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Highly-Efficient Overall Water Splitting Driven by All-Inorganic Perovskite Solar Cells and Promoted by Bifunctional Bimetal Phosphide Nanowire Arrays

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Table S1. HER performance comparison of $Ni_{0.5}Co_{0.5}P$/CP and other representative electrocatalysts in alkaline solutions.

Ref.	**Electrocatalysts (morphology)**	η_{onset} **(mV)**	η_{10} **(mV)**	**Tafel slope (mV/dec)**	**Stability (Activity retention)**	**Electrolyte**
This work	$Ni_{0.5}Co_{0.5}P$ nanowire arrays/carbon paper	10	43	46.4	Stable for 24 h	1.0 M KOH
46	CoP nanowires/carbon cloth	38	110	129	--	1.0 M KOH
47	$NiCo_2S_4$ nanowires/carbon cloth	230	--	141	Almost stable for 12 h	1.0 M KOH
48	WC nanoparticles/CNTs	16	137	106	Almost stable for 1000 cycles	1.0 M KOH
49	NiSn@carbon	100	--	145	Slightly decreased after 100 cycles	1.0 M NaOH
50	WN nanowires/carbon cloth	100	285	170	--	1.0 M KOH
51	Carbon paper/carbon tubes/Co-S	50	190	131	Slightly decreased after 10,000 seconds	1.0 M KOH
52	NiCo-P hollow nanocubes	--	150	61	Slightly decreased after 100 cycles	1.0 M KOH
53	Ni-Fe/nanocarbon	--	219	110	Stable for 1,200 seconds	1.0 M KOH
54	Co-Mo/Ti	--	75	--	Almost stable for 18 h	1.0 M KOH
55	Co/N-doped carbon	~45	260	91.2	Almost stable for 10 h	1.0 M KOH

Table S2. OER performance comparison of $Ni_{0.5}Co_{0.5}P$/CP and other representative electrocatalysts in alkaline solutions.

Ref.	**Electrocatalyst (morphology)**	η_{onset} **(mV)**	η_{10} **(mV)**	**Tafel slope (mV/dec)**	**Stability (Activity retention)**	**Electrolyte**
This work	$Ni_{0.5}Co_{0.5}P$ nanowire arrays/carbon paper	240	260	58.3	Stable for 24 h	1.0 M KOH
58	Graphene-like holey Co_3O_4 nanosheets	230	300	66	Almost stable after 2,000 cycles	0.1 M KOH
59	Ni_1Co_4S@N-doped carbon frameworks	200	280	64	Decrease obviously after 1,000 cycles	0.1 M KOH
60	NiCo-layered double hydroxides/carbon fiber	270	310	64	Decrease after 20 h	1.0 M KOH
61	Phosphorus-doped few-layer graphene	250	330	62	Slightly decreased after 2,000 cycles	1.0 M NaOH
62	$CoSe_2$/CFC	310	356	88	--	1.0 M KOH
63	NiFe layered double hydroxide/reduced graphene oxide nanohybrid	240	250	91	Slightly decreased after 9 h	1.0 M KOH
64	Core–Shell Ni-Co Nanowire Network	250	302	44	Decreased after 10 h	1.0 M KOH
65	$Ni_xCo_{3-x}O_{4-y}$ Nanocages	300	320	53	--	1.0 M KOH
66	Porous carbon cloth	300	360	96	Almost stable for 27 h	1.0 M KOH
67	Porous nickel–iron bimetallic selenide nanosheets	~230	260	47	Almost stable for 28 h	1.0 M KOH

Table S3. Overall water splitting performance comparison of $Ni_{0.5}Co_{0.5}P$/CP and other electrocatalysts reported in the literatures.

