

Atomic Layered NiO/Phosphorus-Doped MnO₂ P-N Junctions: A Pathway to High-Performance Supercapattery Devices

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Supporting Information

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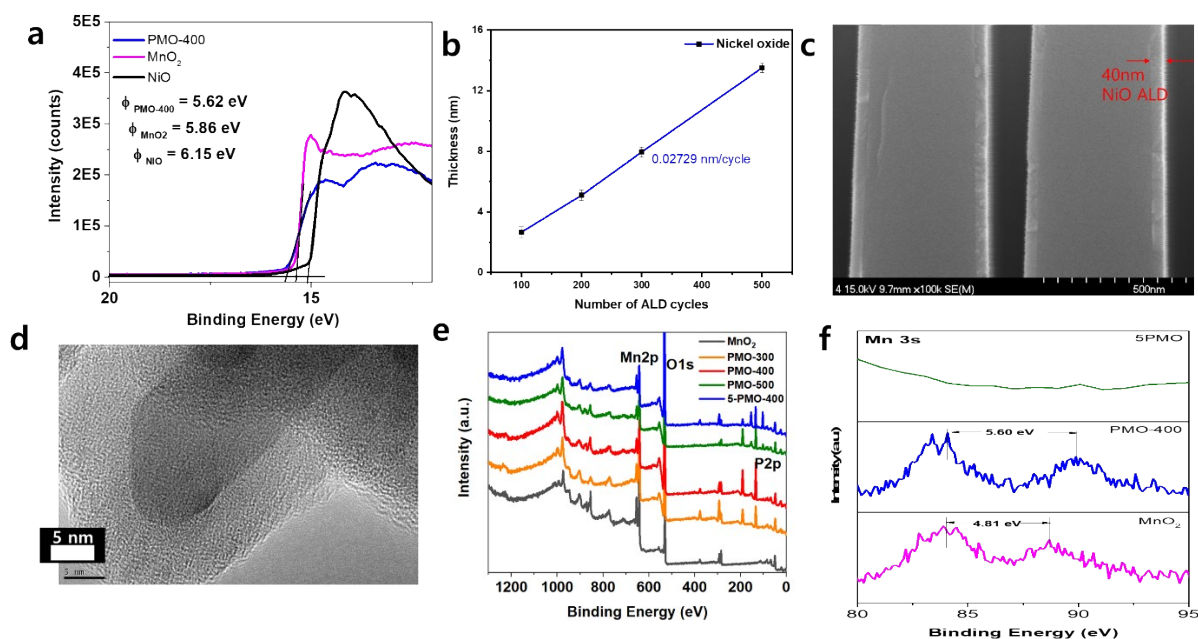


Figure S1. (a) UPS data with corresponding work function for NiO, MnO_2 and PMO-400 ; (b) Linearity process for ALD NiO; (c) 40 nm NiO deposited on patterned silicon wafer; (d) HRTEM image of 7.5 nm NiO deposited PMO-400 electrode; (e) XPS Survey scan of MnO_2 , PMO-300, PMO-400, PMO-500 and 5PMO; and (f) Mn 3s XPS spectra for the prepared MnO_2 , PMO-400 and 5PMO electrodes.

