

Electronic Supplementary Information

Nanostructured Fe-Ni Sulfide: A Multifunctional Material for Energy Conversion and Storage

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Table S1: Comparison of OER catalysis with other reports

Catalyst	Overpotential (mV) at 10 mA/cm ²	Tafel Slope (mV/decade)	Reference
Fe _{0.1} Ni _{0.9} O	297	37	1
Ni _{0.9} Fe _{0.1} /NC	270	45	2
FeNi _{4.34} @FeNi	283	53	3
CoFe ₂ O ₄ NF	~420	82	4
NiCo ₂ O ₄	565	292	5
NiFe/CN _x	360	59	6
NiFe foam	320	-	7
Ni ₃ S ₂	340	150	8
NiS _x	408	56	9
Fe-Ni-O _x /GC	286	48	9
NiSe ₂	323	83.6	10
Fe-Ni ₃ S ₂ /FeNi	282	54	11
FeNiO	277	51	This work
FeNiS	246	49	This work

Table S2: Comparison of HER catalysis with other reports

Catalyst	Overpotential (mV) at 10 mA/cm ²	Tafel Slope (mV/decade)	Reference
NiCo ₂ O ₄ /CC	~350	207	12
NiS	474	124	13
Ni ₃ S ₂	310	96	14
EG/NiFe-LDH	~380	125	15
Ni _{0.9} Fe _{0.1} /NC	231	111	2
NiS ₂	454	128	13
NiCo ₂ S ₄	240	81.3	14
NiFe/NF	269	69	16
Ni ₃ S ₂ /NF	318	74	16
NiFeS/NF	180	53	16
FeNiO	253	129	This work
FeNiS	208	109	This work

Table S3: Comparison for overall water splitting.

Catalyst	Current density (mA/cm ²)	Voltage (V)	Reference
NiFe LDH/NF	10	1.70	17
NiFe/NiCo ₂ O ₄ /NF	10	1.67	18
Fe ₂ Ni ₂ N	10	1.65	19
Ni ₃ S ₄ nanosheets	10	1.61	20
NiSe/NF	10	1.63	21
NiFe-OH-PO ₄ /NF	10	1.64	22
Ni ₂ P	10	1.63	23
NiS	10	1.64	24
Ni ₅ P ₄	10	1.70	25
NiCo ₂ O ₄	10	1.65	26
FeNiS-Pt/C	10	1.535	This work

Table S4: Comparison of supercapacitor performance of some recently reported results.

Samples	Specific capacitance (mF/cm ²)	Current density (mA/cm ²)	Reference
Ni-Co sulfide/NF	2,940	30	27
Ni ₃ S ₂ @Ni(OH) ₂ /3DGN	3,850	19.1	28
NiCo ₂ O ₄ @MnO ₂	~2,000	10	29
Co _{0.67} Ni _{0.33} DHs/NiCo ₂ O ₄ /CFP	1,640	2	30
NiS hollow spheres	2640	4	31
FeOOH	1,110	5	32
Co-Ni double hydroxides	1,480	5	32
Co ₃ O ₄ @NiMoO ₄	5,690	30	33
Co ₃ O ₄	1,100	30	33
FeNiS	4,921	5	This work

