

Supporting Information for

Exfoliation of Metal–Organic Frameworks into Efficient Single-Layer Metal–Organic Nanosheet Electrocatalysts by Synergistic Action of Host-Guest Interactions and Sonication

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Experiment Section

Materials and general methods. Powder X-ray diffraction (PXRD) patterns were measured using a Rigaku D/max 2500v diffractometer. Scanning electron microscopy (SEM) images were obtained by FEI Quanta 200 apparatus working at an acceleration voltage of 5/10 kV. Transmission electron microscopy (TEM) images were recorded on a FEI Talos 200S instrument with STEM aberration corrector. Atomic Force Microscopy (AFM) images were obtained by a Bruker Dimension icon device. Raman spectra were obtained by a Renishaw inVia instrument in the 400–4000 cm^{-1} region.

Synthesis of $[\text{Zn}_2(\text{bdc})_2(\text{dabco})]\cdot 4\text{DMF}\cdot 0.5\text{H}_2\text{O}$ (**3D-Zn**) microcrystals. A mixture of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (500 mg, 1.72 mmol), H_2bdc (280 mg, 1.68 mmol) and dabco (93.7 mg, 0.84 mmol) was dissolved in 20 mL of DMF. Then the mixture was transferred to 50-mL Teflon reactor and stirred at 120 °C for 48 hours. Afterwards, the white powder of **3D-Zn** were separated by centrifugation and washed by DMF (20 mL) thrice, and dried in the vacuum at 80 °C for 24 hours (yield: 74%). Similarly, microcrystals of **3D-Co**, **3D-Ni** and **3D-CoNi** were obtained in a similar way to that described for **3D-Zn** except that $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ or a mixture of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (1.72 mmol, $n/n = 1:1$) was used in place of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, respectively.

Synthesis of $[\text{Zn}_2(\text{bdc})_2(\text{H}_2\text{O})]\cdot \text{guset}$ (**2D-Zn**) microcrystals. The sample of **3D-Zn** was exposed in air for three days, washed with DMF thrice, and dried in the air. Similarly, **2D-Co**, **2D-Ni**, or **2D-CoNi** could be prepared when **3D-Zn** was replaced by **3D-Co**, **3D-Ni**, or **3D-CoNi**, respectively.

Preparation of **2D-Zn-few-layer**. The sample of **3D-Zn** (141 mg, 0.2 mmol) was immersed in H_2O for 30 min at room temperature. Afterwards, the sample was sonicated for 30 min. Then, the

white powder of **2D-Zn-few-layer** were separated by centrifugation and washed by 20 mL H₂O thrice, and dried in air at room temperature (yield: 94%). Similarly, **2D-Co-few-layer**, **2D-Ni-few-layer**, or **2D-CoNi-few-layer** could be prepared when **3D-Zn** was replaced by **3D-Co**, **3D-Ni**, or **3D-CoNi**, respectively.

Preparation of **2D-Zn-single-layer**. The sample of **3D-Zn** (141 mg, 0.2 mmol) was ultraphonic in 50 mL H₂O for 30 min at room temperature. Afterwards, the sample was ultraphonic for 30 min. Then, the white powder of **2D-Zn-single-layer** were separated by centrifugation and washed by 20 mL H₂O thrice, and dried in air at room temperature (yield: 92%). Similarly, **2D-Co-single-layer**, **2D-Ni-single-layer**, or **2D-CoNi-single-layer** could be prepared when **3D-Zn** was replaced by **3D-Co**, **3D-Ni**, or **3D-CoNi**, respectively.

Electrochemical Measurements. Carbon cloth (CC, surface areas = 0.5 cm²) was used as the substrate of working electrode. The common preparation method for CC working electrode is as follows: 4 mg of as-synthesized samples were dispersed in 1 mL of mixed solvents of H₂O and EtOH (4:1, v/v), and then 80 μL of perfluorosulfonic acid-polytetrafluoroethylene copolymer (Nafion) solution (5 wt% in water) was added. The suspension was ultrasonic dispersion for 30 minutes yielding a homogeneous ink. The surface of CC was deposited with 34 μL catalyst ink (catalyst loading of 0.2 mg cm⁻²) and used as working electrode directly after air drying. Similarly, the CC working electrodes with reduced loading mass of **2D-CoNi-single-layer** was prepared through changing the mass of **2D-CoNi-single-layer** dispersed in the solvent without Nafion.

Before the electrochemical measurements, O₂ was bubbled into the electrolyte for 30 minutes at room temperature to prepare the O₂-saturated 0.2 M phosphate buffer solution (PB, pH = 7.0). All the electrochemical tests were performed in a three-electrode electrochemical system controlled by

electrochemical workstation (CHI 660E), using Ag/AgCl and Pt foil as reference electrode and counter electrode, respectively. Considering the solution resistance, all electrode potentials were adjusted to compensate for the Ohmic potential drop losses (R_u) and converted to the reversible hydrogen electrode (RHE) potentials as the following equation: $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.197 \text{ V} + 0.059\text{pH} - IR_u$ [Angew. Chem. Int. Ed. 2019, 58, 139], The IR ($I \times R$) compensation level is 100%, which was done by the method of positive feedback. Before the oxygen evolution reaction (OER) tests, the Cyclic Voltammetry (CV) was used for optimizing the work electrode by the potential cycling between 1.2 and 1.9 V at the sweep rates of 50 mV s^{-1} , and the process was maintained until the voltammogram curves being coincident. Then the linear sweep voltammetry (LSV) was performed at a sweep rate of 5 mV s^{-1} , and the voltage of Chronoamperometry is 1.8 V versus RHE.

Turnover frequency (TOF) calculateion. The TOF value was calculated from the following equation,

$$\begin{aligned} \text{TOF} &= (J \times A) / (4 \times F \times n) \\ &= J / (4 \times F \times m / M) \end{aligned}$$

J is the current density (mA cm^{-2}) at a given overpotential, A is the surface area of the electrode, F is the faraday constant (96485 C mol^{-1}), n is moles of cobalt deposited on the electrode per cm^2 , m is the mass loading of the catalyst (mg cm^{-2}), and M is the molecular weight of the catalyst unified with one active center per formula unit. In this work, all the metal ions in single-layer MOF nanosheets were assumed to exist on the reactive surface and function as the catalytic activity sites. This method has also been used in previous publications (*J. Am. Chem.Soc.* 2010, 132, 16501; *Angew. Chem. Int. Ed.* 2015, 127, 11383).

For example, 0.2 mg **2D-Co-single-layer** cm⁻² supported on CC was used as oxygen electrode, $m = 0.2 \text{ mg cm}^{-2}$, based on Co center, $M = 222.8 \text{ g mol}^{-1}$, $J = 7.14 \text{ mA cm}^{-2}$ at overpotential of 500 mV from LSV curve, $\text{TOF} = 7.14 / (4 \times 96485 \times 0.2 / 222.9) = 0.021 \text{ s}^{-1}$. Similarly, the TOF values for other samples were calculated by the same method, the data listed in Figure S28 and Table S1.

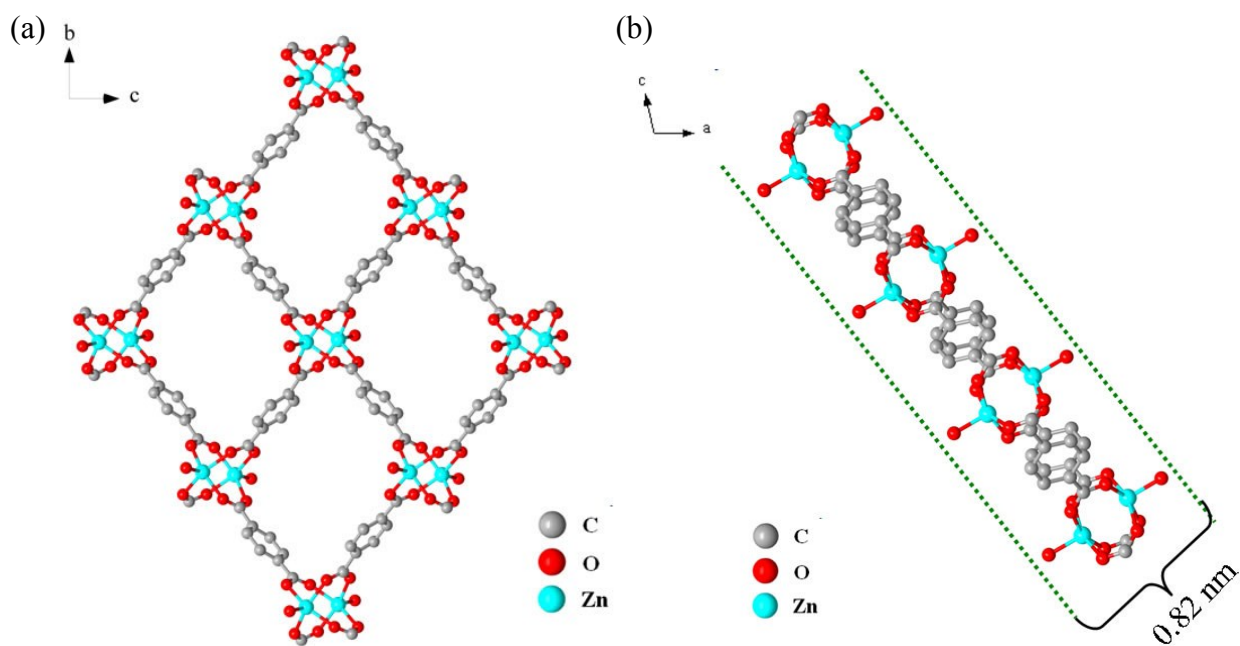


Figure S1. (a) 2D layered structure of **2D-Zn**. (b) The thickness of single coordination layer of **2D-Zn**. Hydrogen atoms, guest molecules are omitted for clarity.

