Supplementary information

Nickel Sulfide Cocatalyst-Modified Silicon Nanowire Arrays for Efficient Seawater-based Hydrogen Generation

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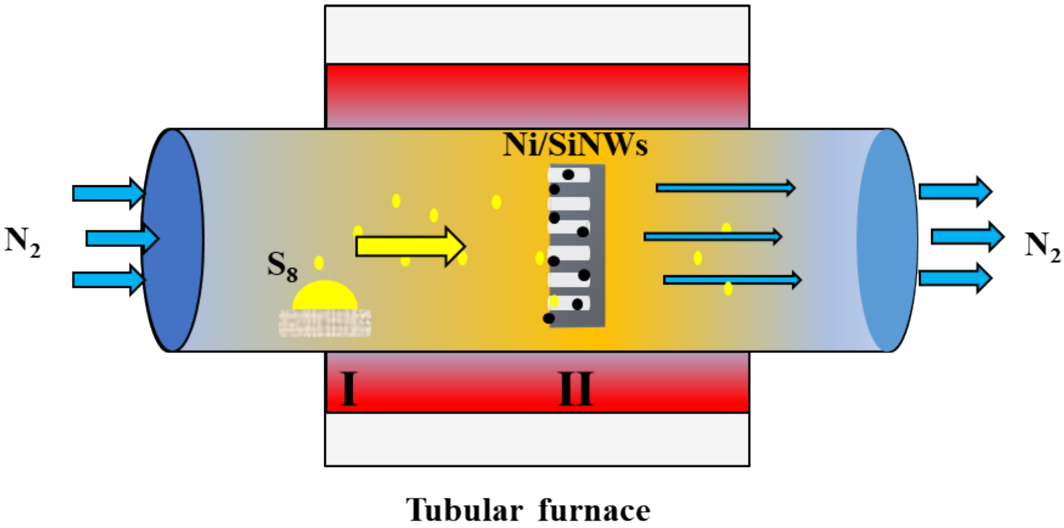

Figure S1. Schematic diagram of the preparation process for NiS_x/SiNWs.

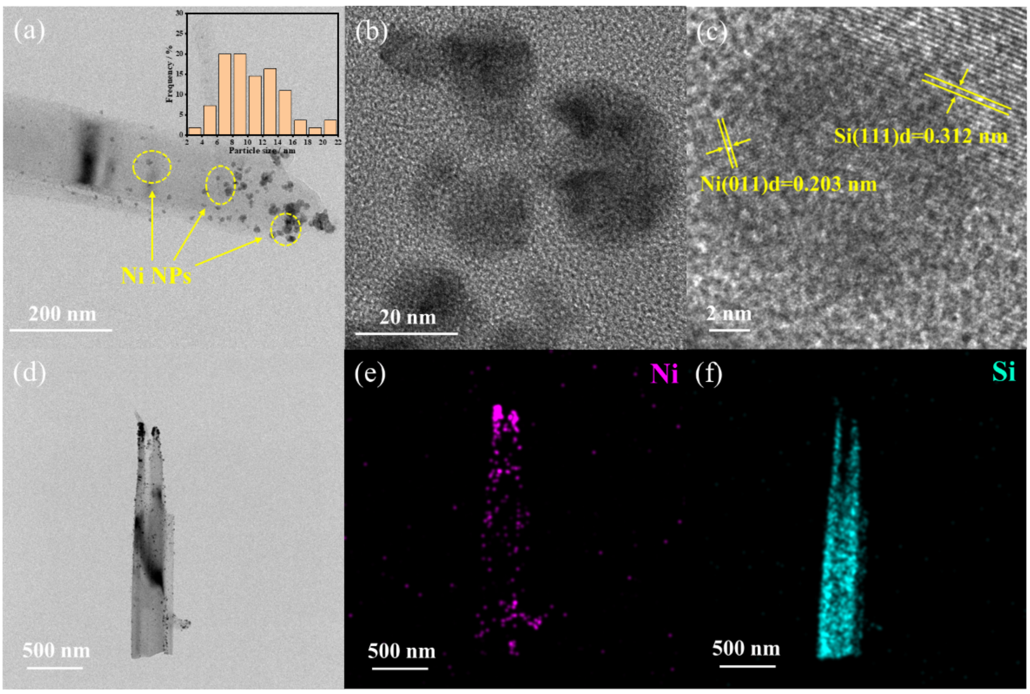

Figure S2. TEM image of Ni/SiNWs (a, b and d), HRTEM image (c), the corresponding elemental maps: (e) Ni and (f) Si.

