Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Ultrafine Co_3O_4 Nanoparticles-Engineered Binary Metal Nitride Nanorods with Interfacial Charge Redistribution for Enhanced Water Splitting

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Synthesis of Co-Zn-(OH-CO_3)

Co-Zn-(OH-CO_3) nanorod arrays were grown on the surface of NF substrate by a hydrothermal method. Typically, the pre-treated NF was dipped in 50 mL solution containing 0.08 M $Co(NO_3)_2.6H_2O$, 0.04 M $Zn(NO_3)_2.6H_2O$, 0.16 M urea, and 0.13 M NH_4F in 100 mL of Teflon-lined stainless-steel autoclave, followed by sealing and heating at 95 °C with heating rate of 2 °C min^{-1} for 12 h. After the hydrothermal reaction was finished, the Co-Zn-(OH-CO_3) sample was rinsed with ethanol and DI water 3 times each, and dried at 60 °C for 1 day in air.

Synthesis of Co-Zn oxide sample

The precursor Co-Zn-(OH-CO_3) was annealed in air at 500 °C for 3 h to convert into Co-Zn oxide sample, as one of the counterparts of the Co_3O_4 NPs/Co-Zn nitride.

Synthesis of Pt/C- and RuO_2-based electrodes

Catalyst ink was prepared by dissolving 2.1 mg of Pt/C or RuO_2 in the mixed solution of 100 μL of DI water, 400 μL of ethanol, 30 μL of Nafion with the association of sonication for 0.5 h. Next, the as-fabricated catalyst ink was coated on nickel foam (1 cm × 1 cm) and then dried at 60 ^{o}C for 24 h.

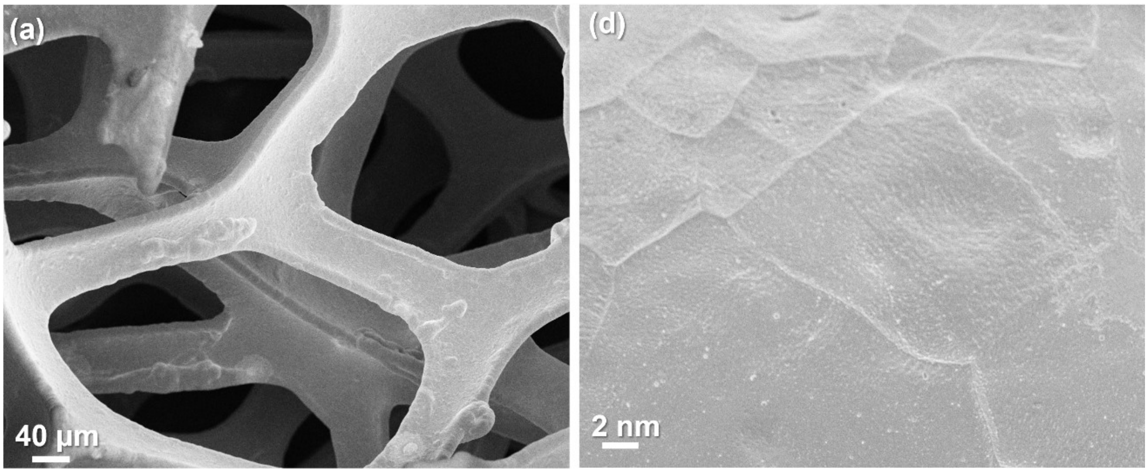

Figure S1. SEM images of nickel foam at different magnifications.