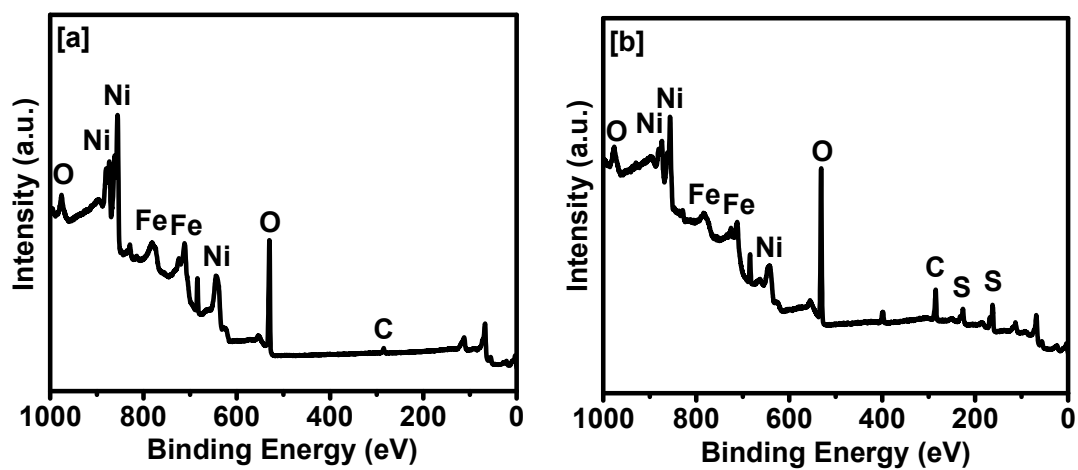


Figure S1: XPS survey spectra of (a) FeNiO and (b) sulfurized FeNiO.

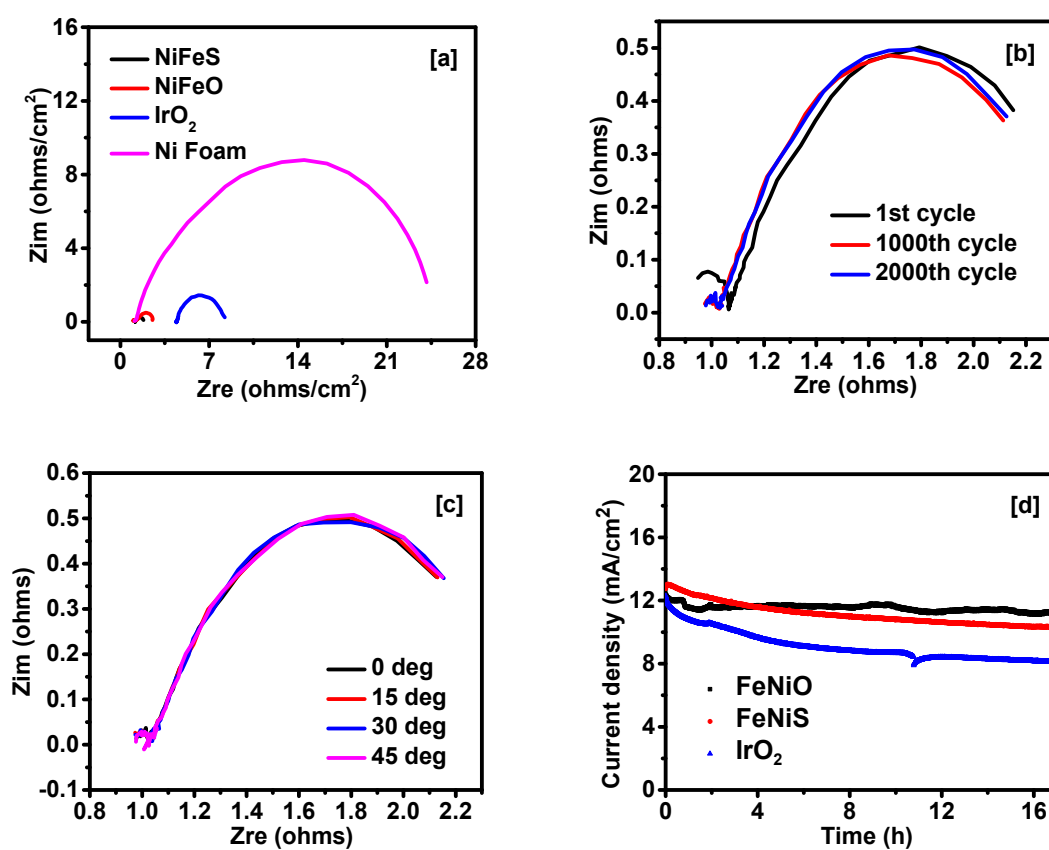


Figure S2: (a) Nyquist plot for all the OER catalytic electrodes at 0.5 V, (b) Nyquist plot at different stability cycles at 0.5 V, (c) Nyquist plot at different bending angles at 0.5 V, and (d) chronoamperometry.