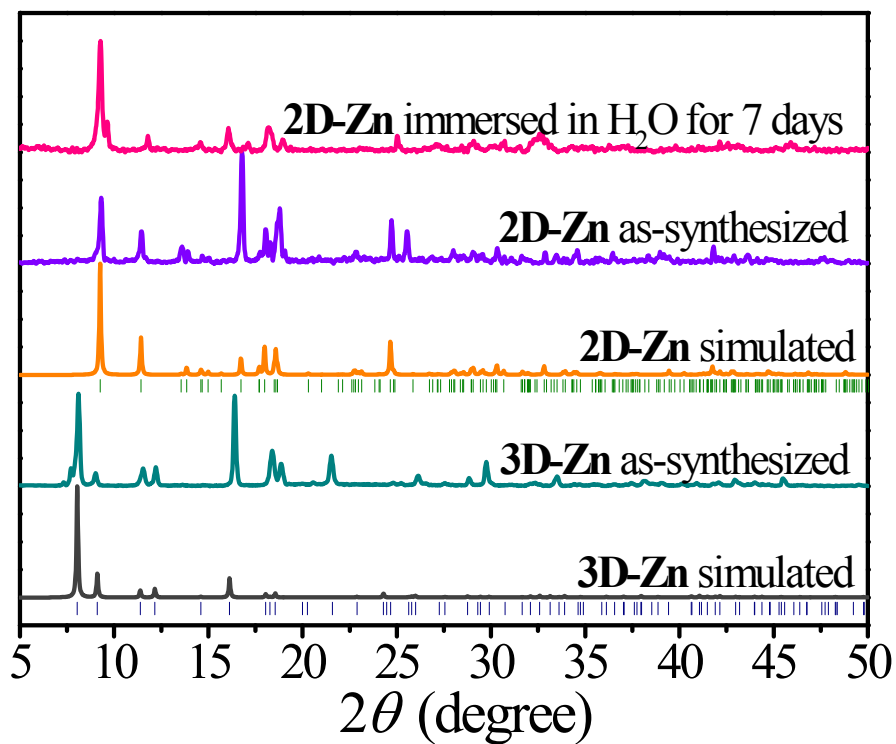


Figure S2. PXRD patterns of (a) 3D-Zn, (b) 2D-Zn before and after immersed in H₂O.

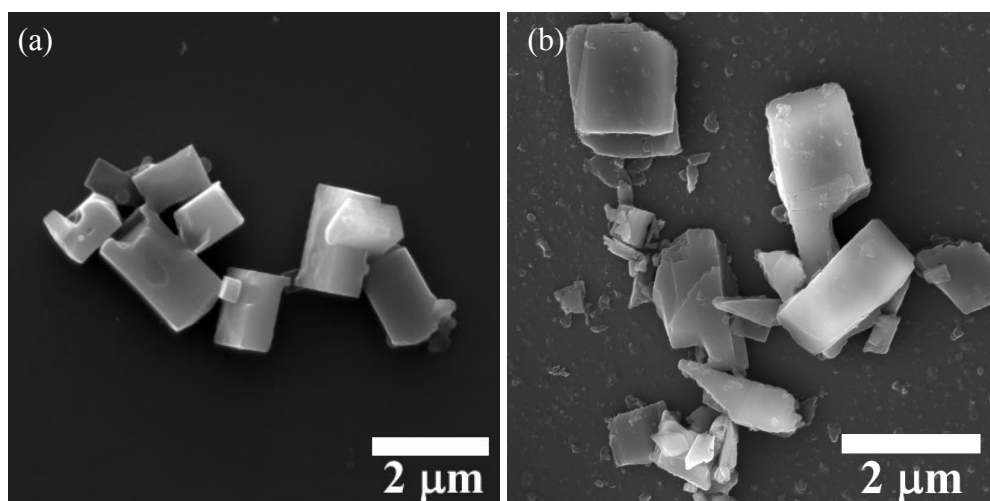


Figure S3. SEM images of (a) 3D-Zn and (b) 2D-Zn.

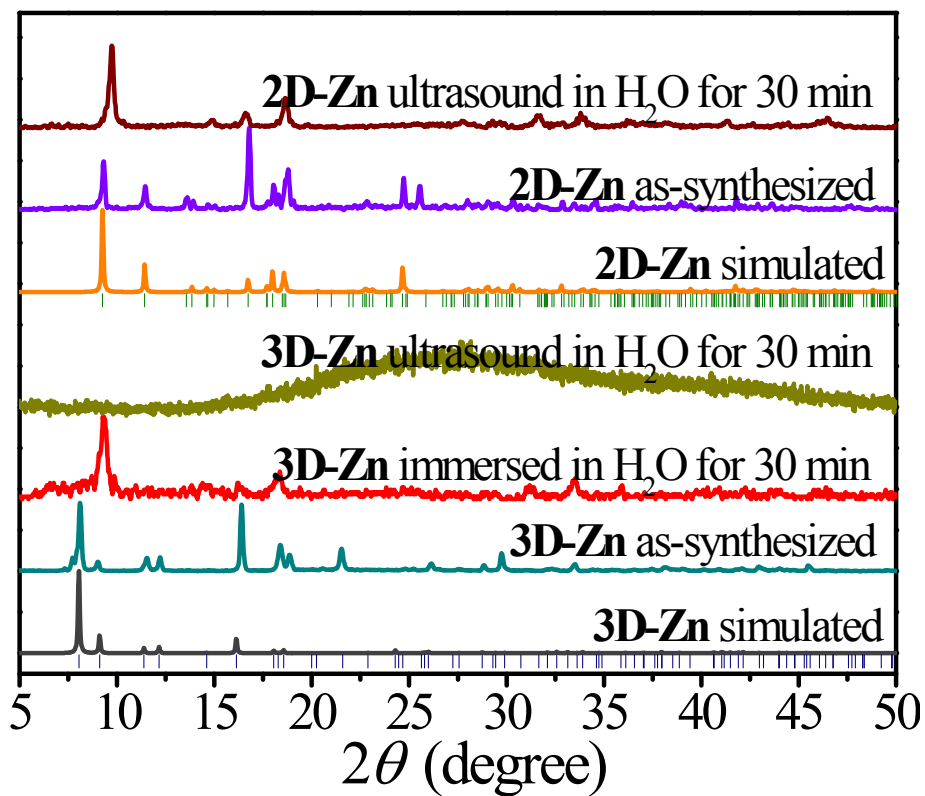


Figure S4. PXRD patterns of exfoliated 3D-Zn generated in different conditions.

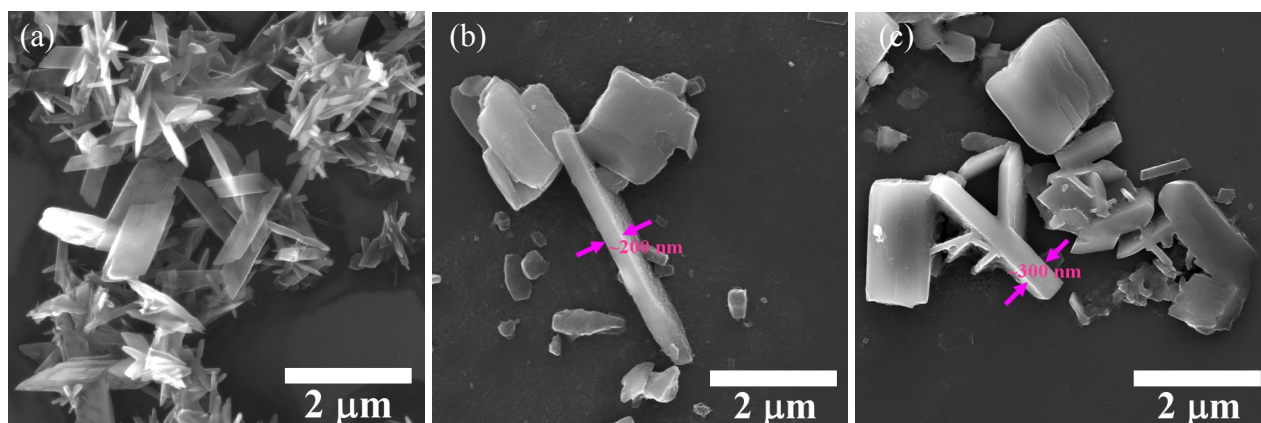


Figure S5. SEM images of 2D-Zn sonicated in different solvents (a) H₂O, (b) MeOH, and (c) EtOH for 30 min.