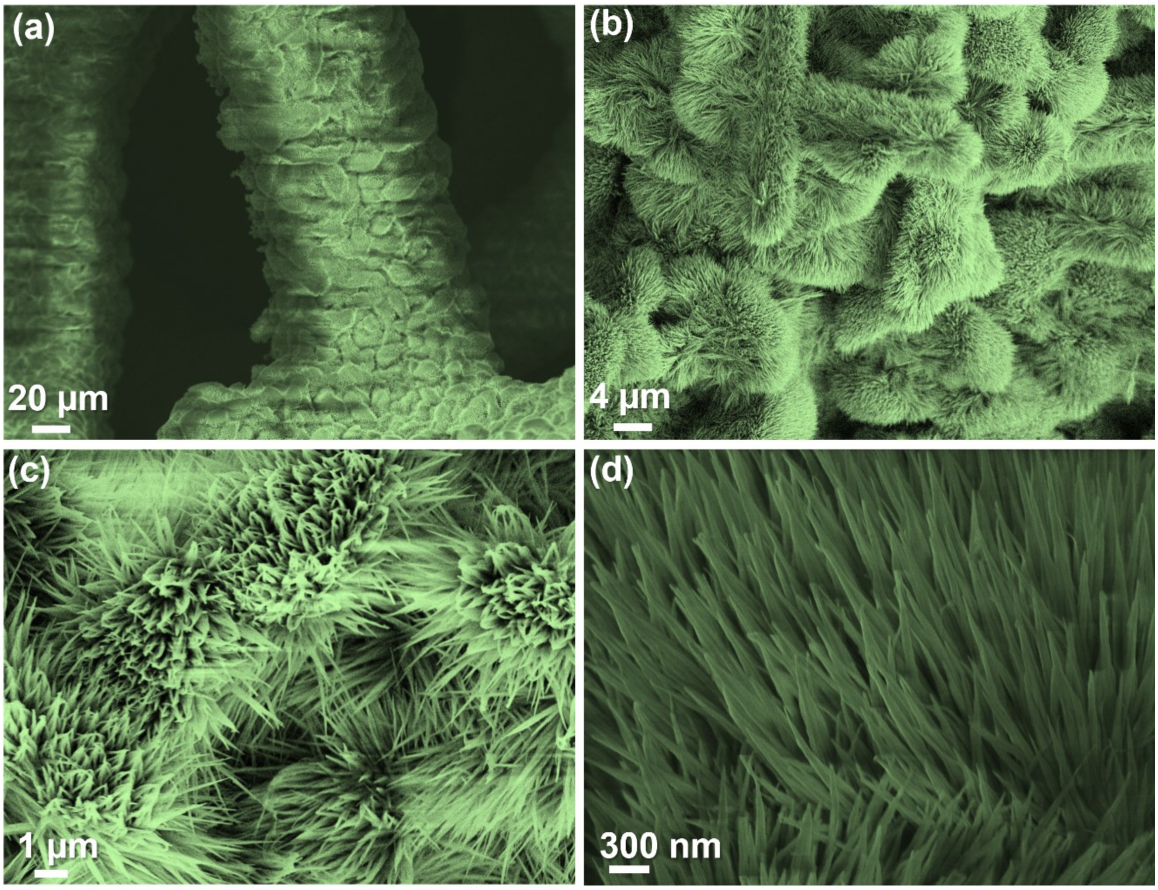

Figure S2. SEM images of Co-Zn-(OH-CO_3) at different magnifications.

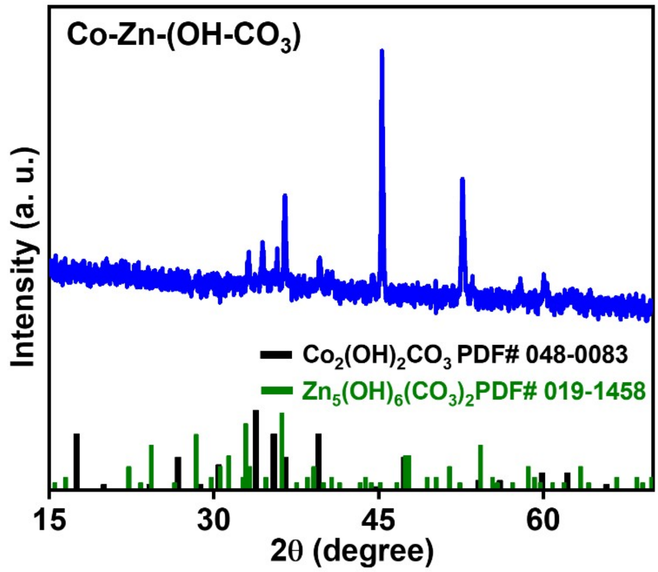

Figure S3. XRD pattern of Co-Zn-(OH-CO_3).

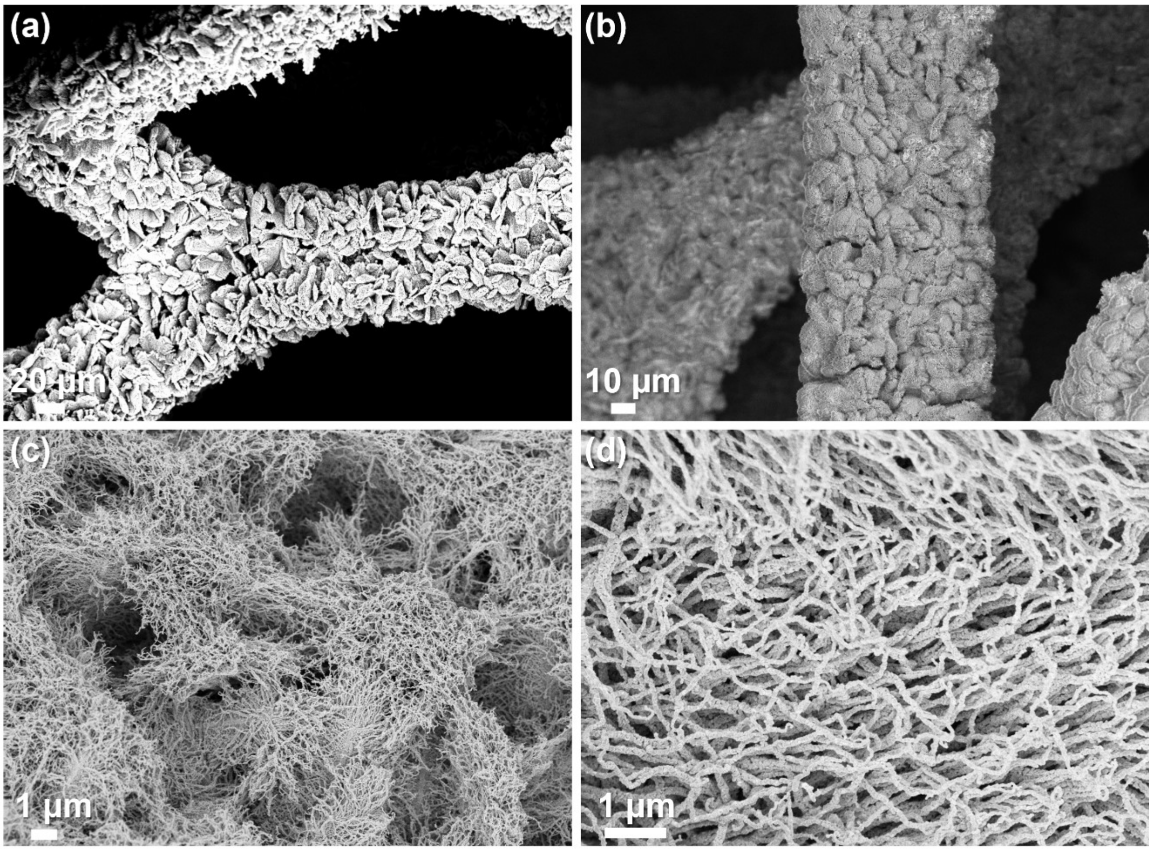

Figure S4. SEM images of Co-Zn nitride at different magnifications.