Ref.	Electrocatalyst (morphology)	η_{10} (V)	Stability (Activity retention)	Electrolyte
This work	3D $Ni_{0.50}Co_{0.50}P$ nanowire arrays/carbon paper	1.61	Extremely stable for 28 h	1.0 M KOH
33	$NiCo_2S_4$ nanowire arrays/Ni foam	1.63	Decreased after 50 h	1.0 M KOH
34	Porous Co-P/NC nanopolyhedrons	1.71	Decreased after 24 h	1.0 M KOH
68	$Cu_{0.3}Co_{2.7}P$/nitrogen-doped carbon (NC)	1.74	Negligible catalytic deactivation after 50 h	1.0 M KOH
69	$CoSe_2$ nanoparticles/carbon fiber	1.63	Stable for 30 h	1.0 M KOH
70	CoO nanoparticle-doped $CoSe_2$ nanobelts	2.18	Increased for 10 h	1.0 M KOH
71	Hierarchical $NiCo_2O_4$ hollow microcuboids	1.65	Stable for 36 h	1.0 M KOH
72	$NiSe_2$ film/Ti foil	1.66	Decreased for 16 h	1.0 M KOH

Table S4. Performance comparison of the overall water splitting system driven by all-inorganic PSCs with the existing photocatalysis systems.

Ref.	Photocatalysts	Solar to hydrogen efficiency (%)
73	Te/SnS_2/Ag	0.49
74	$In_{0.33}Ga_{0.67}N$	3.5
75	Hexagonal CdS	3.2
76	GaN-based nanowire arrays	1.9
77	Mo-doped $BiVO_4$/Au layer	1.1
78	Carbon nitride	0.12

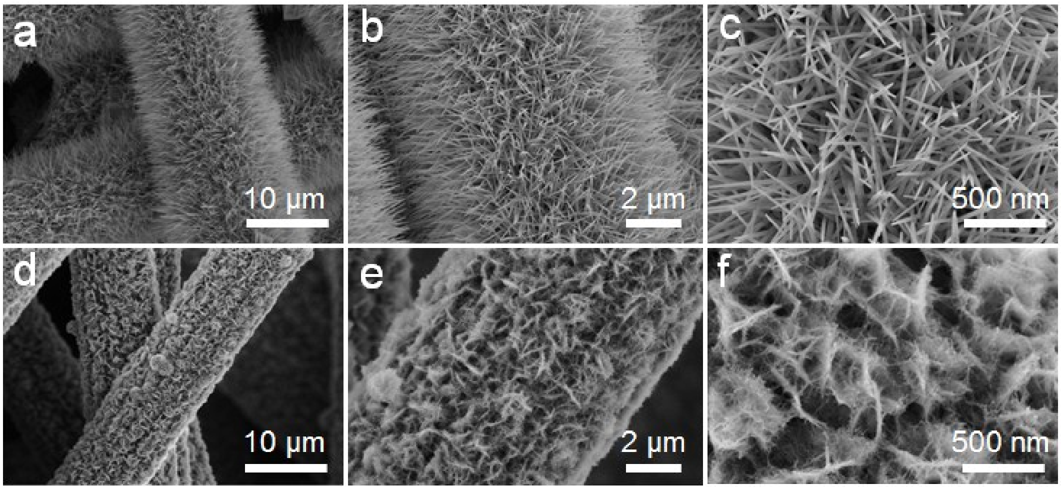

Fig. S1. Morphologic characterizations of control samples. SEM images of (a-c) CoP/CP and (d-f) NiP/CP.

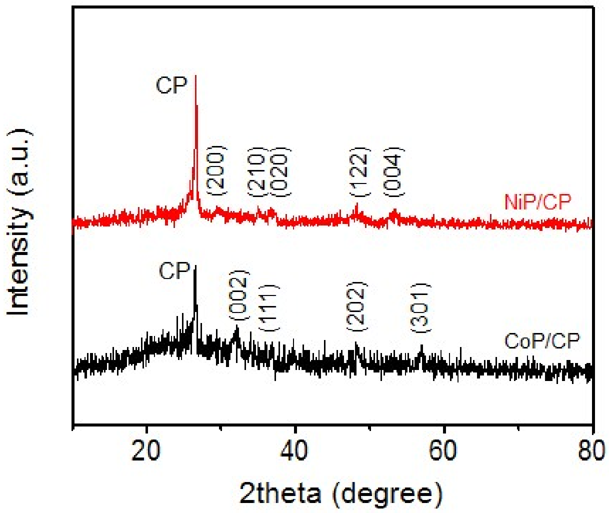

Fig. S2. XRD patterns of control samples (CoP/CP and NiP/CP).

