Supplementary Materials

Two-Dimensional Layered $NiLiP_2S_6$ Crystals as an Efficient Bifunctional Electrocatalyst for Overall Water Splitting

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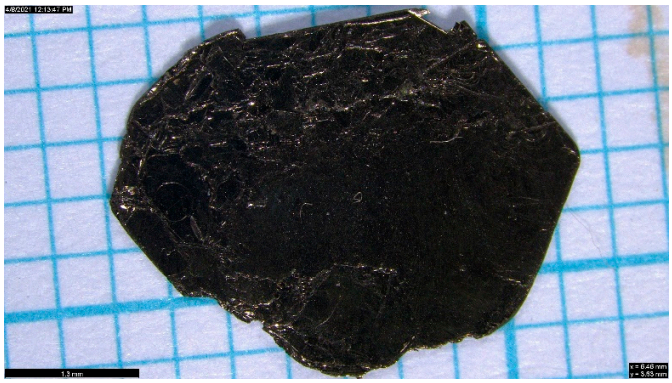
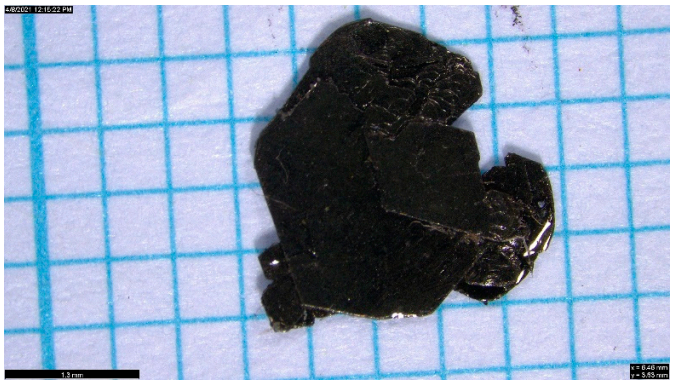
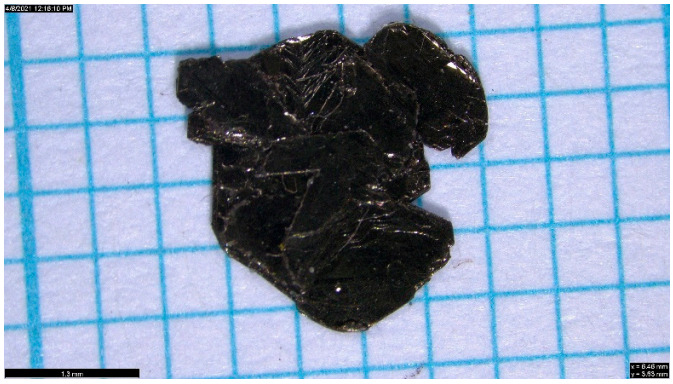

Fig. S1. As Synthesized NLPS crystals

Table S1: Crystallite size and Microstrain

Peak Position	Crystallite Size (nm)	Microstrain (ε) $x10^{-3}$
13.89758	37.65	7.95
28.09179	35.29	4.23
31.02481	33.18	4.08
36.10847	20.34	5.74
49.47916	16.09	5.38
54.56576	24.53	3.22
58.07951	16.14	4.62

Table S2. Structural parameters of the catalysts obtained from Ritveld refinement of XRD powder data

		x	y	z	U	Site	Sym.
1 Li	Li	-0.26520 (3)	1.12328 (15)	-0.06920 (18)	0.183	8j	1
2 Ni	Ni1	-0.48580 (17)	-0.04270 (4)	0.23828 (9)	-0.020	8j	1
3 P	P1	0.26806 (2)	0.04941 (3)	0.54818 (6)	0.208	8j	1
4 P	P2	0.27746 (15)	-0.29010 (10)	0.57554 (7)	-0.054	8j	1
5 S	S1	0.49264 (12)	0.65081 (5)	0.75857 (5)	0.024	8j	1
6 S	S2	0.12902 (9)	0.11480 (5)	0.30761 (5)	0.041	8j	1
7 S	S3	1.03714 (7)	1.01168 (7)	-0.23800 (17)	0.324	8j	1
8 S	S4	-0.34170 (12)	0.27751 (3)	0.49156 (7)	0.393	8j	1
9 S	S5	-0.84110 (11)	0.17045 (9)	-0.21370 (5)	0.046	8j	1
10 S	S6	0.06483 (8)	0.06686 (7)	0.87629 (5)	-0.050	8j	1
NLPS		V = 864.34 (11) Å3					
		Bragg R-factor: 1.952 RF-factor: 1.052					
		Note: ***values in bracket shows the deviations***					