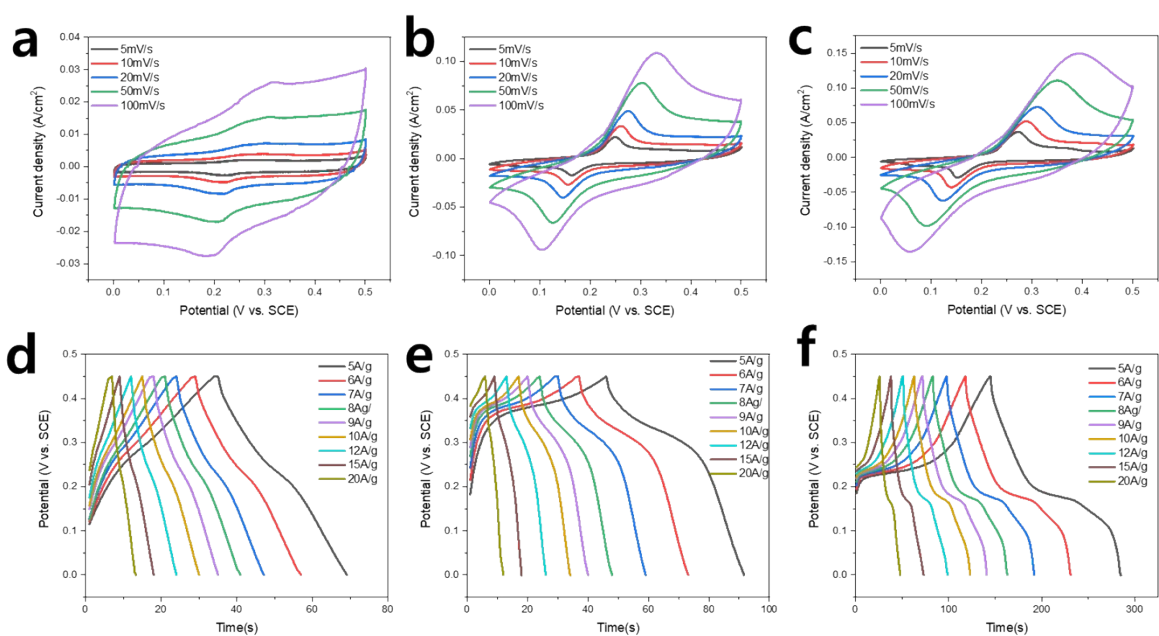


Figure S2. CV and GCD curves of (a, d) MnO₂, (b, e) PMO-300, and (c, f) PMO-500.

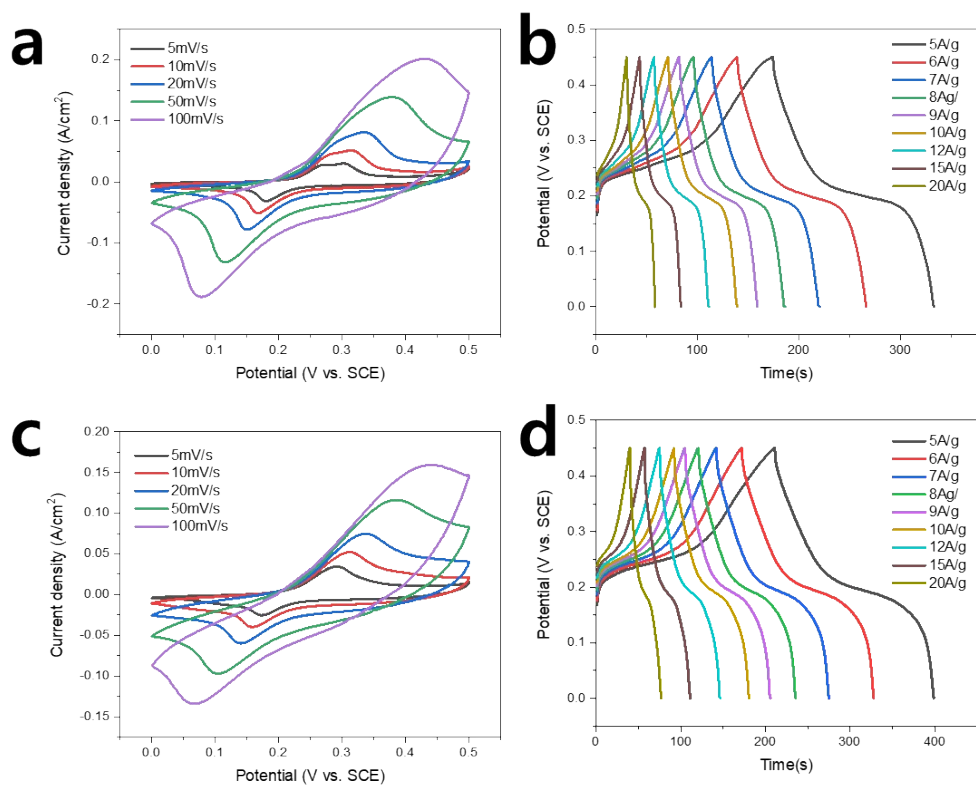


Figure S3. CV and GCD curves of (a, b) 2.5PMO, and (c, d) 7.5PMO electrodes.