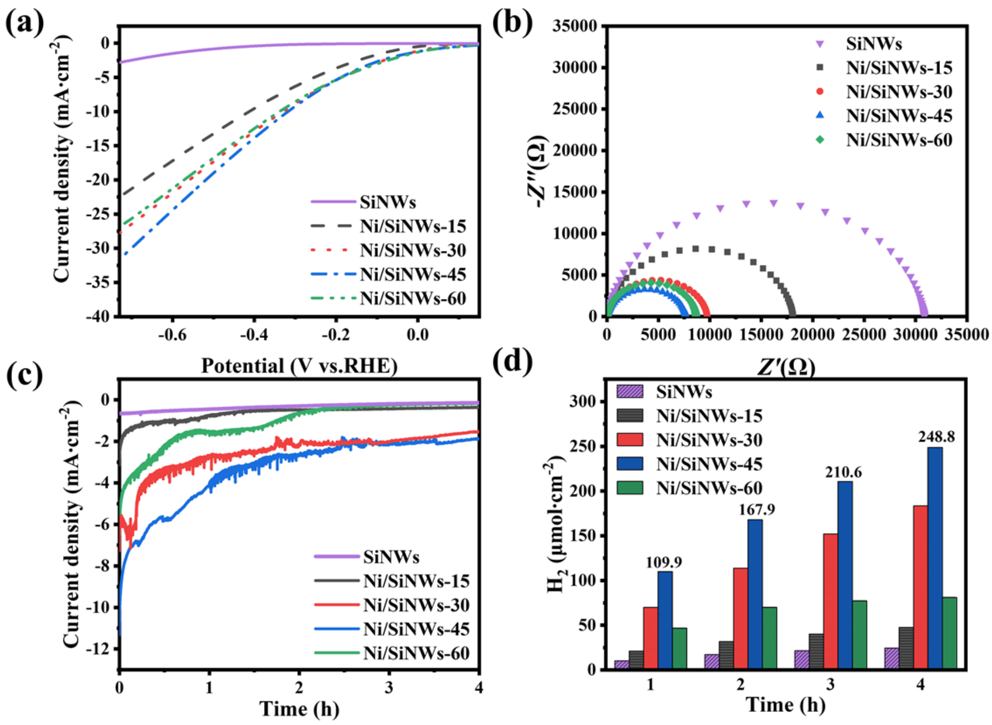

Figure S3. Photoelectrochemical hydrogen evolution performances of Ni/SiNWs: (a) Linear scanning voltammogram, (b) Nyquist impedance spectrogram, (c) PEC stability tests of SiNWs and Ni/SiNWs photocathodes in simulated seawater measured at -0.33 V vs. RHE under 100 mW·cm^{-2} illumination and (d) the corresponding H_2 evolution performance of SiNWs and Ni/SiNWs photocathodes in simulated seawater.

The as-fabricated SiNWs and Ni/SiNWs photocathodes were performed under photoelectrochemical test. As Figure S3a shows, the current density of Ni/SiNWs are significantly higher than SiNWs photocathode under the same potential, which illustrates the superior electrocatalytic activity of Ni nanoparticles. The Ni/SiNWs-45 exhibits the optimum performance, while further increasing the deposition time of Ni, the performance of Ni/SiNWs declines, which may be ascribed to the agglomeration of Ni nanoparticles. Figure S3b is the Nyquist spectra of Ni/SiNWs with different deposition times, the decreased radius of Ni/SiNWs compared to SiNWs also indicates the faster carriers transfer property at the solid/electrolyte interface. The long-time photoelectrochemical performance is illustrated in Figure S3c, all Ni/SiNWs photocathodes exhibits higher current density than SiNWs illustrating the electrocatalytic activity of Ni NPs. However, the performance of Ni/SiNWs photocathode gradually decrease, which could be ascribed to the oxidation of Ni NPs during the PEC process. The Ni 2p XPS result of Ni/SiNWs photocathode after PEC process for 4h also convinced that the Ni^{2+} peak increases and the Ni^0 peak disappears (Figure S4). The corresponding H_2 evolution amount was obtained in Figure S3d, the optimized Ni/SiNWs-45 photocathode exhibits H_2 yield rate of 62.2 μmol·h^{-1}·cm^{-2}, while the unloaded SiNWs photocathode is only 6.13 μmol·h^{-1}·cm^{-2}. Thus, the instability of Ni nanoparticles hampers its application on PEC HER process, although it's excellent catalytic activity.

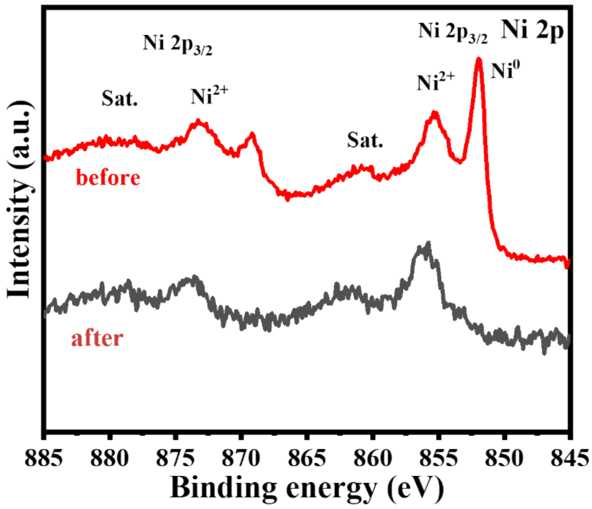

Figure S4. XPS spectrum of Ni 2p in Ni/SiNWs after photoelectrochemical hydrogen evolution process.