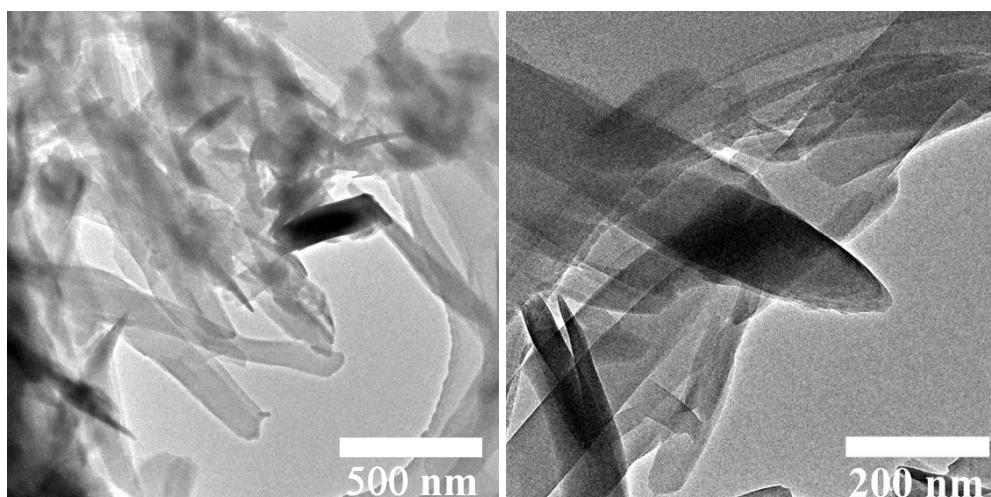


Figure S6. TEM images of 2D-Zn sonicated in H₂O.

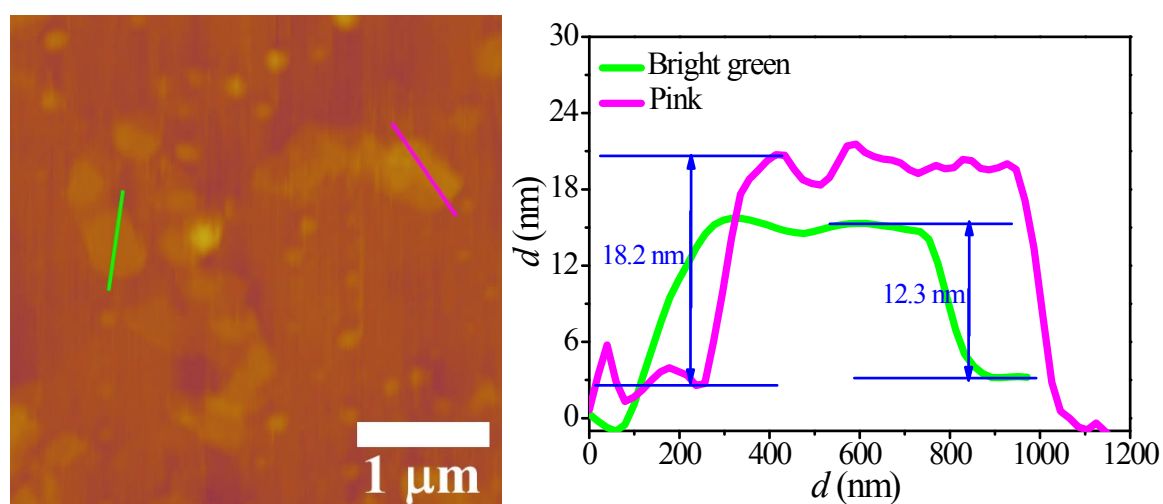


Figure S7. AFM image and the corresponding height profile of 2D-Zn sonicated in H₂O.

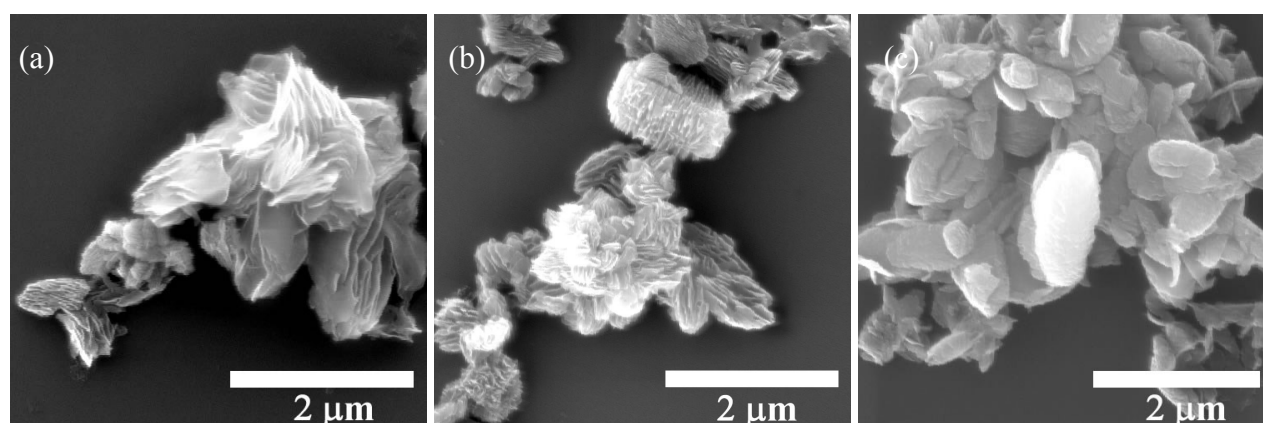


Figure S8. SEM images of 3D-Zn immersed in H₂O for different times (a) 0.5 hour, (b) 12 hours, and (c) 48 hours.

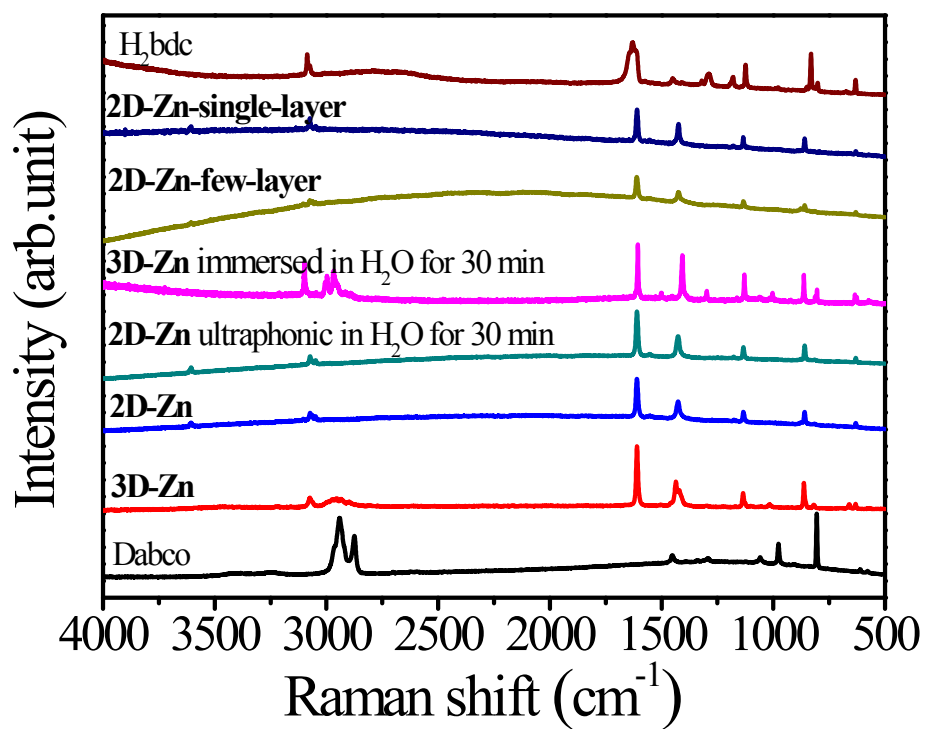


Figure S9. Raman spectra of H₂bdc, dabco, and exfoliated 3D-Zn and 2D-Zn created in different conditions, respectively.

