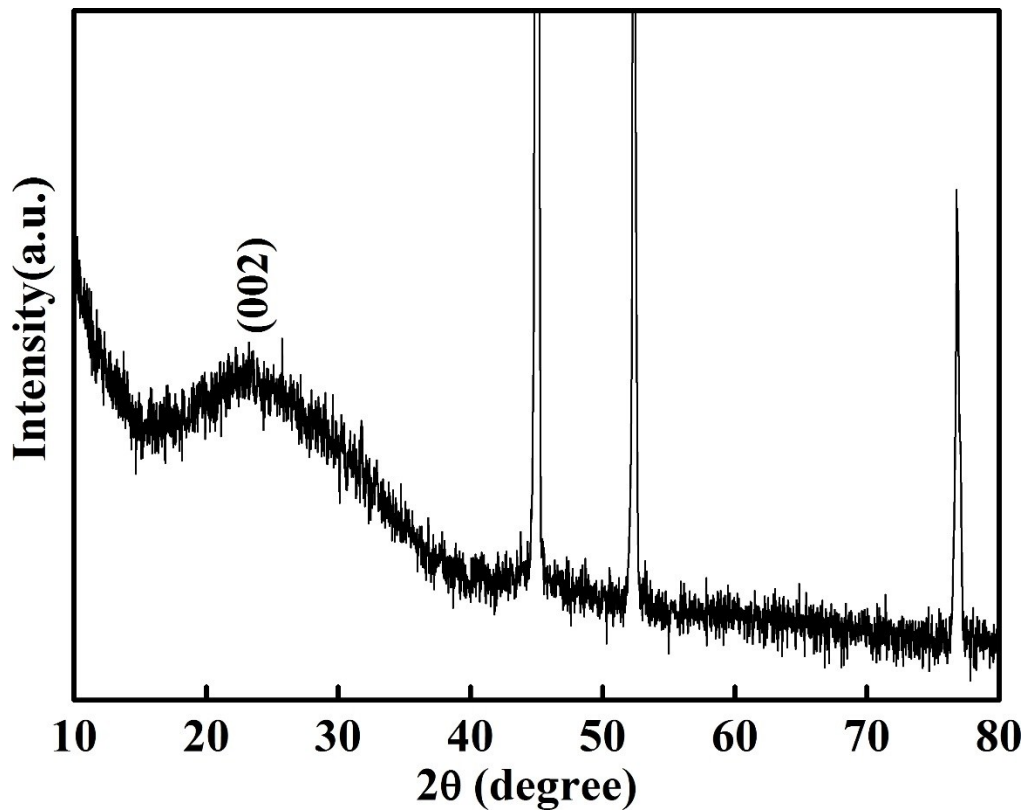


Fig. S1. XRD pattern of the hydrothermally reduced GO.

Note after first publication: This version of the Electronic Supporting Information replaces the version originally published on March 16, 2017.

