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Neutral-pH Overall Water Splitting Catalyzed Efficiently by a Hollow and Porous Structured Ternary Nickel Sulfoselenide Electrocatalyst

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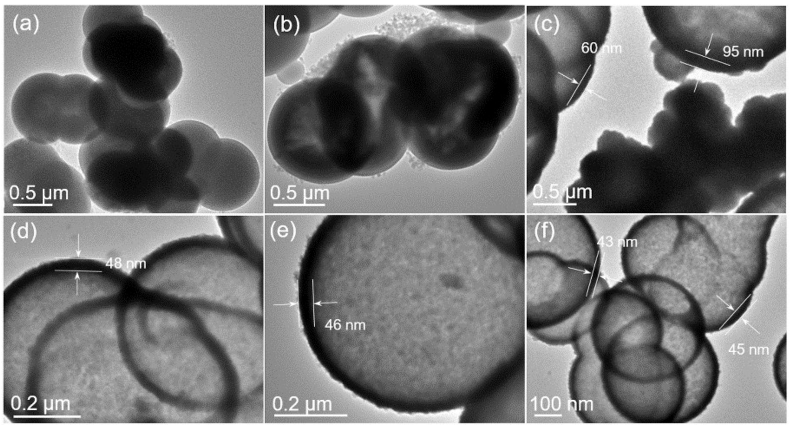

Figure S1. TEM images of the time-dependent formation of hollow NiS_2 spheres. (a) 1 h; (b) 2 h; (c) 4 h; (d) 12 h; (e) 24 h; (f) 36 h. The wall thicknesses of hollow spheres were measured and marked in the images. Figure S1 shows that the NiS_2 solid spheres entirely transform into hollow spheres when the hydrothermal time reaches to 12 h. When continue to extend the hydrothermal time from 12 h to 36 h, the wall thicknesses of hollow spheres slightly decrease from 48 nm to 43 nm.

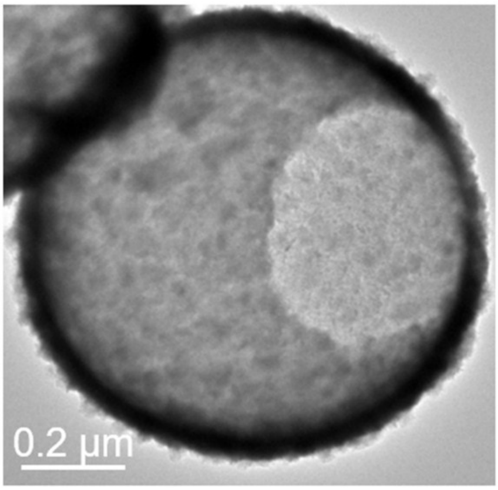

Figure S2. TEM image of a typical hollow NiS_2 microsphere with a broken shell.

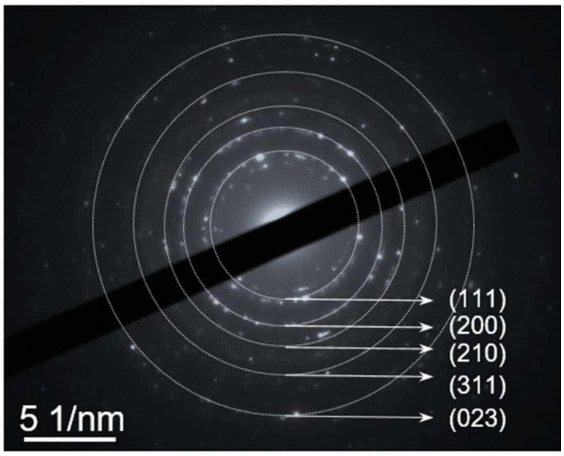

Figure S3. The selective area electron diffraction (SAED) pattern of the $Ni(S_{0.5}Se_{0.5})_2$ electrocatalyst.

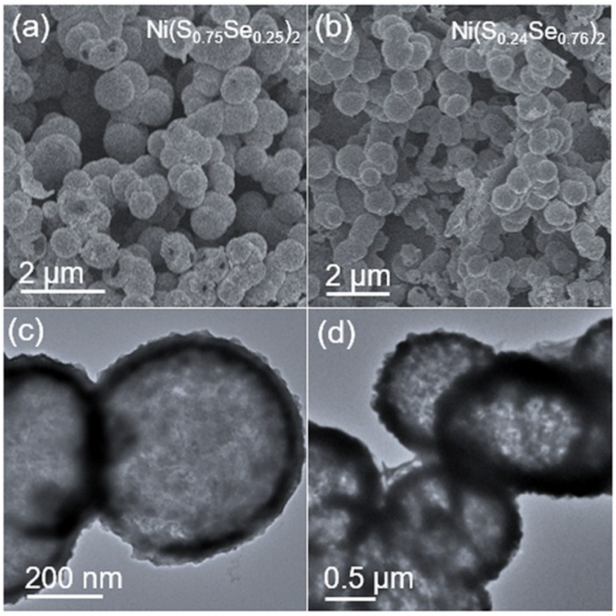

Figure S4. (a, b) SEM and (c, d) TEM images of the $NiS_{2(1-x)}Se_{2x}$ porous/hollow spheres with (a, c) $x = 0.25$ and (b, d) $x = 0.72$.