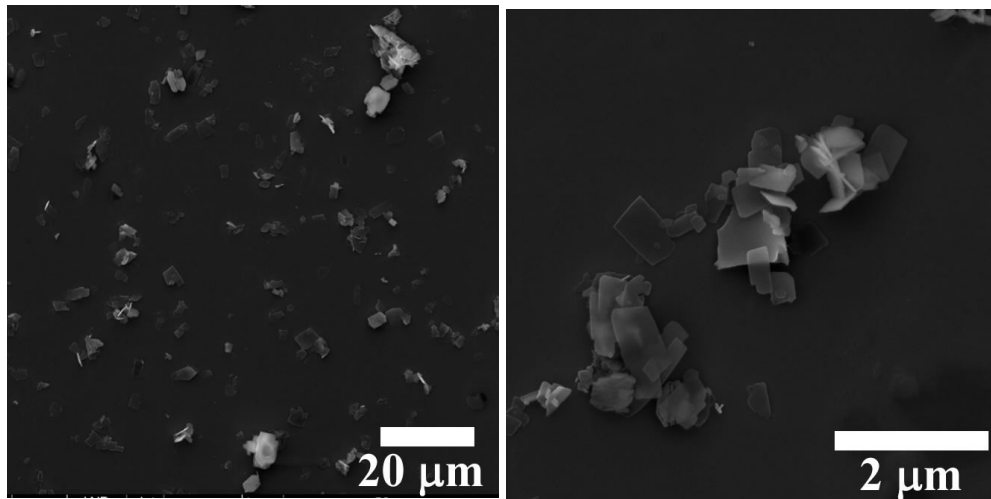


Figure S10. SEM images of 2D-Zn-few-layer.

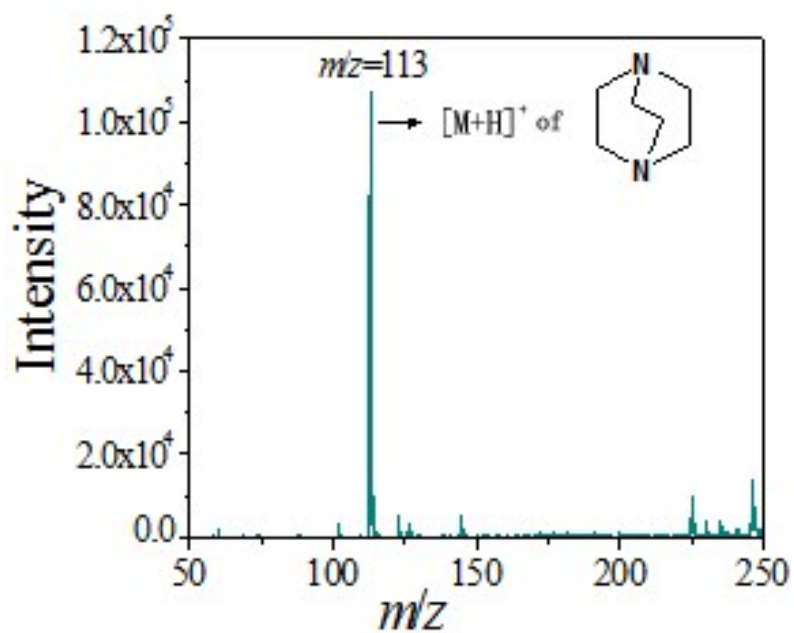


Figure S11. Mass spectrometry of the solution after immersing **3D-Zn** in H_2O for 30 min.

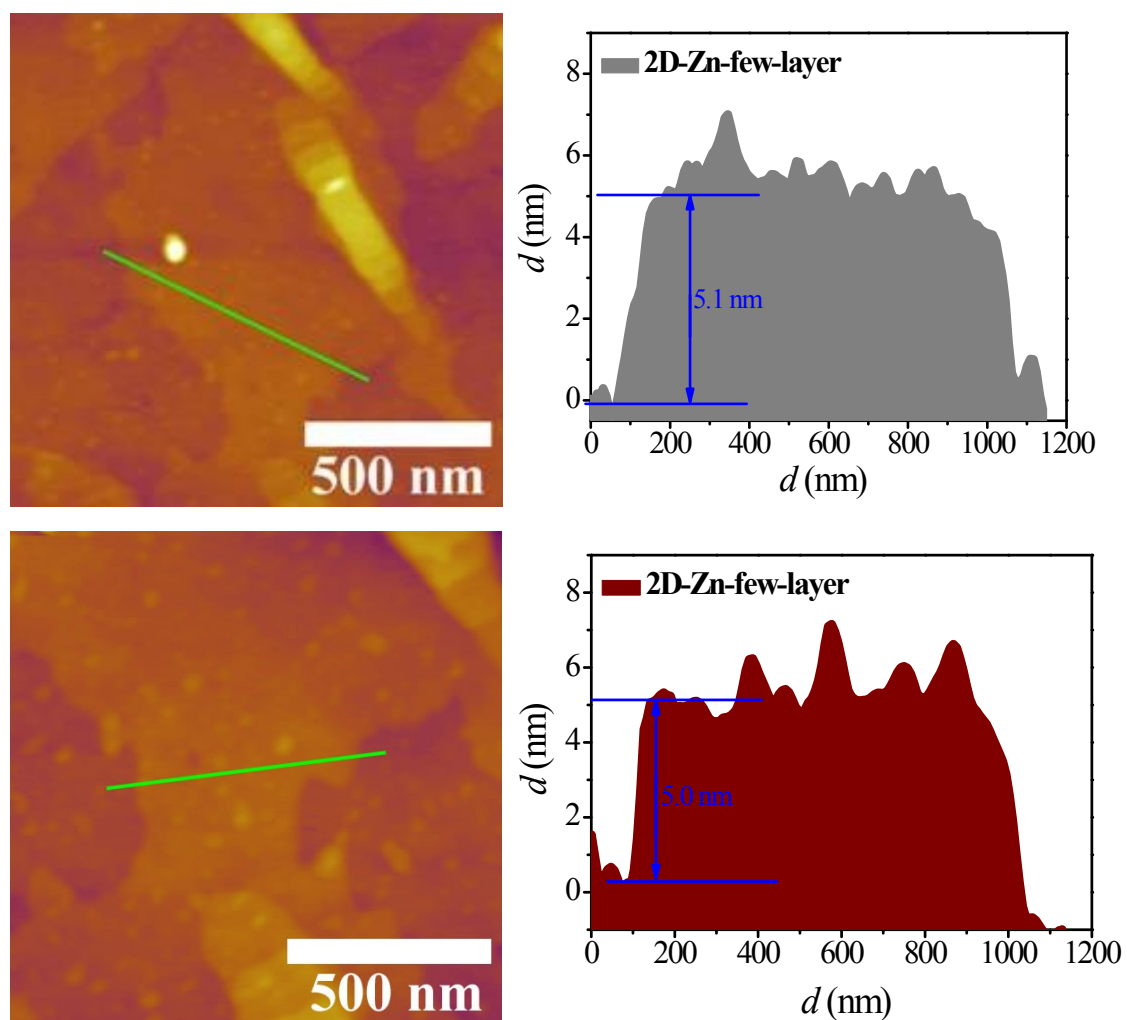


Figure S12. AFM images and the corresponding height profile of **2D-Zn-few-layer**.

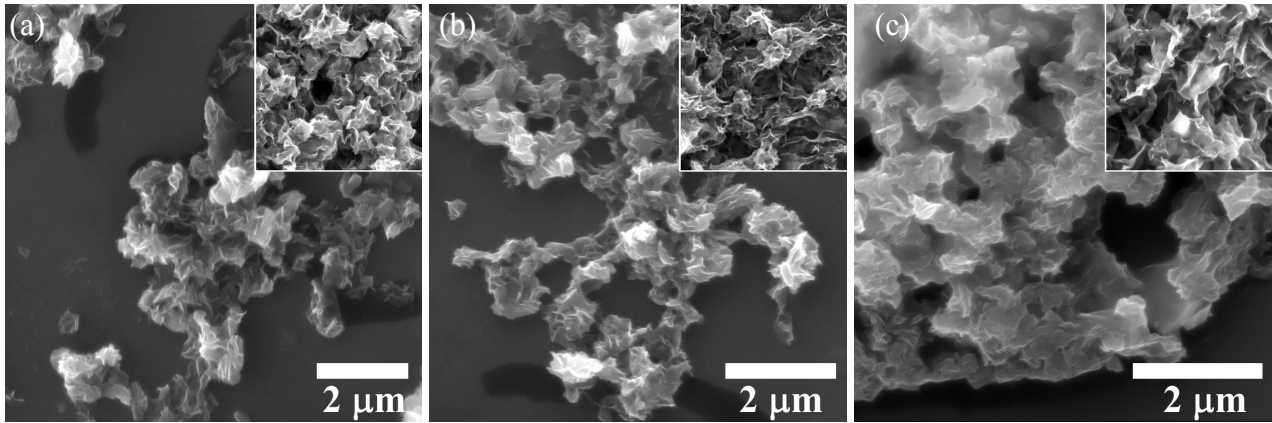


Figure S13. SEM images of **3D-Zn** after sonication in different solvents (a) H₂O, (b) MeOH, and (c) EtOH.