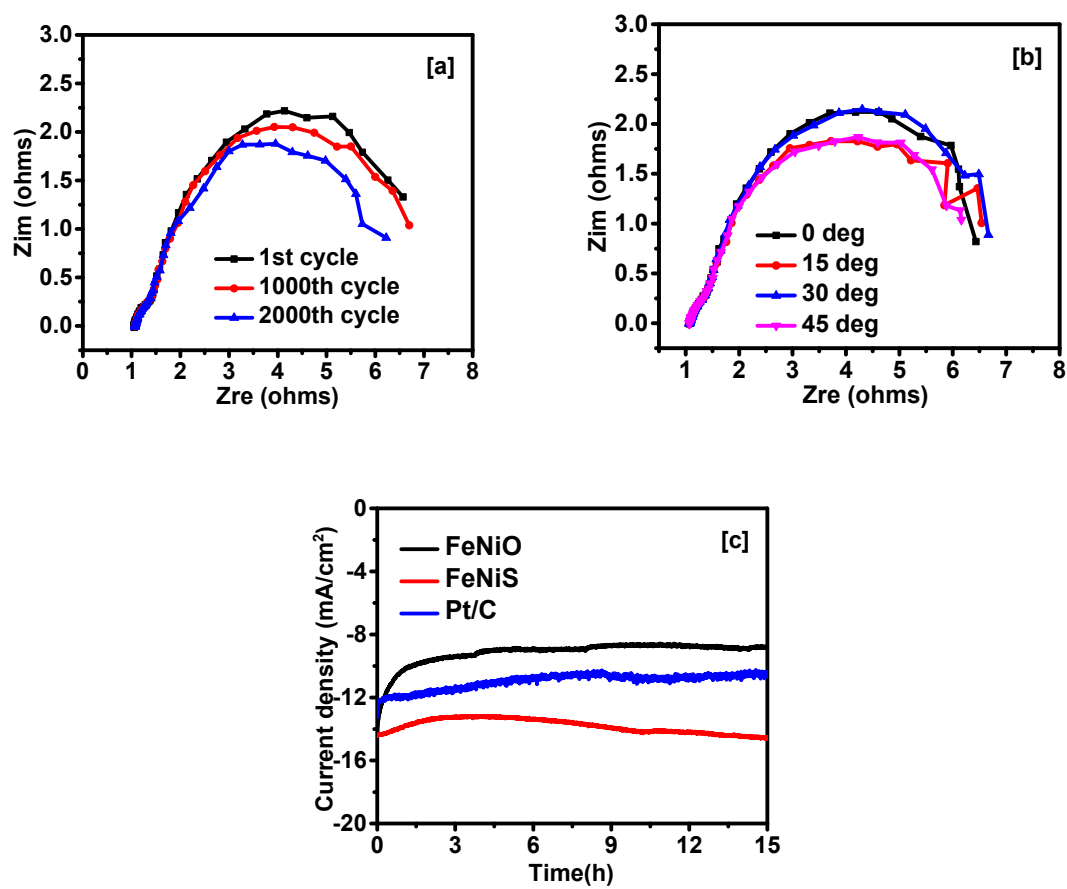


Figure S3: (a) Nyquist plot at different stability cycles at -1.3 V, (b) Nyquist plot at different bending angles at -1.3 V and, (c) chronoamperometry.