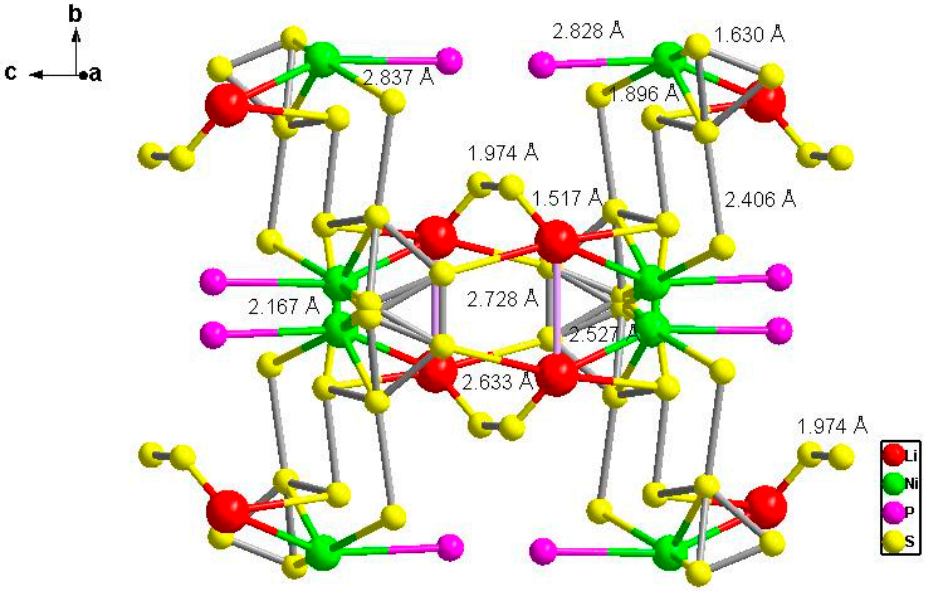

Fig. S2. Inter-atomic distances between indiviual atoms.