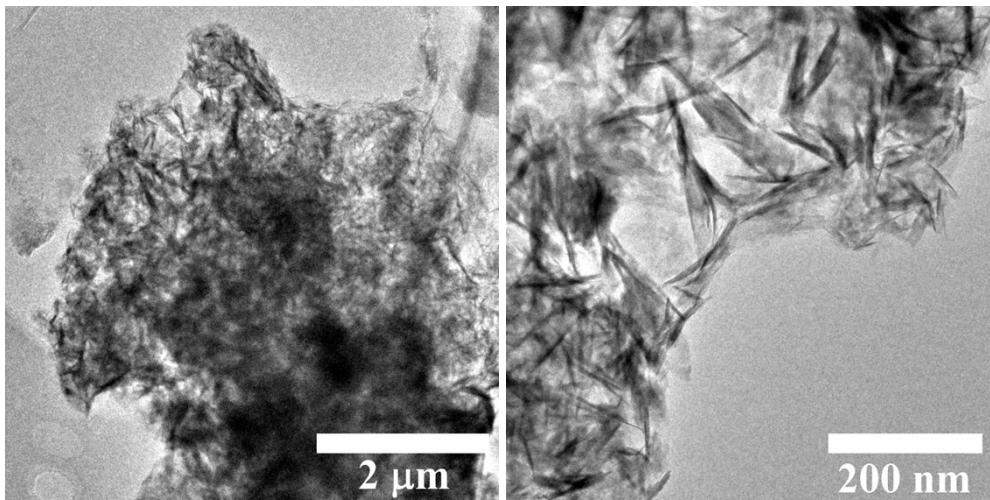


Figure S14. TEM images of **2D-Zn-single-layer**.

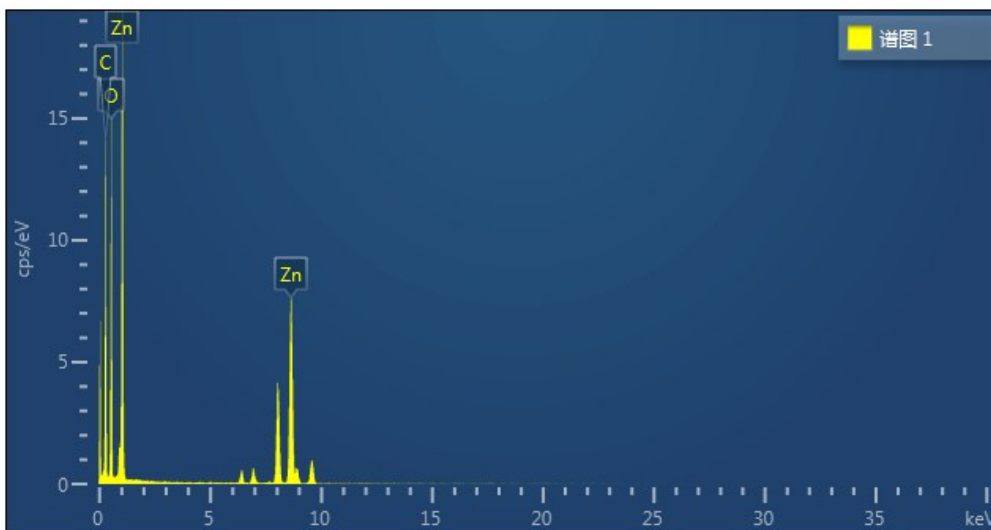


Figure S15. EDS spectrum of **2D-Zn-single-layer**.

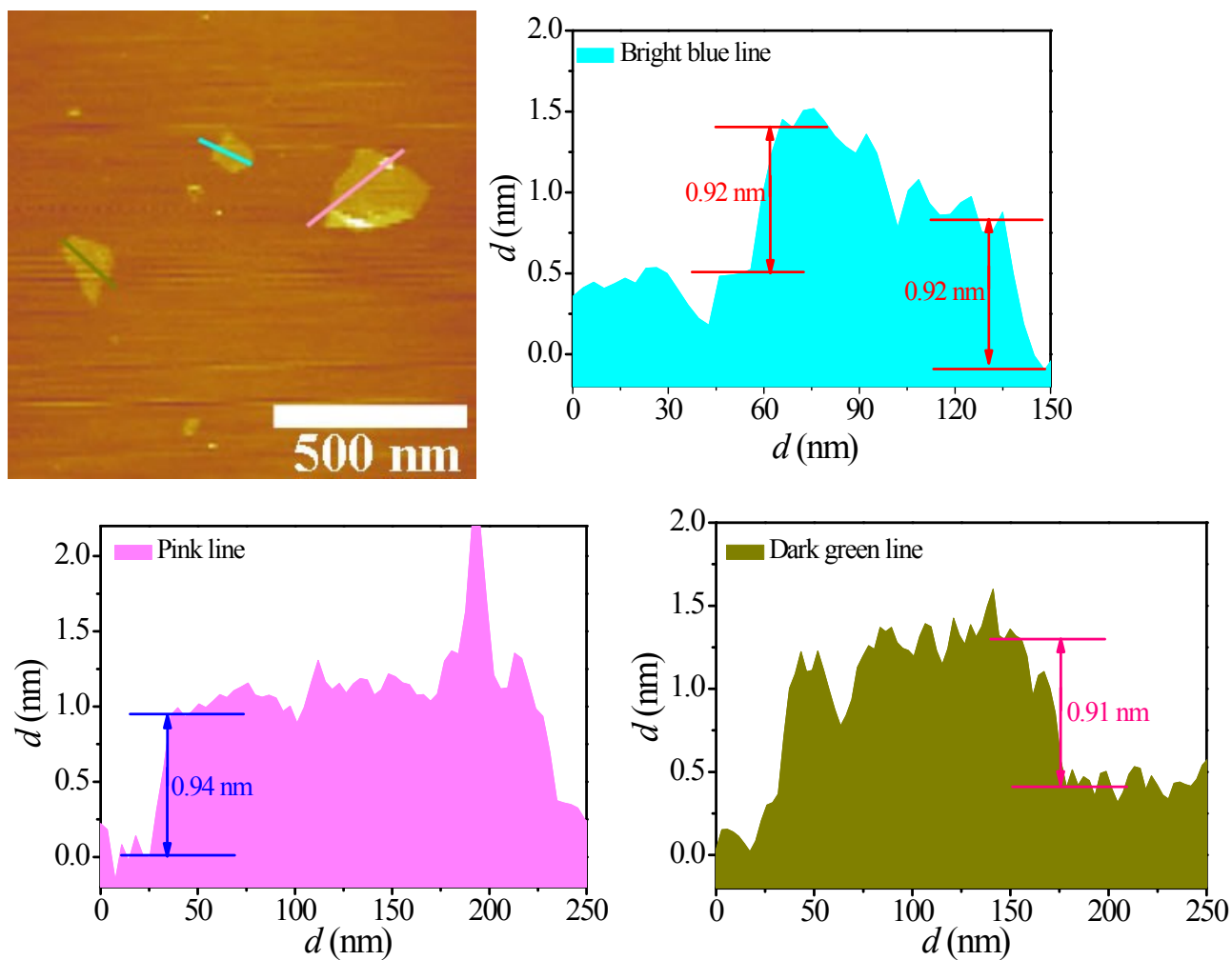


Figure S16. AFM images of **2D-Zn-single-layer**, and the height profile of the nanosheets along the brightly blue line, pink line and dark green line, respectively.



Figure S17. Mass spectrometry of the solution after ultrasonic exfoliation of **3D-Zn**.