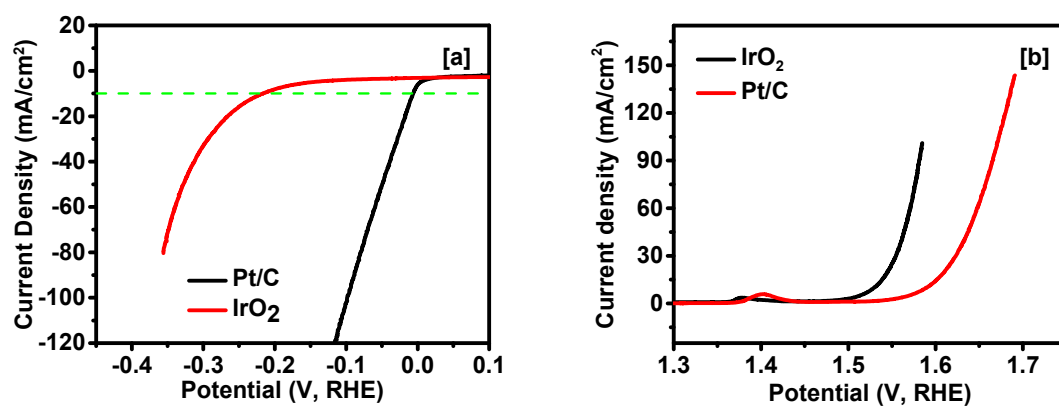


Figure S4: LSV polarization curves for Pt/C and IrO₂: (a) HER and (b) OER.

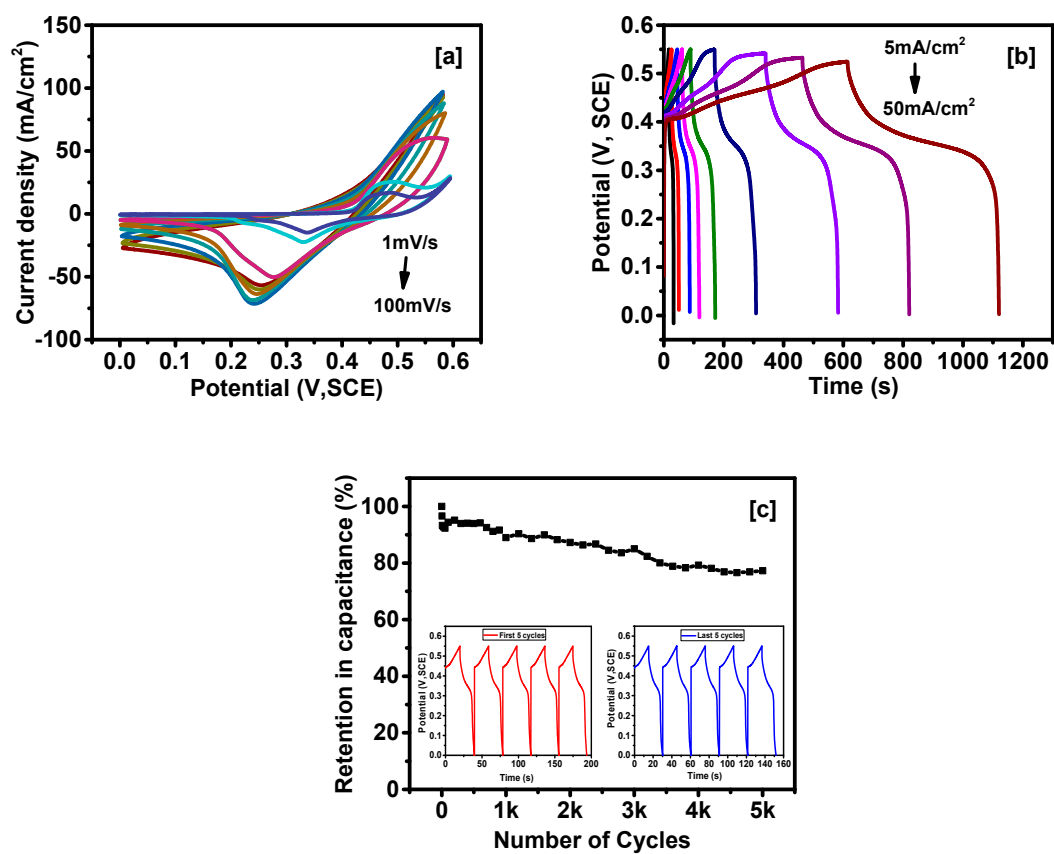


Figure S5: Characteristics of FeNiS: (a) CV curves, (b) GCD curves and (c) cyclic stability plot for FeNiS sample using GCD measurements.