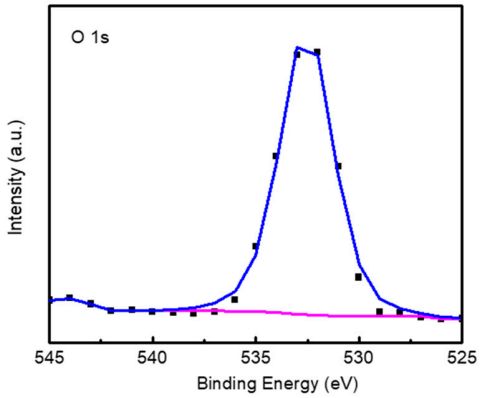

Fig. S3. O 1s spectra of NLPS

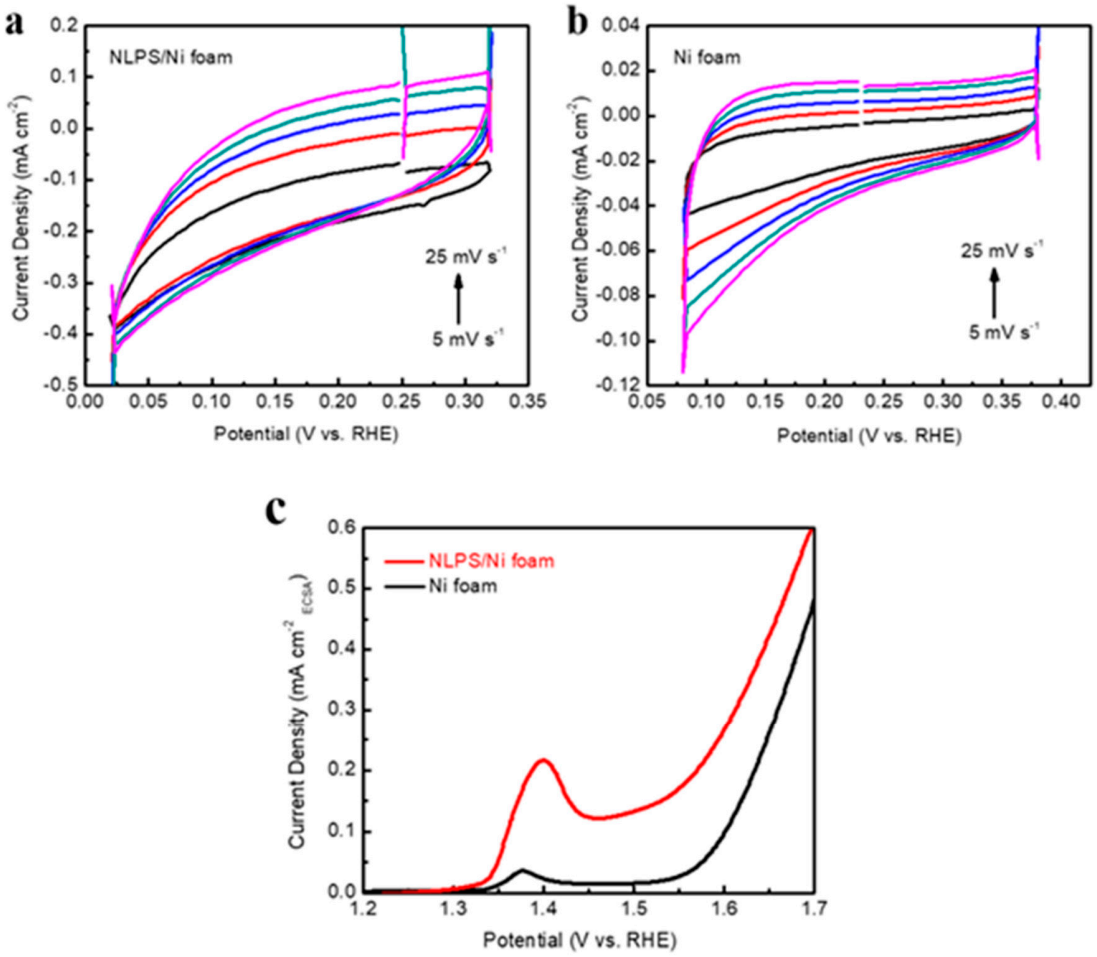

Fig. S4. Cyclic voltammetry at different scan rates (a) NLPS. (b) Ni foam and (c) Overall water splitting of NLPS/Ni foam and Ni foam (Current density was normalized by ECSA)

Supplementary Methods

Calculation of ECSA. The calculation of electrochemically active surface area (ECSA) is based on the measured double layer capacitance of the NLPS/Ni foam and Ni foam electrode in 1 M KOH according to a previous published report.[1] Briefly, a potential range where no apparent Faradaic process happened was determined firstly using the static CV. The charging current ic was measured from the CVs at different scan rates, as shown

in Fig. S4a and b. The relation between i_c, the scan rate (ν) and the double layer capacitance (C_{dl}) was given in eq 1.

$$i_c = vC_{dl} \qquad (1)$$

The electrochemical double-layer capacitance (*C*dl) was determined from the scan-rate dependence of CVs in a potential range where there is no Faradic current. For NLPS/Ni foam, *C*dl = 3.6 mF cm^{-2} and for Ni foam *C*dl = 0.8 mF cm^{-2}. The ECSA can be calculated from the *C*dl according to:

$$ECSA = \frac{C_{dl}}{C_s} \qquad (2)$$

where *C*s is the specific capacitance of a flat standard electrode is Cs = 0.040 mF cm^{-2} in 1 M NaOH is adopted from previous reports.[2] As a result, the ECSA of the NLPS/Ni foam and Ni foam are calculated to be 90 cm^2 and 20 cm^2 according to eq 2. For ECSA normalized activity, the overall water splitting current density was divided by ECSA and the data was presented in **Figure S4c.**

References:

1. Sabhapathy, P.; Liao, C.C.; Chen, W.F.; Chou, T.C.; Shown, I.; Sabbah, A.; Lin, Y.G.; Lee, J.F.; Tsai, M.K.; Chen, K.H.; Chen, L.C. Highly Efficient Nitrogen and Carbon Coordinated N-Co-C Electrocatalyst on Reduced Graphene Oxide Derived from Vitamin-B12 for Hydrogen Evolution Reaction. J. Mater. Chem. A, **2019**, 7, 7179–7185, doi.org/10.1039/C8TA10935D.

2**.** Kibsgaard, J.; Jaramillo, T.F. Molybdenum Phosphosulfide: An Active, Acid-Stable, Earth-Abundant Catalyst for the Hydrogen Evolution Reaction. Angew. Chem. Int. Ed., **2014,** 53, 14433–14437, doi.org/10.1002/anie.201408222