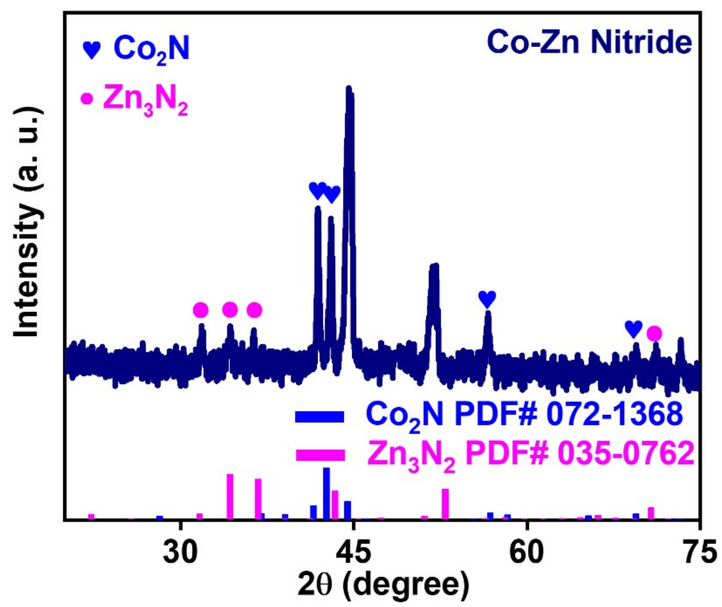

Figure S5. XRD pattern of Co-Zn nitride.

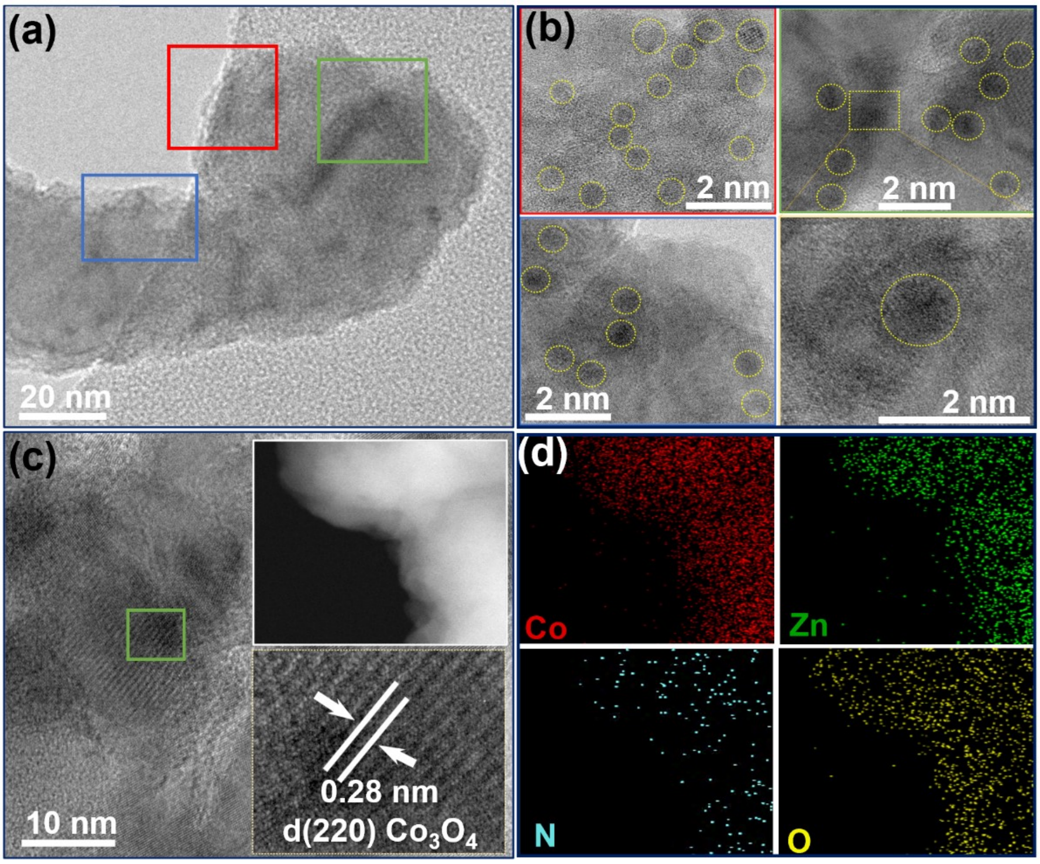

Figure S6. (a) TEM image, (b) and (c) HR-TEM images (the inset of (c) is d(220) crystalline plane of a Co_3O_4 nanocrystal on the Co_3O_4 NPs/Co-Zn nitride (below) and scanning TEM of Co_3O_4 NPs/Co-Zn nitride (up)), and (d) EDS mapping images of the Co_3O_4 NPs/Co-Zn nitride.