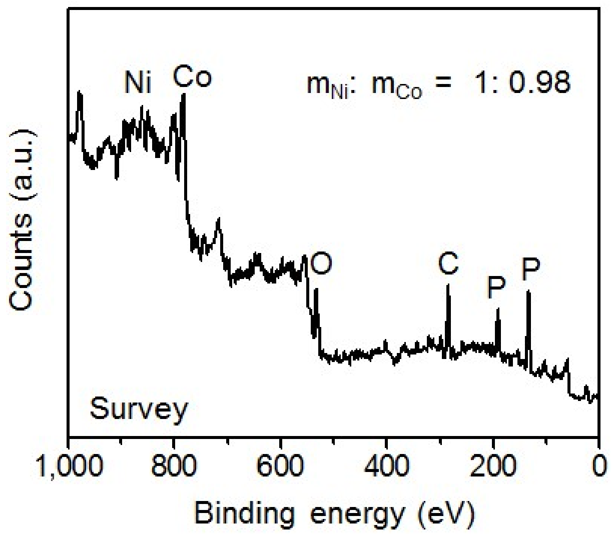

Fig. S3. Survey XPS spectrum of $Ni_{0.5}Co_{0.5}P$/CP. The molar ratio of Ni and Co elements is 1:0.98, consistent well with the initial molar ratio of Ni and Co source materials.

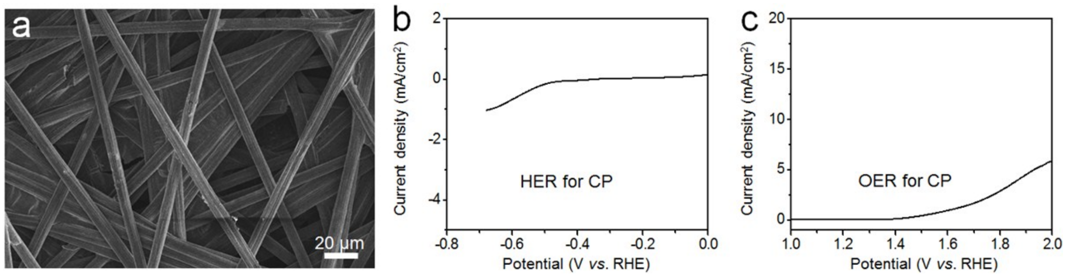

Fig. S4. (a) SEM image of pristine CP. (b) HER and (c) OER performances of pristine CP in 1.0 M KOH solution.

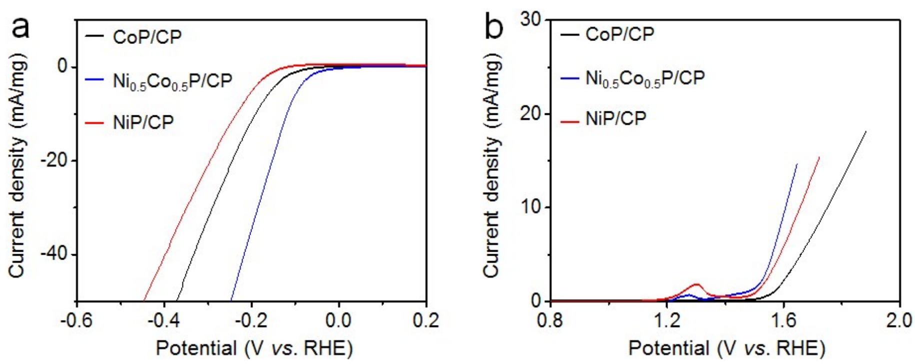

Fig. S5. LSV polarization curves of CoP/CP, $Ni_{0.5}Co_{0.5}P$/CP and NiP/CP catalysts for (a) HER and (b) OER processes.