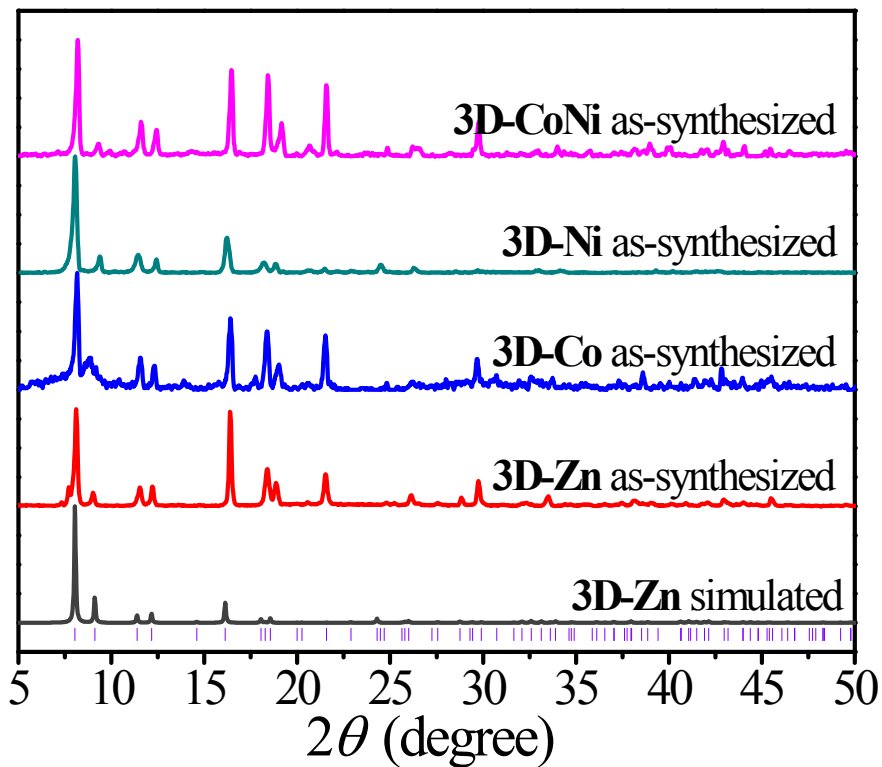


Figure S18. PXRD patterns of **3D-Zn**, **3D-Co**, **3D-Ni**, and **3D-CoNi**.

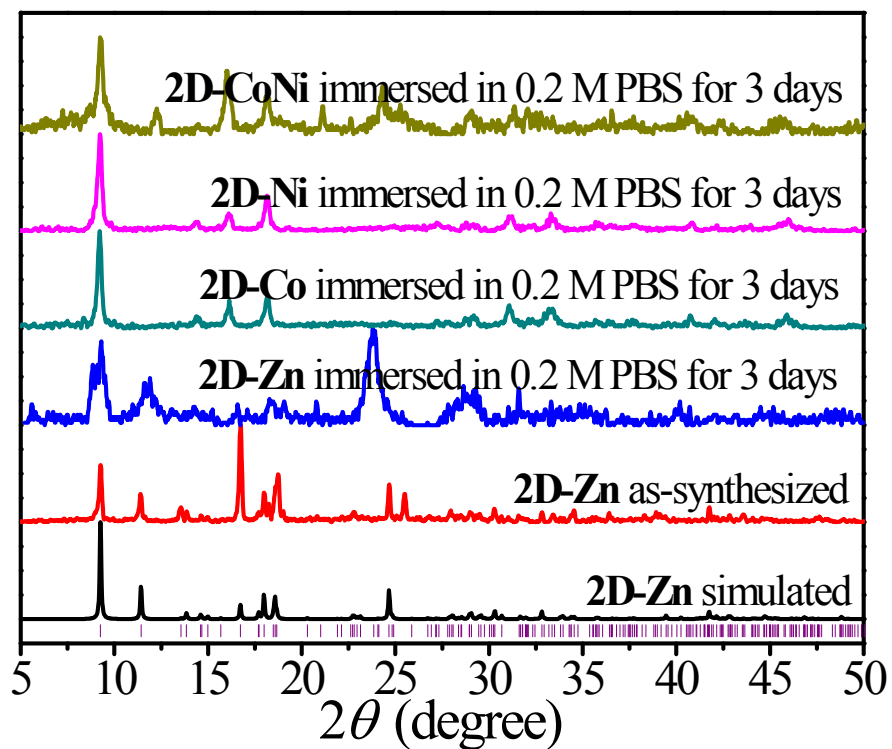


Figure S19. PXRD patterns of **2D-Zn**, **2D-Co**, **2D-Ni** and **2D-CoNi** before and after immersed in 0.2 M PB solution.

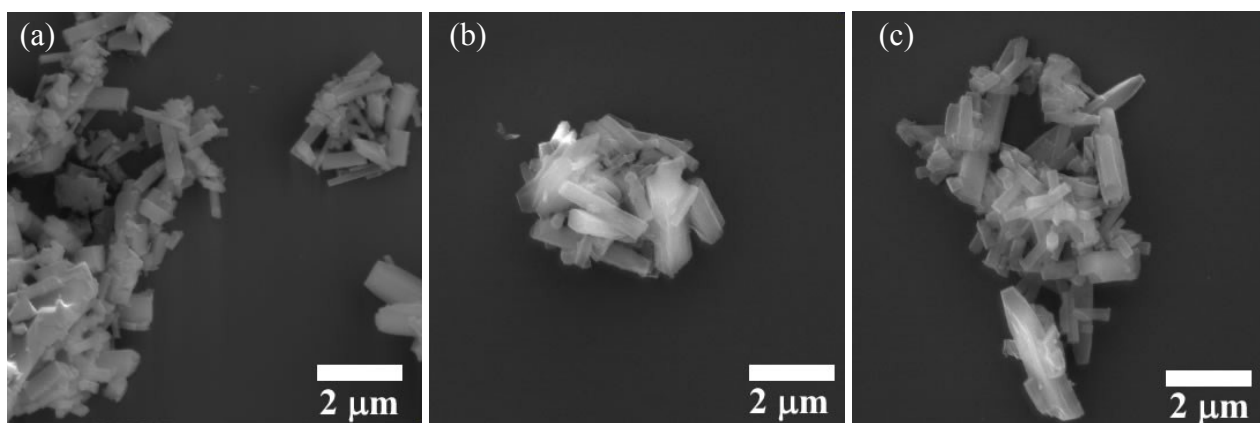


Figure S20. SEM images of **3D-Co**, **3D-Ni** and **3D-CoNi**.

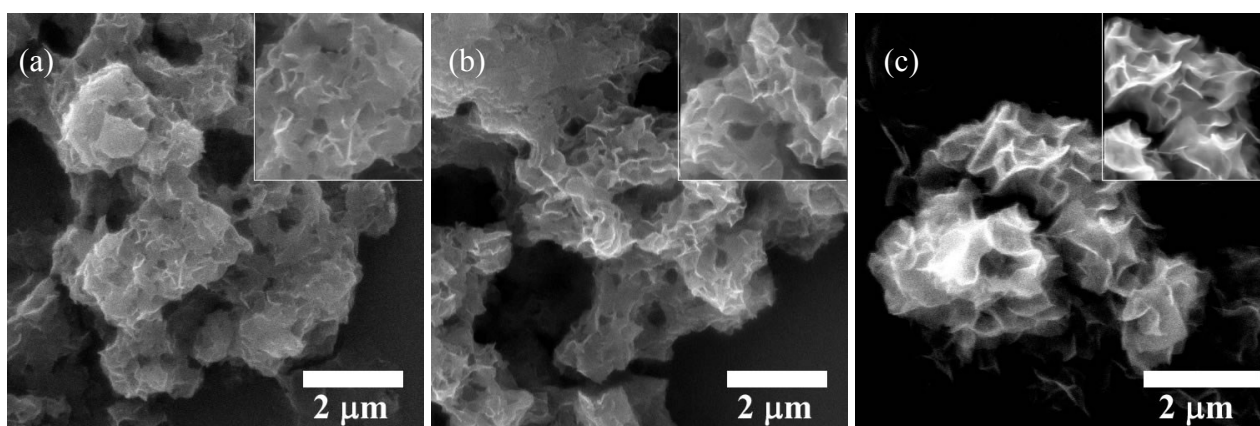


Figure S21. SEM images of **2D-Co-single-layer**, **2D-Ni-single-layer** and **2D-CoNi-single-layer**.