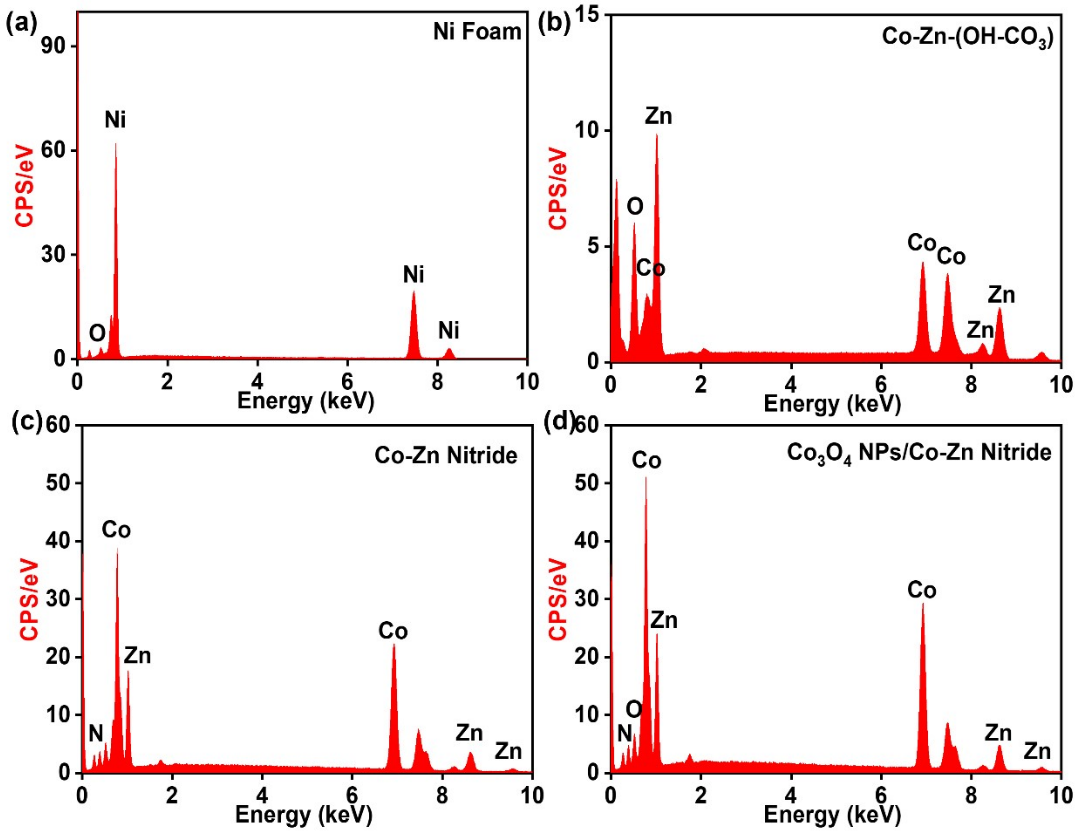

Figure S7. EDS spectra of (a) nickel foam, (b) Co-Zn-(OH-CO_3), (c) Co-Zn nitride, and (d) Co_3O_4 NPs/Co-Zn nitride.

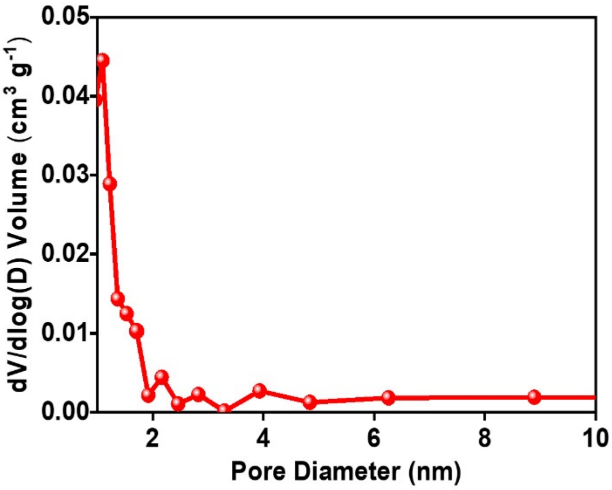

Figure S8. Pore size distribution of the Co_3O_4 NPs/Co-Zn nitride.

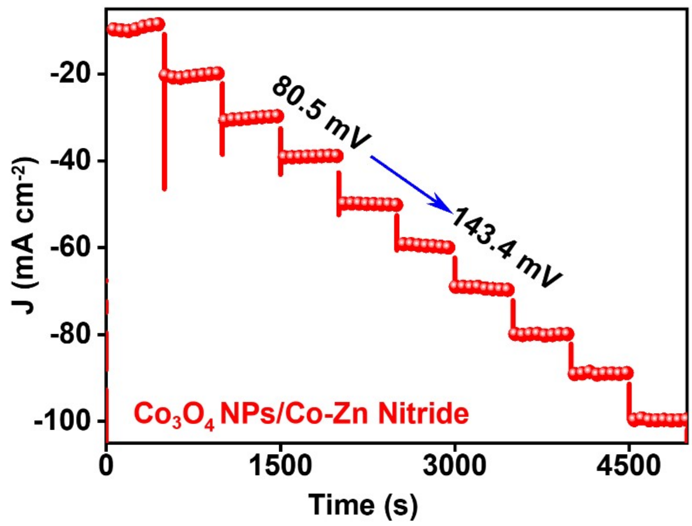

Figure S9. Multi-step chronoamperometric curve of the Co_3O_4 NPs/Co-Zn nitride under HER conditions.