- (1) Fominykh, K.; Chernev, P.; Zaharieva, I.; Sicklinger, J.; Stefanic, G.; Döblinger, M.; Müller, A.; Pokharel, A.; Böcklein, S.; Scheu, C.; et al. Iron-Doped Nickel Oxide Nanocrystals as Highly Efficient Electrocatalysts for Alkaline Water Splitting. *ACS Nano* **2015**, *9*, 5180.
- (2) Zhang, X.; Xu, H.; Li, X.; Li, Y.; Yang, T.; Liang, Y. Facile Synthesis of Nickel–Iron/Nanocarbon Hybrids as Advanced Electrocatalysts for Efficient Water Splitting. *ACS Catal.* **2016**, *6* (2), 580–588.
- (3) Qazi, U. Y.; Yuan, C. Z.; Ullah, N.; Jiang, Y. F.; Imran, M.; Zeb, A.; Zhao, S. J.; Javaid, R.; Xu, A. W. One-Step Growth of Iron-Nickel Bimetallic Nanoparticles on FeNi Alloy Foils: Highly Efficient Advanced Electrodes for the Oxygen Evolution Reaction. *ACS Appl. Mater. Interfaces* **2017**, *9*, 28627.
- (4) Li, M.; Xiong, Y.; Liu, X.; Bo, X.; Zhang, Y.; Han, C.; Guo, L. Facile Synthesis of Electrospun MFe_2O_4 ($M = Co, Ni, Cu, Mn$) Spinel Nanofibers with Excellent Electrocatalytic Properties for Oxygen Evolution and Hydrogen Peroxide Reduction. *Nanoscale* **2015**, *7* (19), 8920–8930.
- (5) Shi, H.; Zhao, G. Water Oxidation on Spinel $NiCo_2O_4$ Nanoneedles Anode: Microstructures, Specific Surface Character, and the Enhanced Electrocatalytic Performance. *J. Phys. Chem. C* **2014**, *118*, 25939.
- (6) Ci, S.; Mao, S.; Hou, Y.; Cui, S.; Kim, H.; Ren, R.; Wen, Z.; Chen, J. Rational Design of Mesoporous NiFe-Alloy-Based Hybrids for Oxygen Conversion Electrocatalysis. *J. Mater. Chem. A* **2015**, *3*, 7986.
- (7) Liang, Y.; Liu, Q.; Asiri, A. M.; Sun, X.; He, Y. Nickel-Iron Foam as a Three-Dimensional Robust Oxygen Evolution Electrode with High Activity. *Int. J. Hydrogen Energy* **2015**, *40*, 13258.
- (8) Zhu, T.; Zhu, L.; Wang, J.; Ho, G. W. In Situ Chemical Etching of Tunable 3D Ni_3S_2 Superstructures for Bifunctional Electrocatalysts for Overall Water