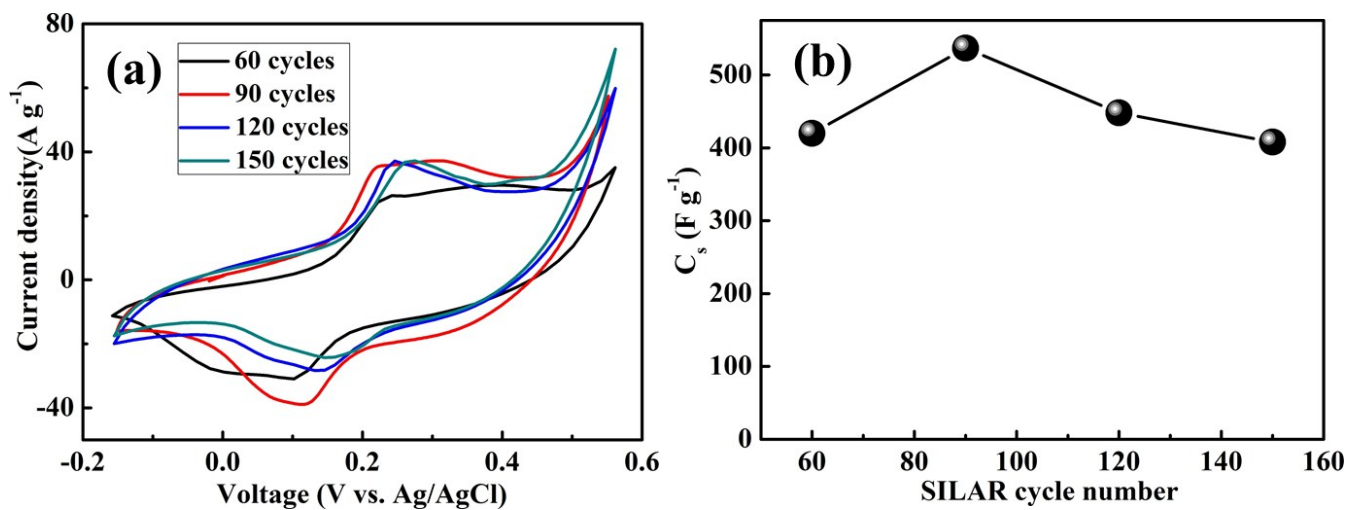


Fig. S2. (a) CV curves of MnS@NF electrodes at a fixed scan rate of 100 mV s⁻¹ in 6M KOH and (b) their variation of C_s upon the number of SILAR cycles.

Note after first publication: This version of the Electronic Supporting Information replaces the version originally published on March 16, 2017.