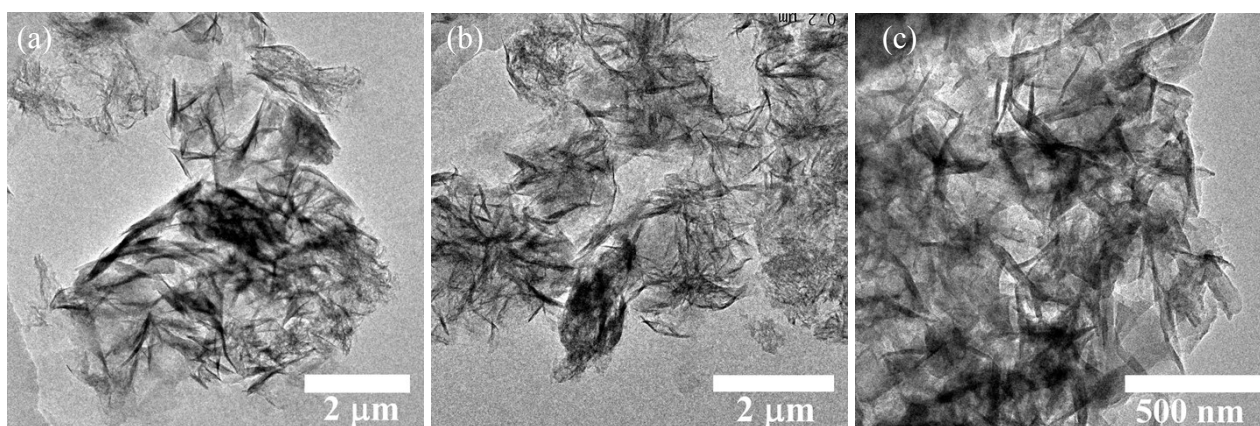


Figure S22. TEM images of **2D-Co-single-layer**, **2D-Ni-single-layer** and **2D-CoNi-single-layer**.

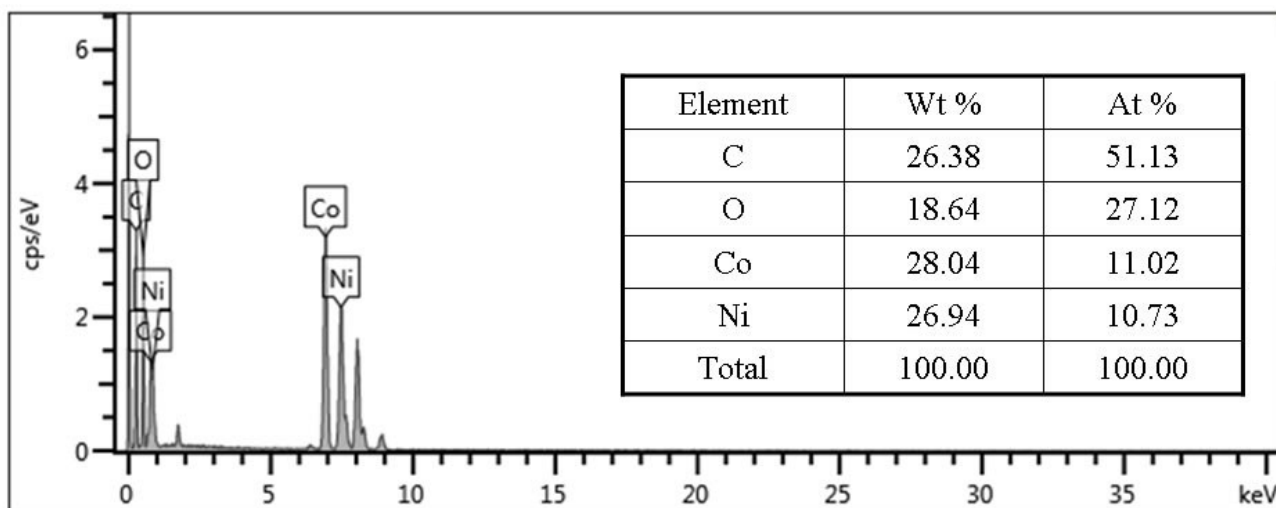


Figure S23. EDS spectrum of 2D-CoNi-single-layer.

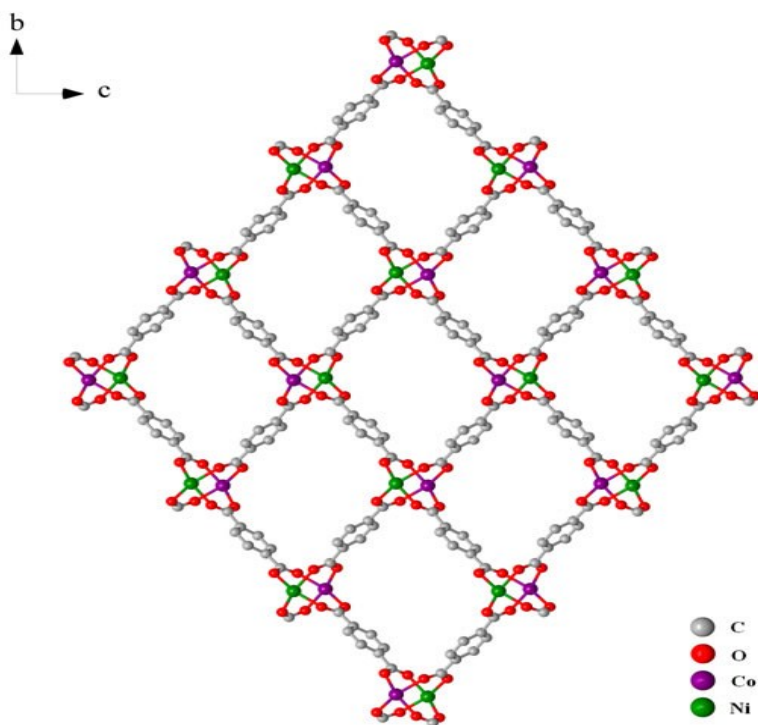


Figure S24. 2D $[\text{CoNi}(\text{bdc})_2]$ layer viewing along the a -axis.

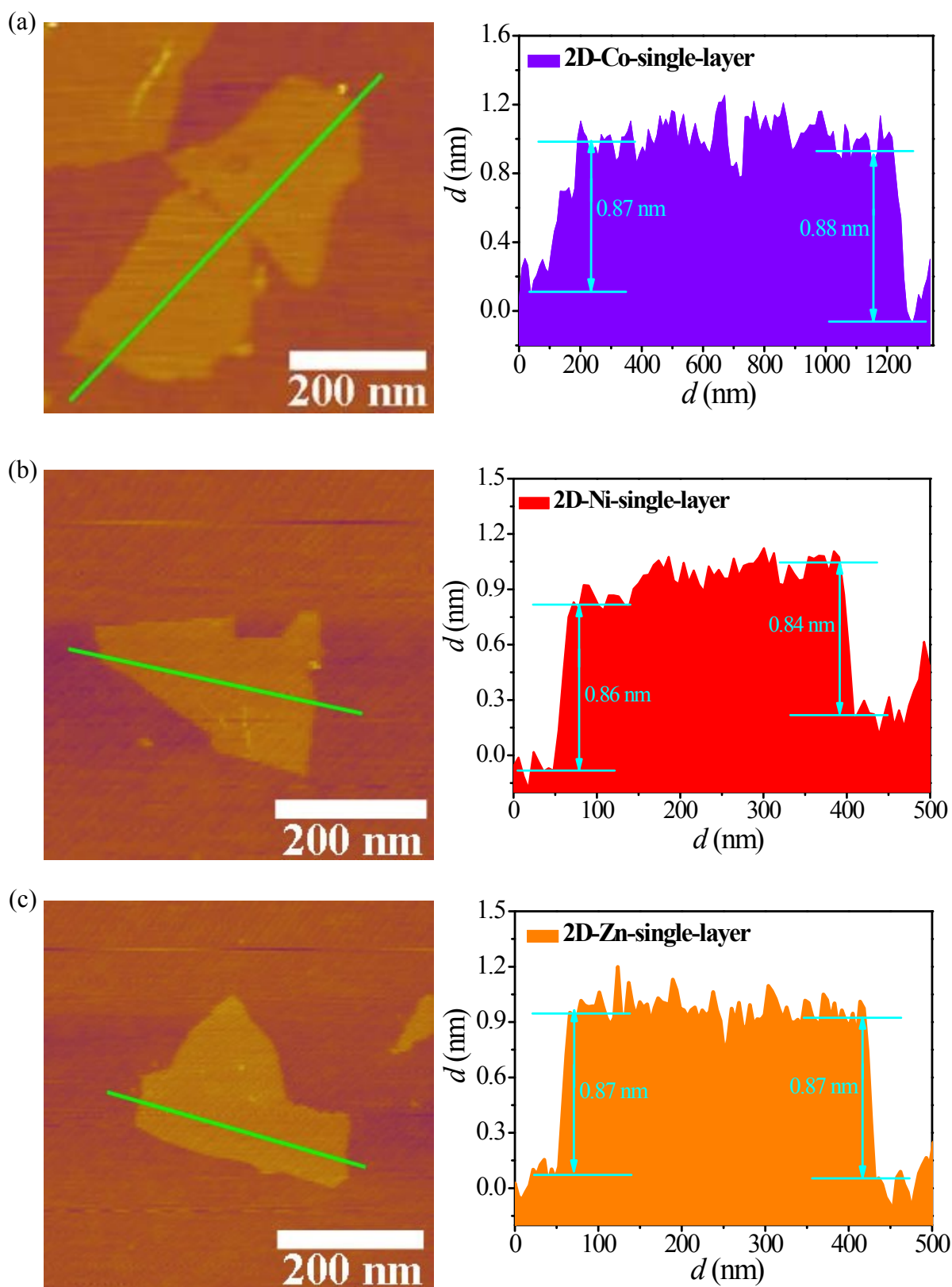


Figure S25. AFM images and the corresponding height profiles of (a) **2D-Co-single-layer**, (b) **2D-Ni-single-layer** and (c) **2D-CoNi-single-layer**.