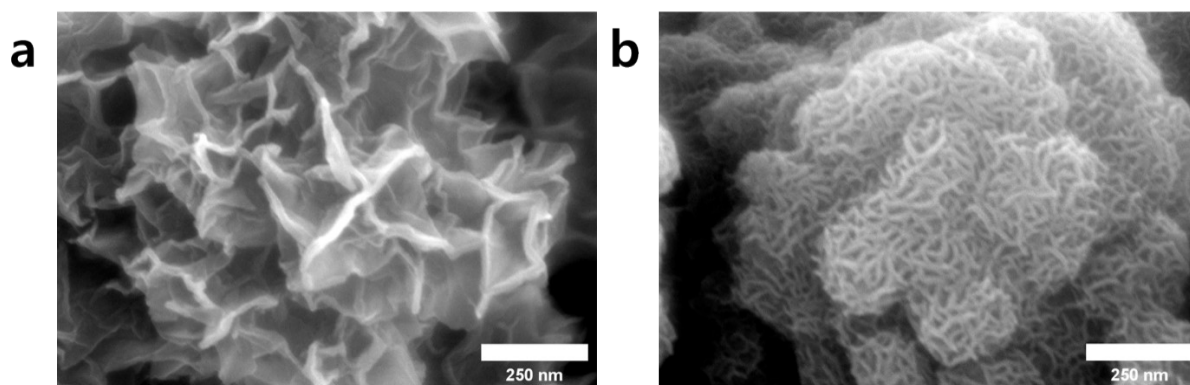


Figure S4. FESEM images of (a) PMO-400 and (b) 5PMO after 20000 charge-discharge cycles.

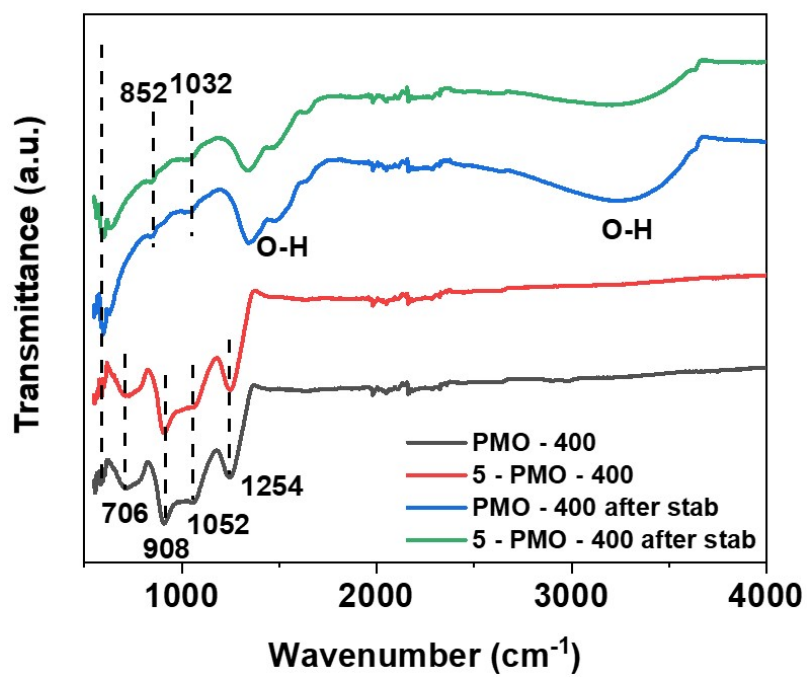


Figure S5. Comparative FTIR spectra for pristine and after 20000 cycles of PMO-400, and 5PMO electrodes.