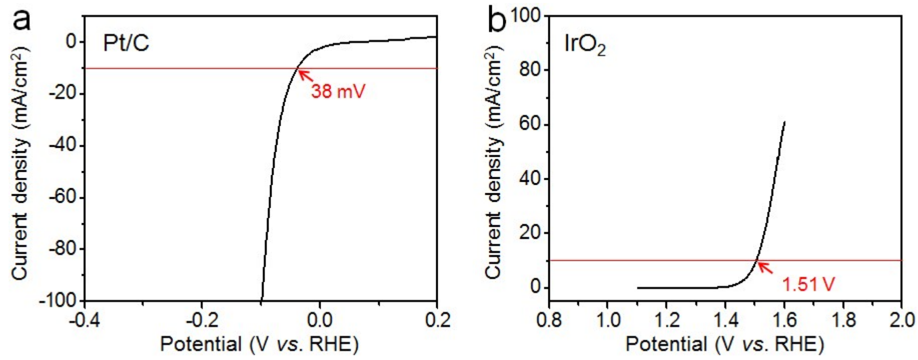

Fig. S6. LSV polarization curves of (a) Pt/C for HER and (b) IrO_2 for OER processes.

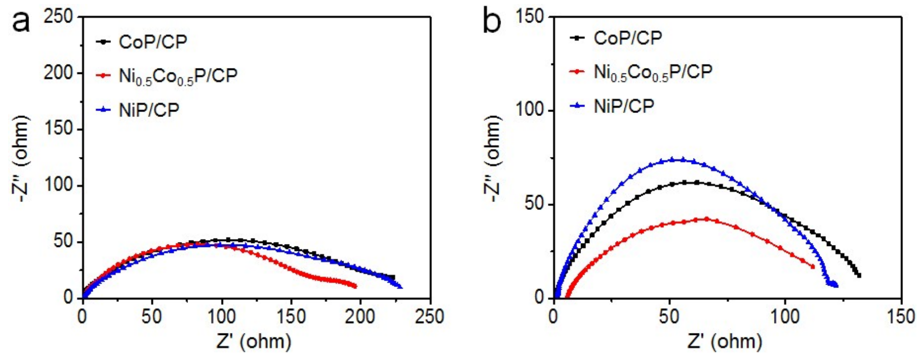

Fig. S7. Electrochemical impedance spectroscopy (EIS) spectra of CoP/CP, $Ni_{0.5}Co_{0.5}P$/CP and NiP/CP electrocatalysts for (a) HER and (b) OER processes.

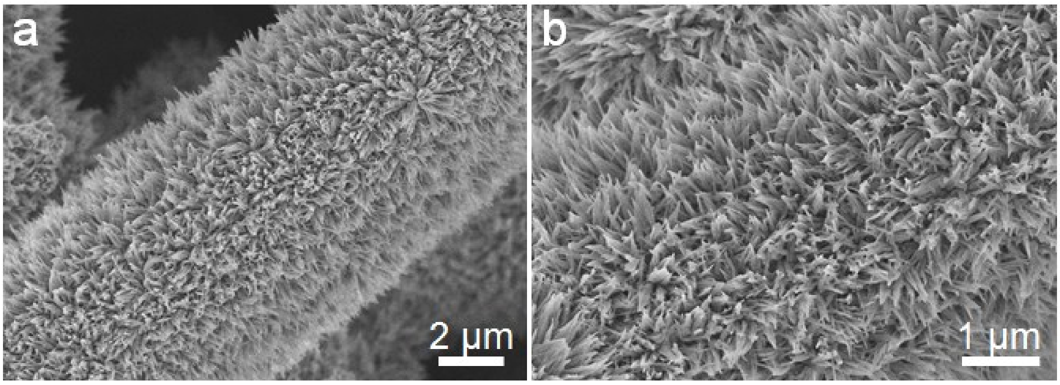

Fig. S8. (a, b) SEM images of $Ni_{0.5}Co_{0.5}P$/CP electrode after long-duration overall water splitting. The $Ni_{0.5}Co_{0.5}P$/CP well retains its initial morphology and nanostructure, suggesting the high structural integrity.

