## Supplementary Information

## Boosted Charge Transport through Au-modified NiFe Layered Double Hydroxide on Silicon for Efficient Photoelectrochemical Water Oxidation

Sungkyun Choi<sup>a</sup>, Sol A Lee<sup>a</sup>, Jin Wook Yang<sup>a</sup>, Woonbae Sohn<sup>a</sup>, Jaehyun Kim<sup>a</sup>, Woo Seok Cheon<sup>a</sup>, Jaemin Park<sup>b</sup>, Jin Hyuck Cho<sup>c</sup>, Chung Won Lee<sup>a</sup>, Sang Eon Jun<sup>a</sup>, Sung Hyuk Park<sup>a</sup>, Jooho Moon<sup>b,\*</sup>, Soo Young Kim<sup>c,\*</sup>, and Ho Won Jang <sub>a,d,\*</sub>



**Fig. S1** *J-V* curves of NiFe LDH/n-Si based photoanodes with different electrodeposition CV range for the deposition of Au on NiFe LDH.



Fig. S2 EDS spectrum of Au-NiFe LDH through HAADF-STEM analysis.



**Fig. S3** (a) STEM image, (b) corresponding EDS map, and (c) TEM image of NiFe LDH. (d) STEM image, (e) corresponding EDS map, and (f) TEM image of Au-NiFe LDH.



Fig. S4 SEM image of electrodeposited Au film on n-Si.



Fig. S5 Au 4f XPS spectra of (a) Au film/n-Si and (b) Au-NiFe LDH/n-Si.



Fig. S6 (a) Fe 2p and (b) Ni 2p XPS spectra for NiFe LDH/n-Si and Au-NiFe LDH/n-Si.



**Fig. S7** Current-potential (*J-V*) curves of Au-NiFe LDH/n-Si with different Au concentration in 1 M NaOH aqueous solution under AM 1.5 G sunlight (100 mW/cm<sup>2</sup>).



**Fig. S8** Current-potential (*J-V*) curves of Au-NiFe LDH/n-Si before and after stability test under AM 1.5 G sunlight (100 mW/cm<sup>2</sup>) at 1.23 V vs. RHE.



**Fig. S9** Wide-scan XPS spectra of Au-NiFe LDH/n-Si, (a) before stability test and (b) after stability test. Au 4f XPS spectra of Au-NiFe LDH/n-Si, (c) before stability test and (d) after stability test. TEM images of Au-NiFe LDH/n-Si, (e) before stability test and (f) after stability test.



**Fig. S10** SEM images of (a) a-NiFe LDH/n-Si and (b) a-Au-NiFe LDH/n-Si. (c) LSVs and (d) stability tests of NiFe LDH and Au-NiFe LDH based photoanodes in buffered NaOH electrolyte.



**Fig. S11** Equivalent circuit of NiFe LDH/n-Si and Au-NiFe LDH/n-Si fitted with EIS data.



**Fig. S12** (a) Mott-Schottky plots of Au-NiFe LDH/n-Si and NiFe LDH/n-Si photoanodes at 50 kHz frequency under light off condition. (b) Amperometric curves of photoanodes under light chopping condition.



**Fig. S13** Curve fitting results of Au L3-edge EXAFS spectra for Au-NiFe LDH/n-Si with (a) Au-O, (b) Au-Ni, and (c) Au-Fe shells.



**Fig. S14** UV-vis (a) transmittance and (b) reflectance spectra of Au-NiFe LDH and NiFe LDH. Tauc plots of (c) NiFe LDH and (d) Au-NiFe LDH.

 Table S1 Atomic fraction of as-synthesized Au-NiFe LDH catalyst.

Element	Ni	Fe	Au	0
Atomic Fraction (%)	15.87	21.47	1.06	61.6

Table S2 DFT calulation results of total free energy with number of atoms in different catalyst systems.

Structure	System	Total free energy (eV)	# atom
	V <sub>Ni</sub>	-913.300	167
NiFe LDH	V <sub>Fe</sub>	-909.274	167
	Au <sub>Ni</sub>	-915.050	168
Au-NiFe LDH	Au <sub>Fe</sub>	-911.544	168

 Table S3 Fitted charge transfer resistances.

	<b>R</b> <sub>ct,1</sub> (Ω·cm²)	<b>R</b> <sub>ct,2</sub> (Ω·cm²)	<b>R</b> <sub>ct,3</sub> (Ω·cm <sup>2</sup> )	
Photoanodes	Contact/n-Si	Au-NiFe LDH/n-Si & NiFe LDH/n-Si	Au-NiFe LDH/electrolyte & NiFe LDH/electrolyte	
Au-NiFe LDH/n-Si	0.65	1.4	305.11	
NiFe LDH/n-Si	0.3	9.59	306.8	

Table S4 Fitted constant phase elements.

Photoanodes	CPE1-T	CPE1-P	CPE2-T	CPE2-P
Au-NiFe LDH/n-Si	6.7E-7	0.79	1.69E-5	0.95
NiFe LDH/n-Si	6.3E-8	1.04	0.0008	0.22

Sample	Reference shell	Radial distance (Å)	Debye-Waller factor (Ų)
Au foil	Au-Au	2.87	
Au-NiFe LDH	Au-Au	2.63±0.3	0.02
	Au-O	1.92±0.12	0.001
	Au-Ni	2.59±0.05	0.01
	Au-Fe	2.6±0.06	0.01

Table S5 EXAFS fitting results with radial distances between Au and other elements.