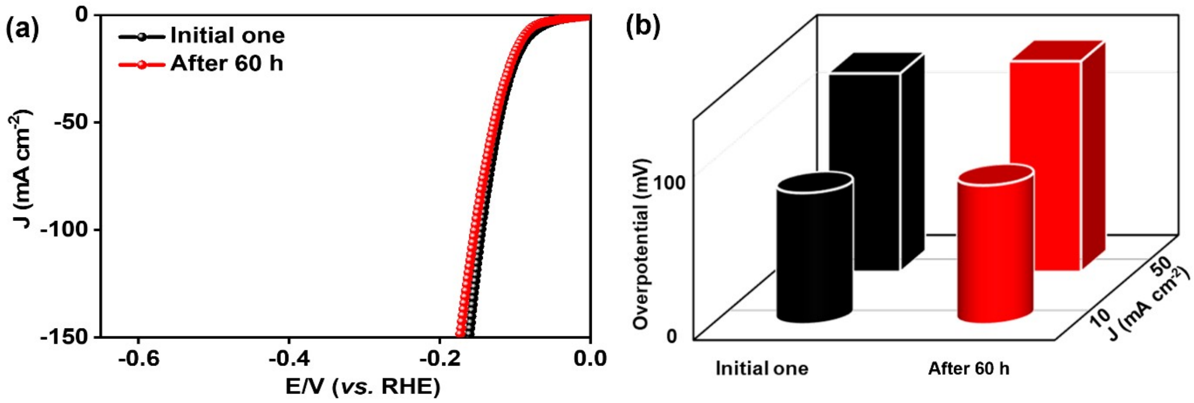

Figure S10. (a) LSV curves and (b) overpotentials at 10 and 50 mA cm^{-2} of the Co_3O_4 NPs/Co-Zn nitride determined before and after HER stability testing.

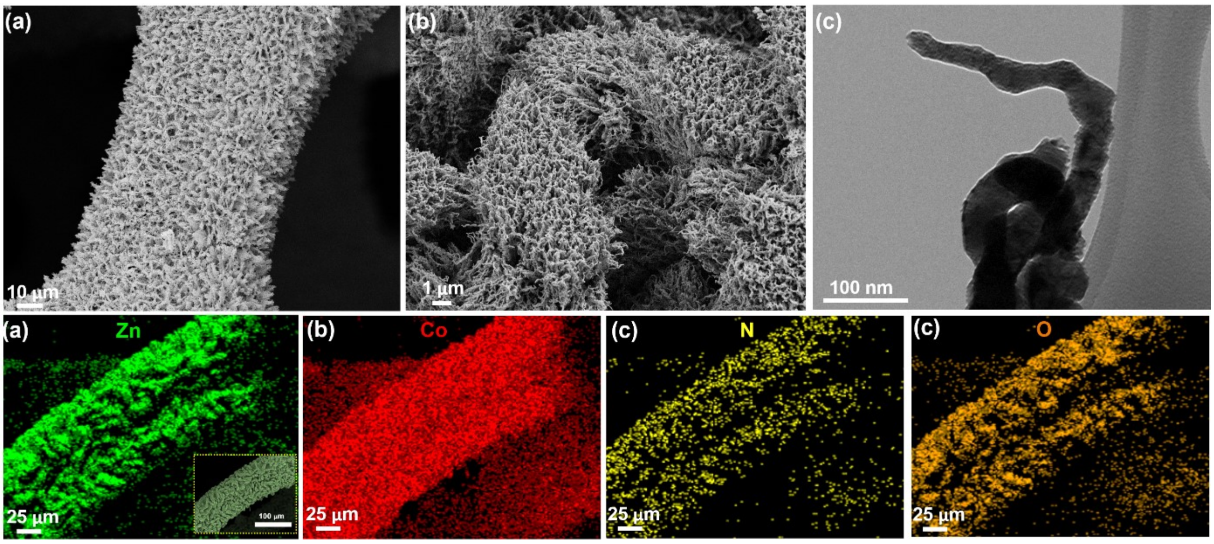

Figure S11. (a) and (b) SEM images, (c) TEM image, (d)-(g) EDS mapping images of the post-HER Co_3O_4 NPs/Co-Zn nitride.

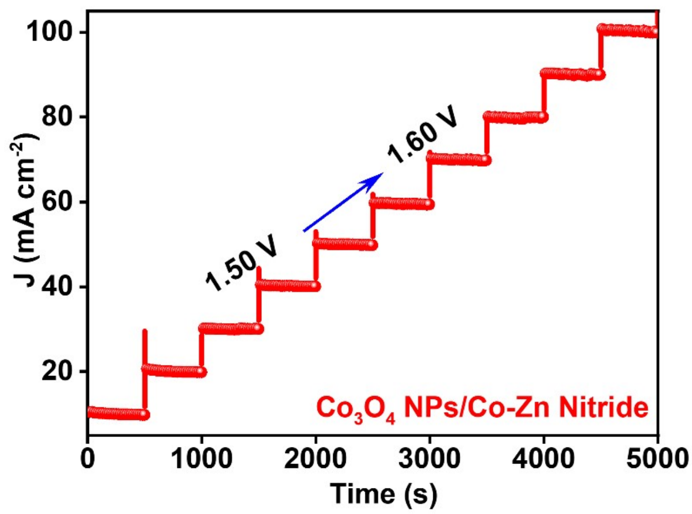

Figure S12. Multi-step chronoamperometric curve of the Co_3O_4 NPs/Co-Zn nitride under OER conditions.

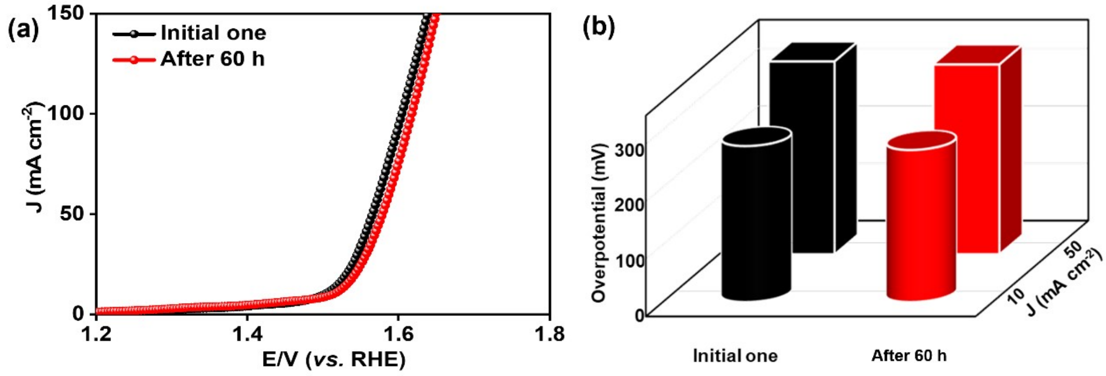

Figure S13. (a) LSV curves and (b) overpotentials at 10 and 50 mA cm^{-2} of the Co_3O_4 NPs/Co-Zn nitride determined before and after OER stability testing.