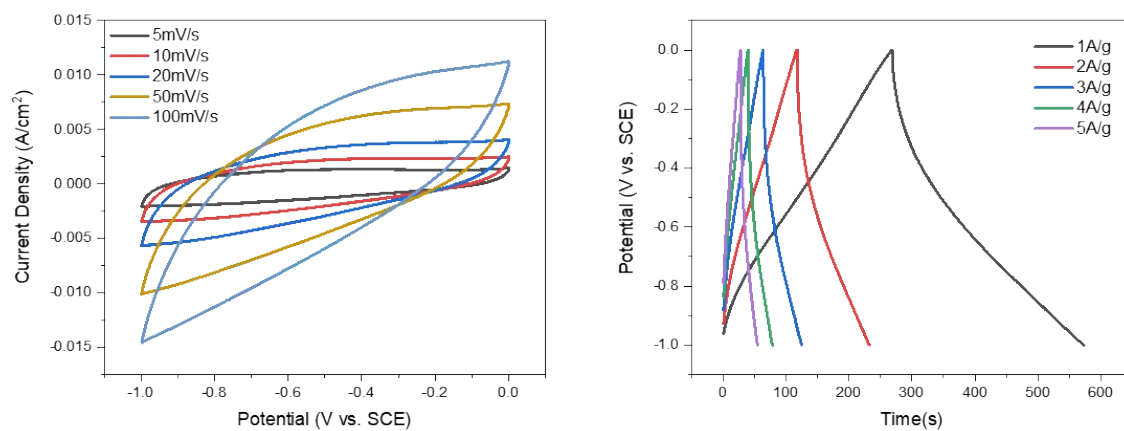


Figure S6. CV and GCD curves of rGO on Ni-foam.