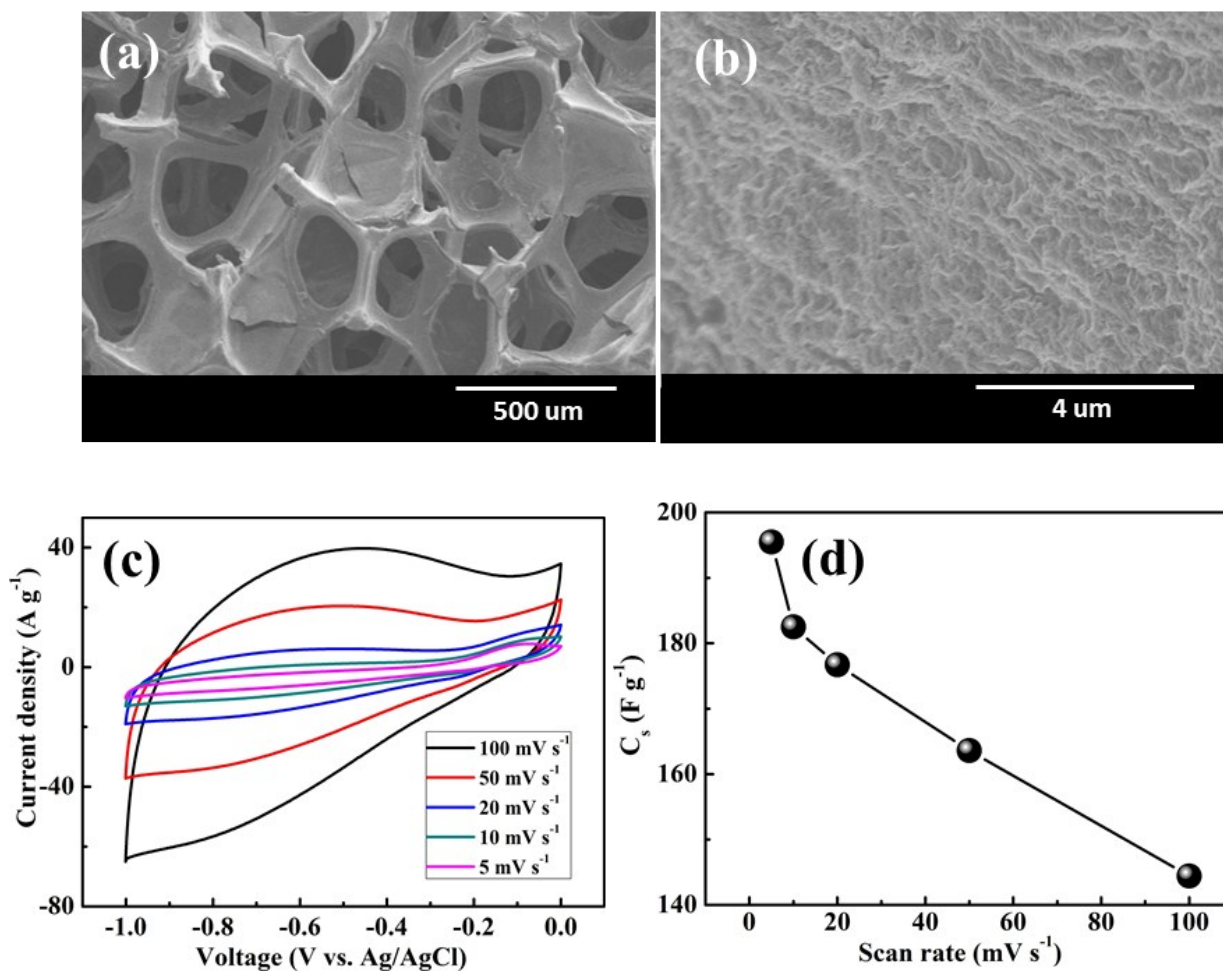


Fig. S3. (a, b) FE-SEM images of the hydrothermally reduced GO on NF, (c) CVs of rGO@NF electrode in 6 M KOH at various scan rates, and (d) the variation of C_s of rGO@NF as a function of the scan rate.

Note after first publication: This version of the Electronic Supporting Information replaces the version originally published on March 16, 2017.

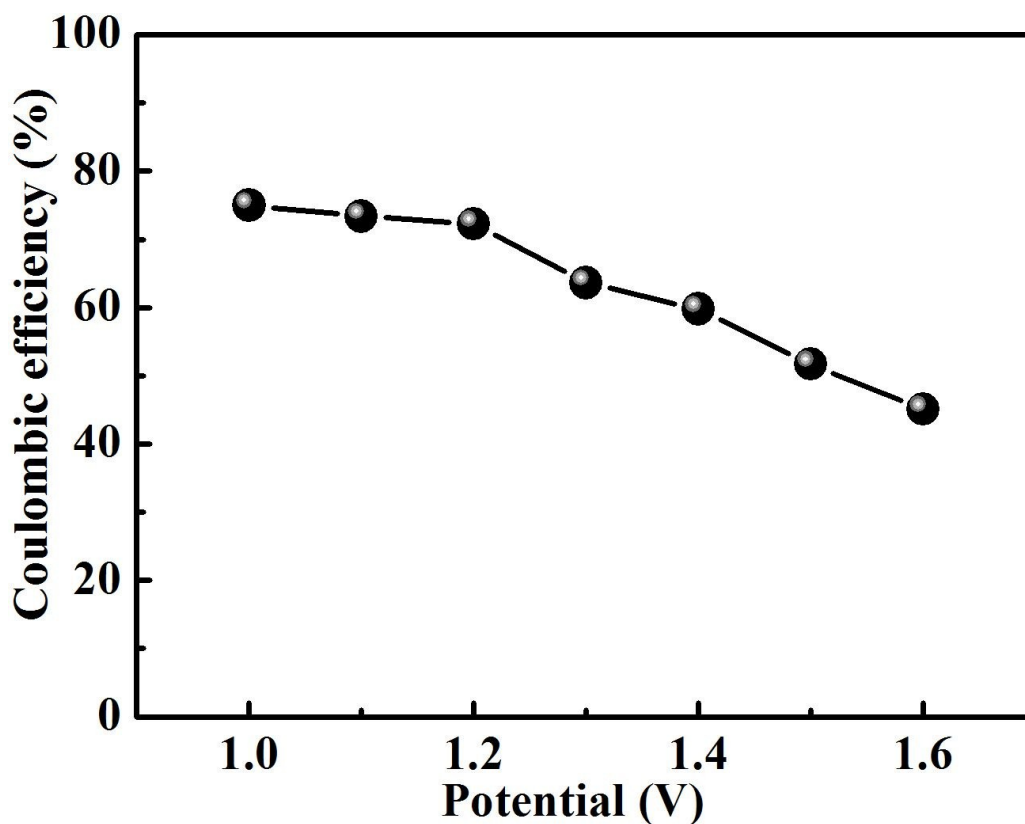


Fig. S4 Coulombic efficiency of the MnS@NF//rGO@NF ASC at various potential windows.