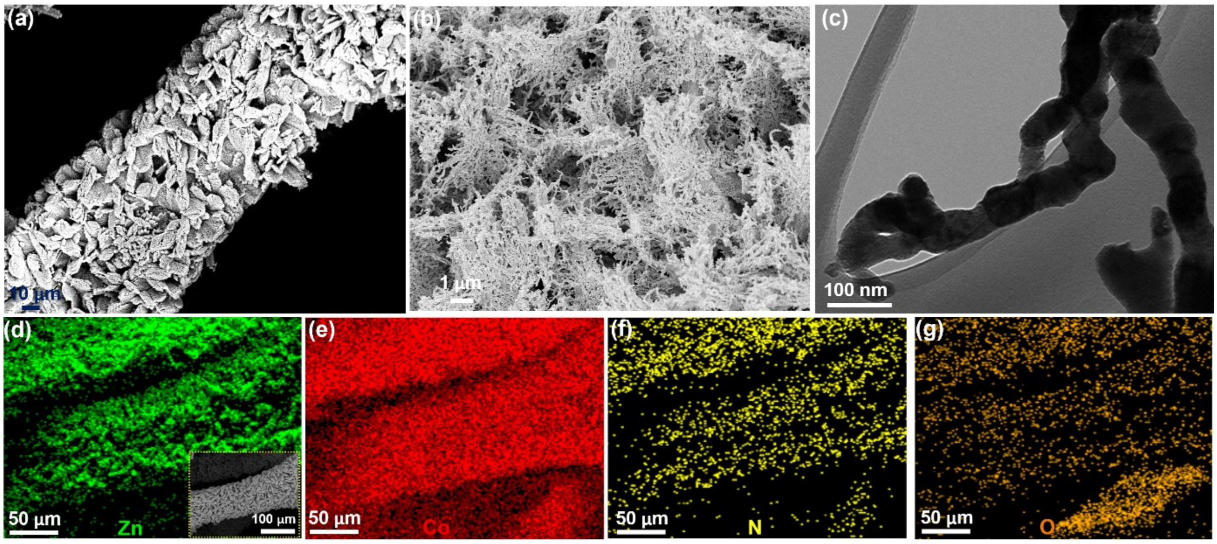

Figure S14. (a) and (b) SEM images, (c) TEM image, (d)-(g) EDS mapping images of the post-OER Co_3O_4 NPs/Co-Zn nitride.

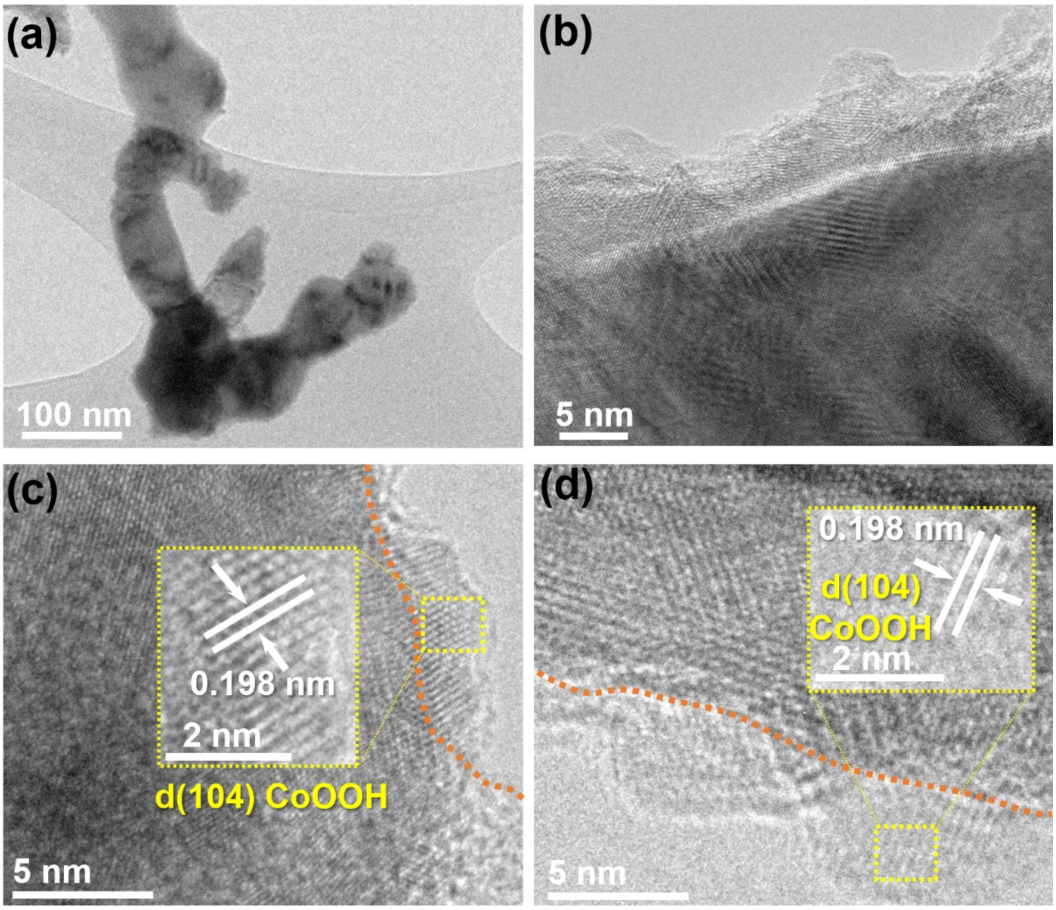

Figure S15. (a) and (b) Magnified TEM images, and (c) and (d) HR-TEM images of the post-OER Co_3O_4 NPs/Co-Zn nitride.