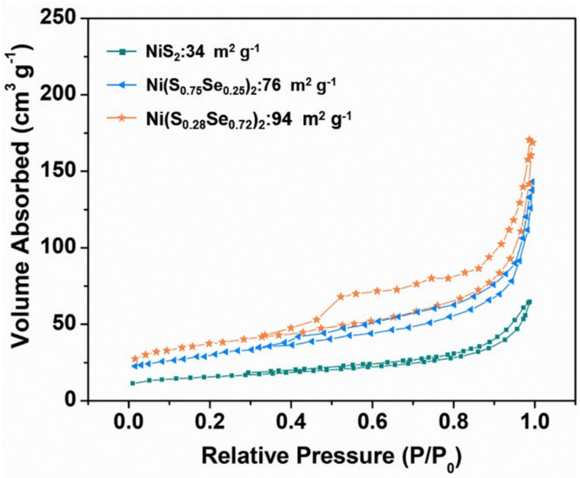

Figure S5. Nitrogen sorption isotherms of NiS_2, $Ni(S_{0.75}Se_{0.25})_2$ and $Ni(S_{0.28}Se_{0.72})_2$ samples.

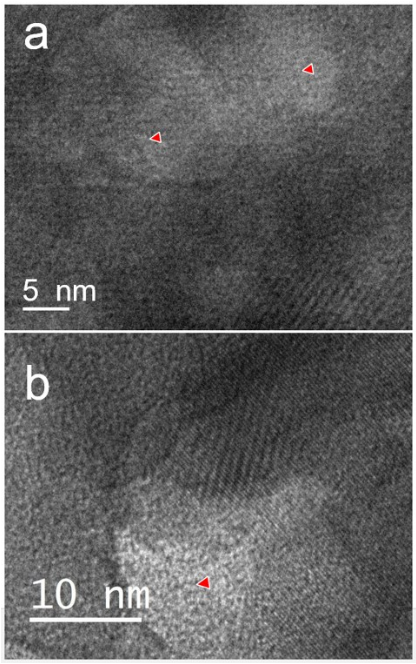

Figure S6. HRTEM images of the $Ni(S_{0.5}Se_{0.5})_2$ catalyst. Red arrows refer to porous structure.

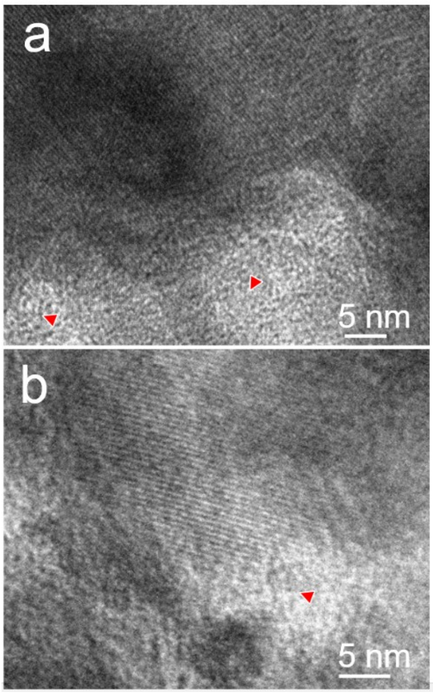

Figure S7. HRTEM images of (a) $Ni(S_{0.75}Se_{0.25})_2$ and (b) $Ni(S_{0.28}Se_{0.72})_2$ catalysts. Red arrows refer to porous structure.

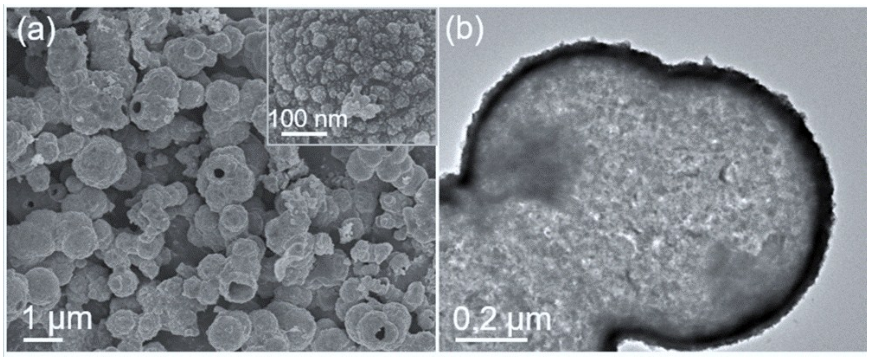

Figure S8. SEM images (a) and TEM image (b) for $Ni(S_{0.5}Se_{0.5})_2$ catalyst after long-term stability test.

Table S1. Chemical composition and electrocatalytic performance of the porous/hollow $NiS_{2(1-x)}Se_{2x}$ catalysts.