- Splitting. *J. Mater. Chem. A* **2016**, *4*, 13916.
- (9) Li, H.; Shao, Y.; Su, Y.; Gao, Y.; Wang, X. Vapor-Phase Atomic Layer Deposition of Nickel Sulfide and Its Application for Efficient Oxygen-Evolution Electrocatalysis. *Chem. Mater.* **2016**, *28*, 1155.
 - (10) Wang, Z.; Li, J.; Tian, X.; Wang, X.; Yu, Y.; Owusu, K. A.; He, L.; Mai, L. Porous Nickel-Iron Selenide Nanosheets as Highly Efficient Electrocatalysts for Oxygen Evolution Reaction. *ACS Appl. Mater. Interfaces* **2016**, *8*, 19386.
 - (11) Yuan, C. Z.; Sun, Z. T.; Jiang, Y. F.; Yang, Z. K.; Jiang, N.; Zhao, Z. W.; Qazi, U. Y.; Zhang, W. H.; Xu, A. W. One-Step In Situ Growth of Iron–Nickel Sulfide Nanosheets on FeNi Alloy Foils: High-Performance and Self-Supported Electrodes for Water Oxidation. *Small* **2017**, *13*, 1604161.
 - (12) Liu, D.; Lu, Q.; Luo, Y.; Sun, X.; Asiri, A. M. NiCo₂S₄ Nanowires Array as an Efficient Bifunctional Electrocatalyst for Full Water Splitting with Superior Activity. *Nanoscale* **2015**, *7*, 15122.
 - (13) Jiang, N.; Tang, Q.; Sheng, M.; You, B.; Jiang, D.; Sun, Y. Nickel Sulfides for Electrocatalytic Hydrogen Evolution under Alkaline Conditions: A Case Study of Crystalline NiS, NiS₂, and Ni₃S₂ Nanoparticles. *Catal. Sci. Technol.* **2016**, *6*, 1077.
 - (14) Sivanantham, A.; Ganesan, P.; Shanmugam, S. Hierarchical NiCo₂S₄ Nanowire Arrays Supported on Ni Foam: An Efficient and Durable Bifunctional Electrocatalyst for Oxygen and Hydrogen Evolution Reactions. *Adv. Funct. Mater.* **2016**, *26*.
 - (15) Hou, Y.; Lohe, M. R.; Zhang, J.; Liu, S.; Zhuang, X.; Feng, X. Vertically Oriented Cobalt Selenide/NiFe Layered-Double-Hydroxide Nanosheets Supported on Exfoliated Graphene Foil: An Efficient 3D Electrode for Overall Water Splitting. *Energy Environ. Sci.* **2016**, *9*, 478.
 - (16) Ganesan, P.; Sivanantham, A.; Shanmugam, S. Inexpensive Electrochemical Synthesis of Nickel Iron Sulphides on Nickel Foam: Super Active and Ultra-Durable Electrocatalysts for Alkaline Electrolyte Membrane Water Electrolysis. *J. Mater. Chem. A* **2016**, *4*, 16394.
 - (17) Luo, J.; Im, J.-H.; Mayer, M. T.; Schreier, M.; Nazeeruddin, M. K.; Park, N.-G.; Tilley, S. D.; Fan, H. J.; Grätzel, M. Water Photolysis at 12.3% Efficiency via Perovskite Photovoltaics and Earth-Abundant Catalysts. *Science* (80-.). **2014**,

345 (6204), 1593 LP – 1596.