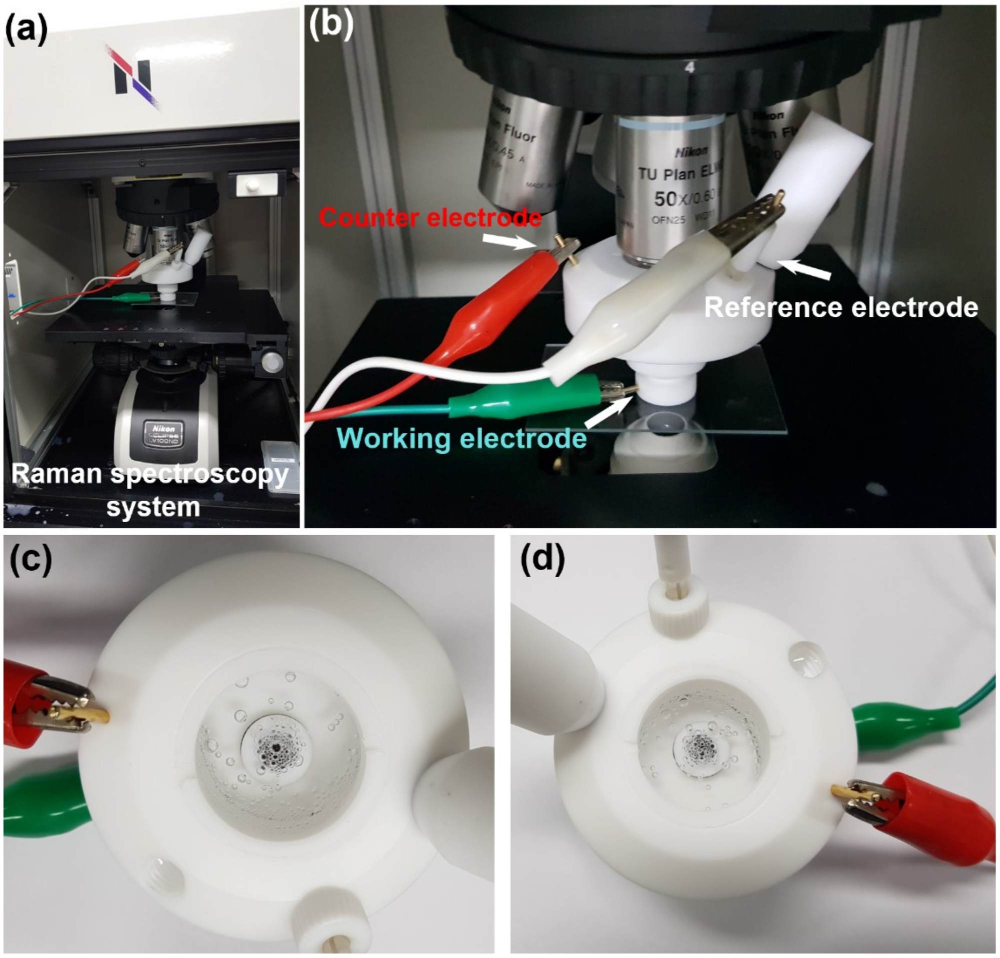

Figure S16. (a) and (b) The photographs of the Raman spectroscopy system. The photographs of Co_3O_4 NPs/Co-Zn nitride sample during *in situ* Raman analysis under (c) HER conditions and (d) OER conditions.

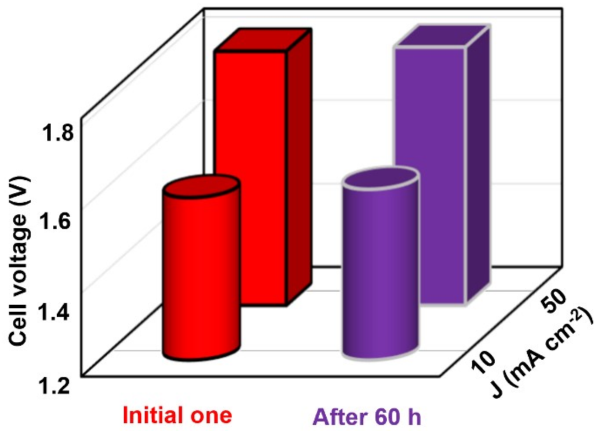

Figure S17. Cell voltages at 10 and 50 mA cm^{-2} of the Co_3O_4 NPs/Co-Zn nitride (-, +) determined before and after stability testing under overall water-splitting.