		NiS_2	$Ni(S_{0.75}Se_{0.25})_2$	$Ni(S_{0.5}Se_{0.5})_2$	$Ni(S_{0.28}Se_{0.72})_2$
selenization process	feed mass ratio [a)]	—	1:2	1:5	1:10
	reaction time (h)	—	2	2	5
S:Se ratio from ICP		—	0.745:0.253	0.494:0.506	0.282:0.718
η_{10} [b)] (mV)	HER	245	171	124	141
	OER	665	595	501	540
Tafel slope (mV dec^{-1})	HER	106	86	81	92
	OER	182	105	94	121
C_{dl} (mF cm^{-2})		4.6	8.7	12.9	9.8
C_{dl}-normalized activity [c)]		0.41	0.74	1.55	1.32
BET surface area (m^2 g^{-1})		34	76	91	94
BET-normalized activity [d)]		0.04	0.09	0.22	0.13

a) feed mass ratio: mass ratio of NiS_2 to Se powder (g/g). b) η_{10}: overpotential requirement for current density of 10 mA cm^{-2}. c) and d) : HER current densities at -150 mV *vs.* RHE normalized to C_{dl} and BET surface area, respectively.

Table S2. Comparison of the HER performance of $Ni(S_{0.5}Se_{0.5})_2$ with other earth-abundant HER electrocatalysts in neutral electrolyte.

Catalysts	Support	Mass loading (mg cm^{-2})	η vs. RHE (mV) @j=10 mA cm^{-2}	Tafel slope (mV dec^{-1})	Electrolyte	Reference
$Ni(S_{0.5}Se_{0.5})_2$	Ni foam	0.75	124	81	1 M PBS	This work
CoP nanowire/CC	Carbon choth	0.92	106	93	1 M PBS	[1]
MoP/CFP	Carbon paper	2.8	165	105	1 M PBS	[2]
MoS_2/Ti plate	Ti plate	1.5	200	152	1 M PBS	[3]
FeP NAs	Glass carbon	N.A.	202	71	1 M PBS	[4]
CoP NS	Ti plate	2.0	149	58	1 M PBS	[5]
$Ni_{0.1}Co_{0.9}P$	Carbon paper	0.58	125	103	1 M PBS	[6]
Ni-doped FeP/C	Carbon paper	0.4	117	81	1 M PBS	[7]
Amorphous Co-S film	FTO	1.5	160	93	1 M PBS	[8]
Co-C-N complex	Glass carbon	1.25	107	273	1 M PBS	[9]
CoP-MNA/NF	Ni foam	0.92	189	180	0.5 M PBS	[10]
3D MoS_2/N-GAs	Glass carbon	0.7	261	230	1 M PBS	[11]

Table S3. Comparison of the OER performance of $Ni(S_{0.5}Se_{0.5})_2$ with other earth-abundant OER electrocatalysts in neutral electrolyte.

Catalysts	Support	Mass loading (mg cm^{-2})	η vs. RHE (mV) @j=10 mA cm^{-2}	Tafel slope (mV dec^{-1})	Electrolyte	Ref.
$Ni(S_{0.5}Se_{0.5})_2$	Ni foam	0.75	501	94	1 M PBS (pH 7)	This work
Co_3S_4 ultrathin nanosheets	Glassy carbon	N.A.	700	151	PBS (pH 7)	[12]
a-Co_2P	Glassy carbon	N.A.	592	94.4	0.1 M PBS	[13]
1-D CoHCF	Glass substrate	1.0	880	N.A.	PBS (pH 7)	[14]
Co-Bi NS/G	Glass carbon	0.285	570 mV @ 14.4	160	PBS (pH 7)	[15]
Bi_2WO_6 CNPs	Glass carbon	0.34	540	N.A.	0.5 M Na_2SO_4 (pH 6.6)	[16]
$CuCo_2O_4$/NrGO	Glass carbon	0.8	540	79	0.1 M PBS (pH 7.6)	[17]

N.A. stands for not given.

Table S4. Comparison of recent bifunctional electrocatalysts for overall water splitting in neutral electrolytes.

Catalysts	Support	Mass loading (mg cm^{-2})	Electrolyte	HER η_{10} (mV)	HER Tafel slope (mV dec^{-1})	OER η_{10} (mV)	OER Tafel slope (mV dec^{-1})	E_{10} (V)	Ref.
$Ni(S_{0.5}Se_{0.5})_2$	Ni foam	0.75	1 M PBS (pH 7)	124	81	501	94	1.87	This work
S-$NiFe_2O_4$	Ni foam	N.A.	1 M PBS (pH 7)	197	81.3	494	118.1	1.95	[18]
CoO/$CoSe_2$-Ti	Ti mesh	2.0	0.5 M PBS	337	131	510	137	2.18	[19]
$Ni_{0.1}Co_{0.9}P$	Carbon paper	0.58	1 M PBS (pH 7)	125	103	570	133	1.89	[6]

N.A. stands for not given.

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