Table S1. Parameter values for fitting the Nyquist plots of the as-prepared MnS@NF electrode before cycling and after 5000 cycles in a 3 electrode system.

Parameter	Before cycling	Parameter	After 5000 cycles
C (mF)	0.49	C' (mF)	0.50
R _s (Ω)	0.48	R' _s (Ω)	0.63
R _{ct} (Ω)	1.20	A' _{w1} (Ω s ^{-0.5})	14.2
A _w (Ω s ^{-0.5})	65.6	A' _{w2} (Ω s ^{-0.5})	99.5
W _{or} (Ω s ^{-0.5})	15.5	-	-
W _{oc} (Ω s ^{-0.5})	0.082	-	-

Note after first publication: This version of the Electronic Supporting Information replaces the version originally published on March 16, 2017.

Table S2. Parameter values for fitting the Nyquist plots of the as-prepared

Parameter	Before cycling	Parameter	After 2000 cycles
R_s (Ω)	0.72	C'_1 (mF)	1.40
R_{ct1} (Ω)	1083	C'_2 (mF)	1.19
R_{ct2} (Ω)	12.4	R'_s (Ω)	1.66
P_1	0.00019	R'_{ct} (Ω)	2078
n_1	0.78	A'_w ($\Omega\text{ s}^{-0.5}$)	4947
P_2	0.00029	-	-
n_2	0.63	-	-

MnS@NF//rGO@NF ASC before cycling and after 2000 cycles.

Table S3. Comparison of the energy and power densities of different MnS-based asymmetric supercapacitors

Ref. No.	Symmetric/Asymmetric supercapacitor		Electrolyte	Potential window (V)	C_s (F g⁻¹)	Highest energy density (Wh kg⁻¹)	Highest power density (kW kg⁻¹)
	Positive electrode	Negative electrode					

Note after first publication: This version of the Electronic Supporting Information replaces the version originally published on March 16, 2017.

1.	MnS nanocrystals	Activated carbon	KOH agar gel	0 ~ 1.6	110.4 F g ⁻¹ at 1 A g ⁻¹	37.6	5.9
2.	Tetrapod nanorod MnS nanocrystals	Activated carbon	2 M KOH aqueous	0 ~ 1.6	59.8 F g ⁻¹ at 1 mV s ⁻¹	13.1	4.45
3.	α -MnS/ N-doped rGO	Nitrogen-doped rGO	3 M KOH aqueous	0 ~ 1.6	77.9 F g ⁻¹ at 1 A g ⁻¹	27.7	20
4.	MnS/GO-NH ₃	Activated carbon	2 M KOH aqueous	0 ~ 1.6	73.6 F g ⁻¹ at 1 mV s ⁻¹	14.9	4.6
5.	MnS microfibers	MnS microfibers	PVA-KOH gel	-0.6 ~ 0.6	68.3 F g ⁻¹ at 3 mA	18.9	0.25
6.	MnS nanoclusters (This work)	rGO	PVA-KOH gel	0 ~ 1.6	104 F g⁻¹ at 5 mV s⁻¹	34.1	12.8

References:

1. T. Chen, Y. Tang, Y. Qiao, Z. Liu, W. Guo, J. Song, S. Mu, S. Yu, Y. Zhao and F. Gao, *Sci. Rep.*, 2016, 6, 23289-23297.
2. Y. Tang, T. Chen and S. Yu, *Chem. Comm.*, 2015, 51, 9018-9021.
3. H. Quan, B. Cheng, D. Chen, X. Su, Y. Xiao and S. Lei, *Electrochim. Acta*, 2016, 210, 557-566.
4. Y. Tang, T. Chen, S. Yu, Y. Qiao, S. Mu, J. Hu and F. Gao, *J. Mater. Chem. A*, 2015, 3, 12913-12919.
5. R. B. Pujari, A. C. Lokhande, A. A. Yadav, J. H. Kim and C. D. Lokhande, *Mater. Des.*, 2016, 108, 510-517.