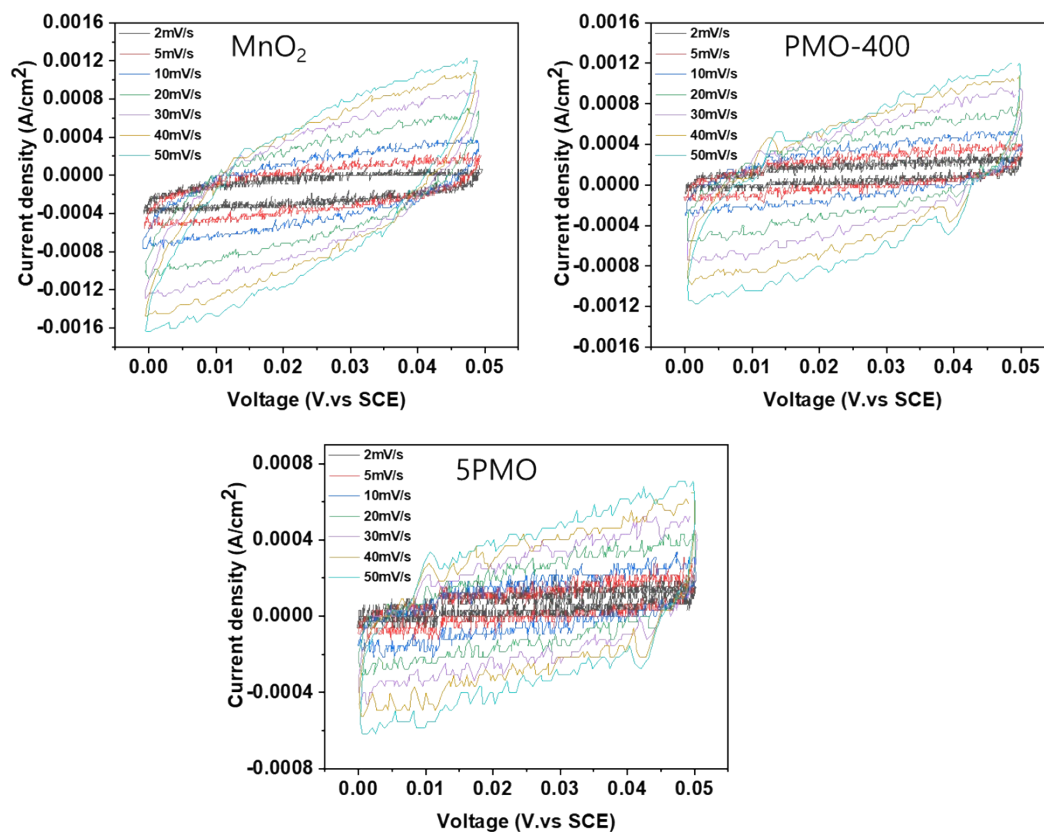


Figure S7. CV curves of MnO_2 , PMO-400 and 5PMO electrodes at different scan rates.

Table S1. Electrochemical performance of 5PMO electrode compared with MnO₂-based systems.

Sl. No.	Electrode material	Electrolyte	Specific capacitance (F/g)	Rate Capability (%)	Cycling Stability (at cycles)	Ref.
1	P-Co ₂ MnO _{4-x}	3M KOH	838F/g at 1A/g	74.5% (1 to 10A/g)	80.3% at 10,000cycle	[1]
2	Cobalt Manganese Phosphate	1M KOH	571F/g at 2.2A/g		88% at 8,000 cycle (3A/g)	[2]
3	Mn _{0.5} Co _{0.5} (HPO ₄)	3M KOH	1727F/g at 1A/g	77.3% (1 to 10A/g)		[3]
4	MnO ₂ -CNFs cable	1M Na ₂ SO ₄	324.55F/g at 0.5A/g		62% at 100 cycle (1A/g)	[4]
5	MnO ₂ /nitrogen doped Carbon	1M Na ₂ SO ₄	480.3F/g at 0.5mA/cm ²	70% (0.5 to 40A/cm ²)	97% at 10,000 cycle (0.5mA/cm ²)	[5]
6	Alpha-MnO ₂	1M Na ₂ SO ₄	235F/g at 1A/g	76.6% (0.5 to 10A/g)	95% at 3,000 cycle (3A/g)	[6]
7	MnO ₂ /Ant-nest like hierarchical porous carbon	6M KOH	662F/g at 1A/g	50.3% (1 to 10A/g)	-	[7]
8	Mn ³⁺ /Mn ⁴⁺ ratio controlled MnO ₂ / CC	1M Na ₂ SO ₄	408.1F/g at 1A/g	46% (1 to 16A/g)	99.4% at 2,000 cycle (10A/g)	[8]
9	PANI/Ag@MnO ₂ nanorod	2M KOH	1028.66F/g at 1A/g	69.1% (1 to 20A/g)	91.3% at 5,000 cycle (10A/g)	[9]
10	5nm NiO ALD P-MnO ₂	2M KOH	2294.78F/g at 5A/g	79.0% (5 to 20A/g)	85.8% at 20,000 cycle (20A/g)	This work

Table S2. Device performance of 5PMO//rGO device compared with MnO₂-based systems.