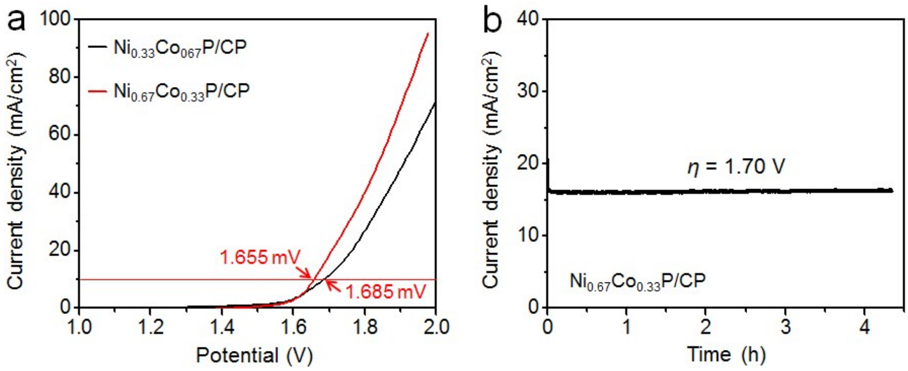

Fig. S9. (a) LSV polarization curves of the overall water splitting system based on $Ni_{0.33}Co_{0.67}P$/CP and $Ni_{0.67}Co_{0.33}P$/CP control samples with $Ni_xCo_{1-x}P$/CP||$Ni_xCo_{1-x}P$/CP symmetric electrode configuration. (b) Time-dependent current density of $Ni_{0.67}Co_{0.33}P$/CP||$Ni_{0.67}Co_{0.33}P$/CP electrolyzer in 1.0 M KOH solution.

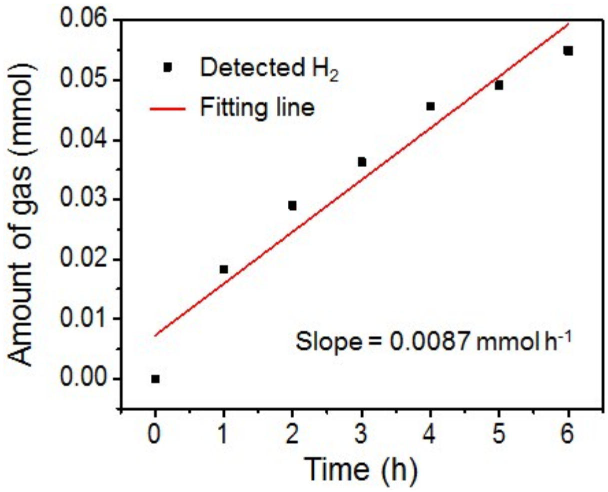

Fig. S10. The amount of generated H_2 during the long-term overall water splitting process of $Ni_{0.5}Co_{0.5}P/CP||Ni_{0.5}Co_{0.5}P/CP$ electrolyzer driven by all-inorganic PSCs.

The overall energy conversion efficiency was calculated as follows:

$$\eta_{overall} = E_{H2}/E_{light}$$

where E_{H2} represents the energy of generated H_2 driven by all-inorganic PSCs, E_{light} stands for the total energy of simulated sunlight. The $\eta_{overall}$ also can be calculated below:

$$\eta_{overall} = UQ*F_{electric\text{-}to\text{-}H2}/P_{sunlight}St = UIt*F_{electric\text{-}to\text{-}H2}/P_{sunlight}St$$

During the tests, after running 6 h, the detected working voltage is about 2.21 V and the Q is about 27.93 C. $P_{sunlight}$ is 100 mW cm^{-2}, S is the total active area of all-inorganic PSCs for absorbing sunlight (2 × 0.18 cm^{-2}).

According to Fig. S10, the mole number of generated H_2 (n) after 6 h is about 0.0549 mmol. Thus, the $\eta_{overall}$ can be obtained:

$$\eta_{overall} = UQ\times (2 \times 6.02*10^{23} \times 54.9*10^{-6} \times 1.66*10^{-19}/Q)/P_{sunlight}St$$

Therefore, the $\eta_{overall}$ can be calculated to be 3.12%.