- (18) Xiao, C.; Li, Y.; Lu, X.; Zhao, C. Bifunctional Porous NiFe/NiCo₂O₄/Ni Foam Electrodes with Triple Hierarchy and Double Synergies for Efficient Whole Cell Water Splitting. *Adv. Funct. Mater.* **2016**, *26* (20), 3515–3523.
- (19) Jiang, M.; Li, Y.; Lu, Z.; Sun, X.; Duan, X. Binary Nickel–Iron Nitride Nanoarrays as Bifunctional Electrocatalysts for Overall Water Splitting. *Inorg. Chem. Front.* **2016**, *3*, 630.
- (20) Ren, J. T.; Yuan, Z. Y. Hierarchical Nickel Sulfide Nanosheets Directly Grown on Ni Foam: A Stable and Efficient Electrocatalyst for Water Reduction and Oxidation in Alkaline Medium. *ACS Sustain. Chem. Eng.* **2017**, *5*, 7203.
- (21) Tang, C.; Cheng, N.; Pu, Z.; Xing, W.; Sun, X. NiSe Nanowire Film Supported on Nickel Foam: An Efficient and Stable 3D Bifunctional Electrode for Full Water Splitting. *Angew. Chemie Int. Ed.* **2015**, *54* (32), 9351–9355.
- (22) Lei, Z.; Bai, J.; Li, Y.; Wang, Z.; Zhao, C. Fabrication of Nanoporous Nickel–Iron Hydroxylphosphate Composite as Bifunctional and Reversible Catalyst for Highly Efficient Intermittent Water Splitting. *ACS Appl. Mater. Interfaces* **2017**, *9* (41), 35837–35846.
- (23) Stern, L.-A.; Feng, L.; Song, F.; Hu, X. Ni₂P as a Janus Catalyst for Water Splitting: The Oxygen Evolution Activity of Ni₂P Nanoparticles. *Energy Environ. Sci.* **2015**, *8*, 2347.
- (24) Zhu, W.; Yue, X.; Zhang, W.; Yu, S.; Zhang, Y.; Wang, J.; Wang, J. Nickel Sulfide Microsphere Film on Ni Foam as an Efficient Bifunctional Electrocatalyst for Overall Water Splitting. *Chem. Commun.* **2016**, *52*, 1486.
- (25) Ledendecker, M.; Krick Calderón, S.; Papp, C.; Steinrück, H.-P.; Antonietti, M.; Shalom, M. The Synthesis of Nanostructured Ni₅P₄ Films and Their Use as a Non-Noble Bifunctional Electrocatalyst for Full Water Splitting. *Angew. Chemie Int. Ed.* **2015**, *54* (42), 12361–12365.
- (26) Gao, X.; Zhang, H.; Li, Q.; Yu, X.; Hong, Z.; Zhang, X.; Liang, C.; Lin, Z. Hierarchical NiCo₂O₄hollow Microcuboids as Bifunctional Electrocatalysts for Overall Water-Splitting. *Angew. Chemie - Int. Ed.* **2016**, *55*, 6290.
- (27) Li, Y.; Cao, L.; Qiao, L.; Zhou, M.; Yang, Y.; Xiao, P.; Zhang, Y. Ni–Co Sulfide Nanowires on Nickel Foam with Ultrahigh Capacitance for Asymmetric Supercapacitors. *J. Mater. Chem. A* **2014**, *2*, 6540.

- (28) Zhou, W.; Cao, X.; Zeng, Z.; Shi, W.; Zhu, Y.; Yan, Q.; Liu, H.; Wang, J.; Zhang, H. One-Step Synthesis of Ni₃S₂ Nanorod@Ni(OH)₂ Nanosheet Core–Shell Nanostructures on a Three-Dimensional Graphene Network for High-Performance Supercapacitors. *Energy Environ. Sci.* **2013**, *6*, 2216.
- (29) Yu, L.; Zhang, G.; Yuan, C.; Lou, X. W. (David). Hierarchical NiCo₂O₄@MnO₂ Core–Shell Heterostructured Nanowire Arrays on Ni Foam as High-Performance Supercapacitor Electrodes. *Chem. Commun.* **2013**, *49*, 137.
- (30) Huang, L.; Chen, D.; Ding, Y.; Feng, S.; Wang, Z. L.; Liu, M. Nickel–Cobalt Hydroxide Nanosheets Coated on NiCo₂O₄ Nanowires Grown on Carbon Fiber Paper for High-Performance Pseudocapacitors. *Nano Lett.* **2013**, *13*, 3135.
- (31) Tran, V. C.; Sahoo, S.; Shim, J.-J. Room-Temperature Synthesis of NiS Hollow Spheres on Nickel Foam for High-Performance Supercapacitor Electrodes. *Mater. Lett.* **2018**, *210*, 105.
- (32) Chen, J.; Xu, J.; Zhou, S.; Zhao, N.; Wong, C.-P. Amorphous Nanostructured FeOOH and Co–Ni Double Hydroxides for High-Performance Aqueous Asymmetric Supercapacitors. *Nano Energy* **2016**, *21*, 145.
- (33) Cai, D.; Wang, D.; Liu, B.; Wang, L.; Liu, Y.; Li, H.; Wang, Y.; Li, Q.; Wang, T. Three-Dimensional Co₃O₄@NiMoO₄ Core/Shell Nanowire Arrays on Ni Foam for Electrochemical Energy Storage. *ACS Appl. Mater. Interfaces* **2014**, *6*, 5050.