Sl. No.	Positive Electrode Material	Negative Electrode Material	Energy density (Wh/kg)	Power density (W/kg)	Cycling Stability (at cycles)	Ref.
1	P-Co ₂ MnO _{4-x}	Activated carbon	25.18	800.07	89.5% at 10,000 cycle	[1]
2	Cobalt Manganese Phosphate	rGO	45.7	1650	87% at 6,000 cycle (2.5A/g)	[2]
3	Mn _{0.5} Co _{0.5} (HPO ₄)	G-ink	56.16	599.92	95.5% at 5,000 cycle (5A/g)	[3]
4	MnO ₂ -CNFs cable	MnO ₂ -CNFs cable	16.7	400		[4]
5	MnO ₂ /nitrogen doped Carbon	1T-MoS ₂ /Gr	3.62	18.7	90.1% at 10,000 cycle (10mV/s)	[5]
6	Alpha-MnO ₂	Activated carbon	28.9	200	94% at 5,000 cycle (1A/g)	[6]
7	MnO ₂ /Ant-nest like hierarchical porous carbon	MnO ₂ /Ant-nest like hierarchical porous carbon	14.5	5000	93.4% at 5,000 cycle (1A/g)	[7]
8	Mn ³⁺ /Mn ⁴⁺ ratio controlled MnO ₂ / CC	FeOOH/C	55.9	1240	-	[8]
9	PANI/Ag@MnO ₂ nanorod	AC	49.66	1599.75	88.6% at 5,000 cycle (10A/g)	[9]
10	5nm NiO ALD P-MnO ₂	rGO	71.975	1599	87.0% at 23,000 cycle (10A/g)	This work

References:

- [1] K.-S. Ahn, R. Vinodh, B.G. Pollet, R.S. Babu, V. Ramkumar, S.-C. Kim, K. Krishnakumar, H.-J. Kim, A high-performance asymmetric supercapacitor consists of binder free electrode materials of bimetallic hydrogen phosphate ($\text{MnCo}(\text{HPO}_4)$) hexagonal tubes and graphene ink, *Electrochimica Acta*, 426 (2022) 140763.
- [2] S. Dang, Y. Wen, T. Qin, J. Hao, H. Li, J. Huang, D. Yan, G. Cao, S. Peng, Nanostructured manganese dioxide with adjustable $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio for flexible high-energy quasi-solid supercapacitors, *Chemical Engineering Journal*, 396 (2020) 125342.
- [3] J.M. Jeong, S.H. Park, H.J. Park, S.B. Jin, S.G. Son, J.M. Moon, H. Suh, B.G. Choi, Alternative-Ultrathin Assembling of Exfoliated Manganese Dioxide and Nitrogen-Doped Carbon Layers for High-Mass-Loading Supercapacitors with Outstanding Capacitance and Impressive Rate Capability, *Advanced Functional Materials*, 31 (2021) 2009632.
- [4] P.K. Katkar, S.J. Marje, V.G. Parale, C.D. Lokhande, J.L. Gunjekar, H.-H. Park, U.M. Patil, Fabrication of a high-performance hybrid supercapacitor based on hydrothermally synthesized highly stable cobalt manganese phosphate thin films, *Langmuir*, 37 (2021) 5260-5274.
- [5] C.-S. Liu, C.-L. Huang, H.-C. Fang, K.-Y. Hung, C.-A. Su, Y.-Y. Li, MnO_2 -based carbon nanofiber cable for supercapacitor applications, *Journal of Energy Storage*, 33 (2021) 102130.
- [6] Q. Lu, X. Wang, M. Chen, B. Lu, M. Liu, T. Xing, X. Wang, Manganese dioxide/ant-nest-like hierarchical porous carbon composite with robust supercapacitive performances, *ACS Sustainable Chemistry & Engineering*, 6 (2018) 7362-7371.
- [7] M.B. Poudel, M. Shin, H.J. Kim, Polyaniline-silver-manganese dioxide nanorod ternary composite for asymmetric supercapacitor with remarkable electrochemical performance, *International Journal of Hydrogen Energy*, 46 (2021) 474-485.
- [8] Z. Wang, J. Gu, S. Li, G.C. Zhang, J. Zhong, X. Fan, D. Yuan, S. Tang, D. Xiao, One-step polyoxometalates-assisted synthesis of manganese dioxide for asymmetric supercapacitors with enhanced cycling lifespan, *ACS Sustainable Chemistry & Engineering*, 7 (2018) 258-264.
- [9] F. Xiang, X. Zhou, X. Yue, Q. Hu, Q. Zheng, D. Lin, An oxygen-deficient cobalt-manganese oxide nanowire doped with P designed for high performance asymmetric supercapacitor, *Electrochimica Acta*, 379 (2021) 138178.