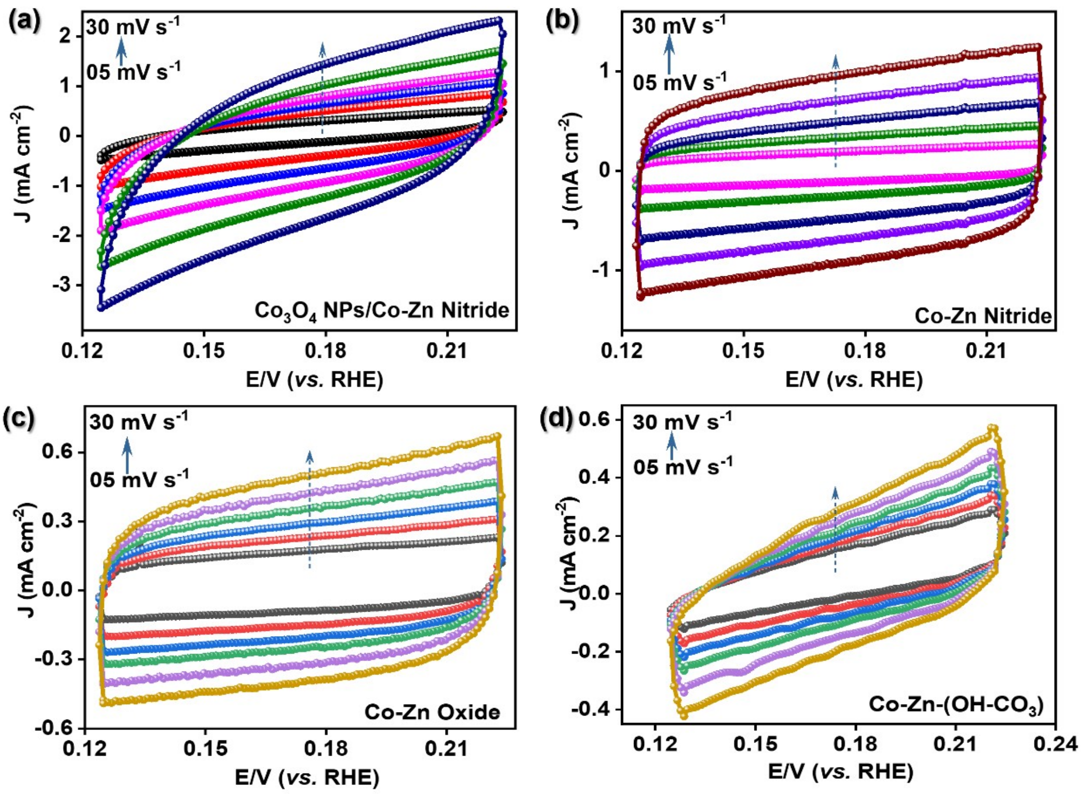

Figure S18. CV curves at different scan rates of (a) the Co_3O_4 NPs/Co-Zn nitride, (b) Co-Zn nitride, (c) Co-Zn oxide, and (d) Co-Zn-(OH-CO_3).

Table S1. The Co percentage in the Co-Zn nitride and Co_3O_4 NPs/Co-Zn nitride samples by XPS analysis

Samples	**Co percentage (at %)**
Co-Zn nitride	23.43
Co_3O_4 NPs/Co-Zn nitride	37.51
Co percentage of Co_3O_4 NPs: 14.08 at %	

Table S2. HER overpotential of the Co_3O_4 NPs/Co-Zn nitride at current density of 10 mA cm^{-2} compared to those of other noble-metal-free HER electrocatalysts.

Catalysts	Overpotential (10 mA cm^{-2})	References
NiCoP/CNF	130	Adv. Energy Mater. 2018, 8, 20, 1800555.
Ni/Mo_2C- NCNFs	143.0	Adv. Energy Mater. 2019, 9, 1803185
CoP/TiO_x	337	Small, 2020, 16, 2, 1905075.
MoP/NPG	126	Appl. Catal., B: Environ, 2020, 260, 118196.
1D-DRHA MoS_2	119.0	Appl. Catal. B, 2019, 258, 117964
FeCo/Co_2P@NPCF	260	Adv. Energy Mater. 2020, 10, 10, 1903854
MoS_2–Ni_3S_2 HNRs/NF	98.0	ACS Catal. 2017, 7, 4, 2357–2366
Co-P/FTO	254	Angew. Chem. Int. Ed. 2020,59, 39, 17172-17176.
MoS_x@NiO	406.0	Adv. Funct. Mater. 2019, 29, 1807562
CoP@FeCoP/NC YSMPs	141	Chem. Eng. J. 2021, 403, 126312.
$SrRuO_3$/CNT	109.0	ACS Appl. Energy Mater. 2019, 2, 956−960
Co_3O_4 NPs/Co-Zn nitride	**80.5**	**This work**

Table S3. OER overpotential of Co_3O_4 NPs/Co-Zn nitride at current density of 10 mA cm^{-2} compared to those of other noble-metal-free OER electrocatalysts.

Catalysts	Overpotential at 10 mA cm^{-2}	References
CoS_x@Cu_2MoS_4-MoS_2/NSG	351.4	Adv. Energy Mater. 2020, 10, 8, 1903289.
Co_2P/CoNPC	328	Adv. Funct. Mater, 2020, 32, 36, 2003649.
$Co_{1.5}Fe_{0.5}P$	278	Angew. Chem. Int. Ed. 2020, 59, 1, 465-470.
MoS_x@NiO	406.0	Adv. Funct. Mater. 2019, 29, 1807562
D-CoP-HoMSs	294	Angew. Chem. Int. Ed., 2021, 133, 13, 7002-7007
CoP (MoP)-$CoMoO_3$/CN	296	ACS Appl. Mater. Interfaces. 2019, 11, 7, 6890-6899.
D-CoP-HoMSs	294	Angew. Chem. Int. Ed., 2021, 133, 13, 7002-7007
O-CoP–2	310	Adv. Funct. Mater, 2020, 30, 7, 1905252.
Ni-CoP	290	Nano Lett. 2021, 21, 1, 823–832
Mn-Co-P YS	330	Chem. Eng. J. 2021, 405, 126580.
Co_3O_4 NPs/Co-Zn nitride	**271.7**	**This work**