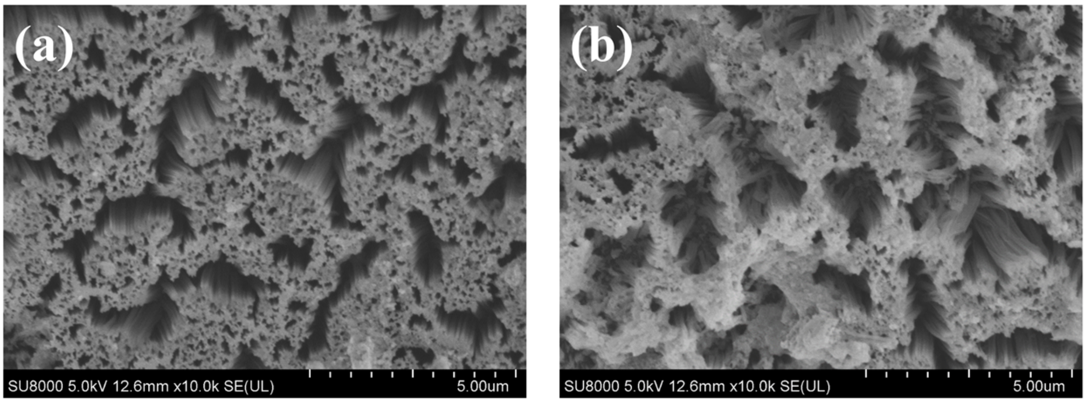

Figure S5. SEM images of NiS_x/SiNWs: (a) before photoelectrochemical hydrogen evolution process, (b) after photoelectrochemical hydrogen evolution process.

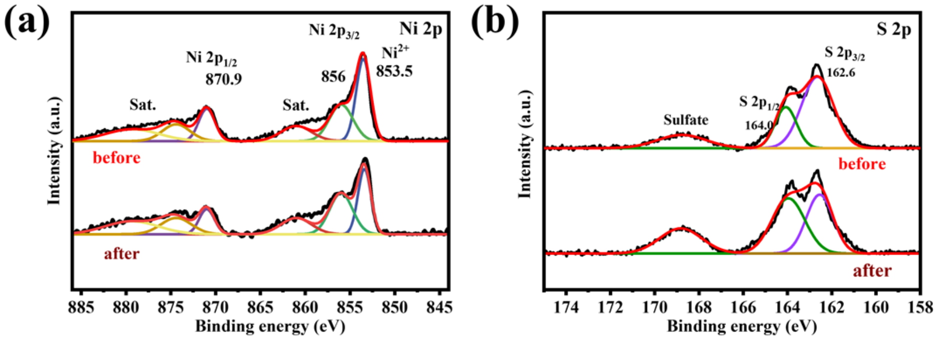

Figure S6. High resolution XPS spectra of (a) Ni 2p and (b) S 2p in NiS_x/SiNWs after photoelectrochemical hydrogen evolution process.

Table S1. Fitting results of EIS curves for SiNWs and NiS_x/SiNWs samples

Samples	Rs	Rct	CPE-T	CPE-P
SiNWs	45.22	21072	1.407×10^{-5}	0.995
NiS_x/SiNWs	22.58	4994	6.607×10^{-5}	0.802

Table S2. Comparison with the similar reported works in literature

Photocathode	Electrolyte	Hydrogen evolution potential at -10 $mA \cdot cm^{-2}$ (V vs. RHE)	V vs. RHE/ H_2 evolution rate($\mu mol \cdot h^{-1} \cdot cm^{-2}$)	Refs
NiS_x/SiNWs	**simulated seawater**	**-0.316**	**-0.33/189.15**	**This work**
RuCo@Ti	simulated seawater	-0.387	~	1
$PtNi_x$	natural seawater	-0.38	~	2
Co_3O_4	natural seawater	-0.950	~	3
SiNWs@Mo S_2/NiS_2	0.5 $mol \cdot L^{-1}$ Na_2SO_4	-0.560	-0.50/183	4
MoS_2/SiNWs	0.5 $mol \cdot L^{-1}$ H_2SO_4	-0.300	0/226.5	5
PANI/GO/ TiO_2	simulated seawater	~	0.07/72.5	6
AlGaN/ GaN heteroepitaxial films	natural seawater	~	-0. 4/95	7

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