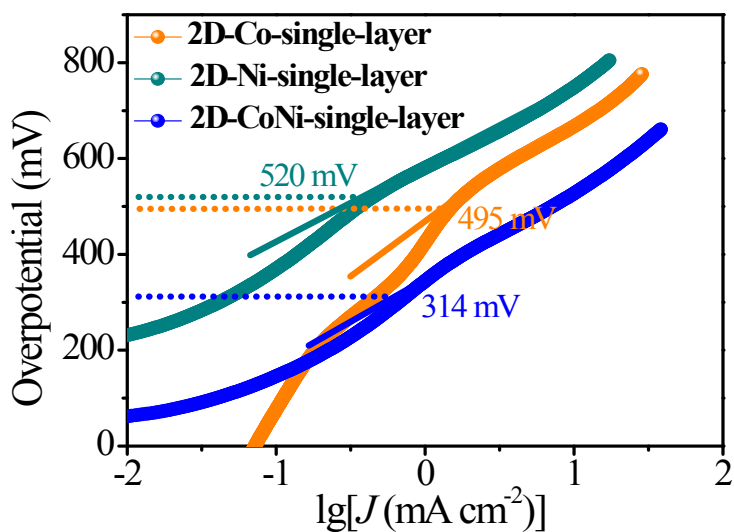


Figure S26. Onset potentials of 2D-Co-single-layer, 2D-Ni-single-layer and 2D-CoNi-single-layer.

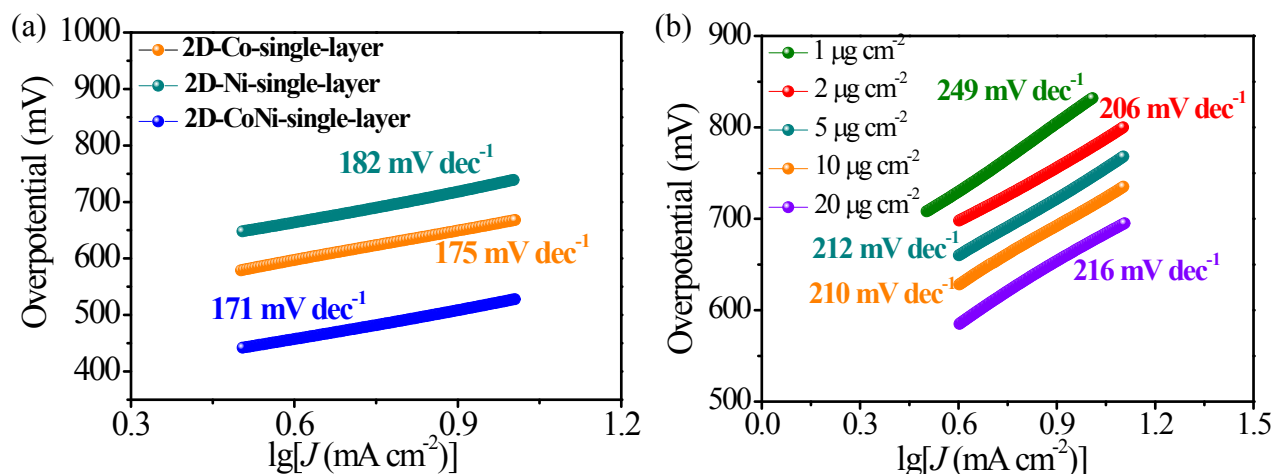


Figure S27. (a) Tafel slopes for 2D-Co-single-layer, 2D-Ni-single-layer and 2D-CoNi-single-layer with the loading mass of 0.2 mg cm^{-2} . (b) Tafel slopes for 2D-CoNi-single-layer with different loading mass.

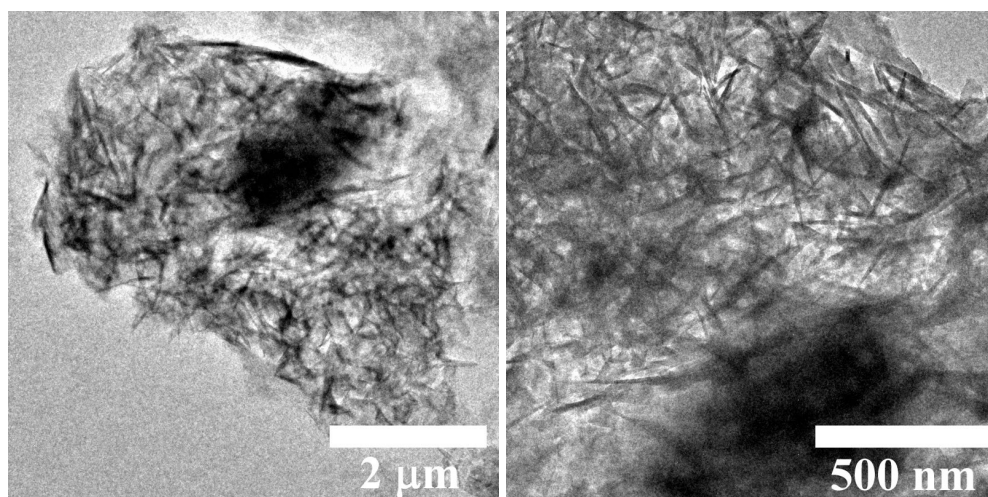


Figure S28. TEM image of **2D-CoNi-single-layer** after OER testing.

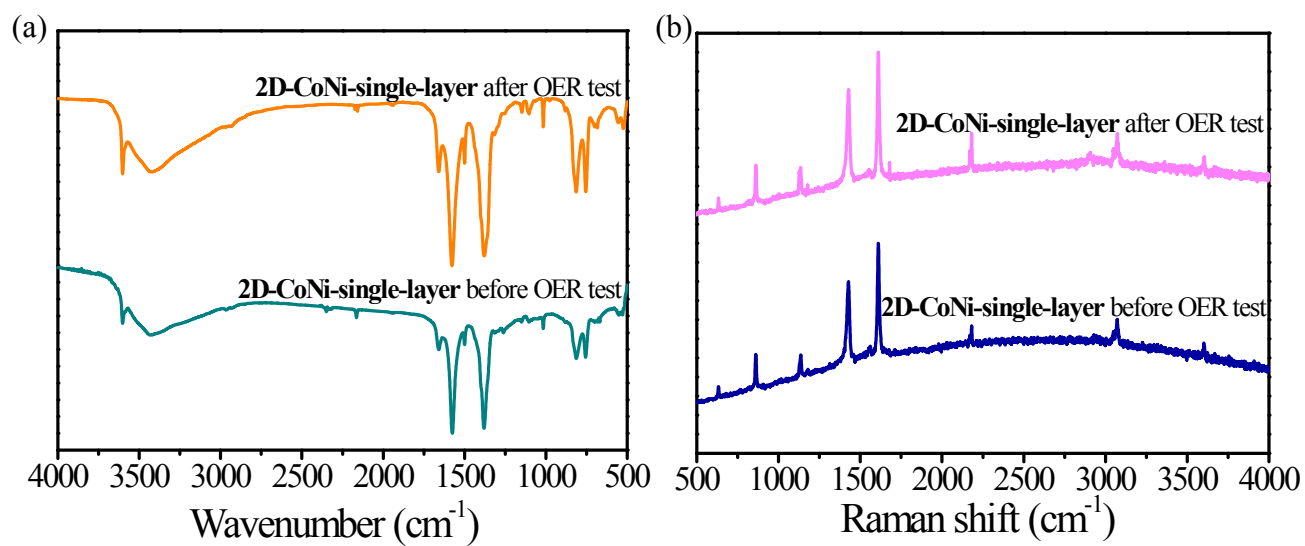


Figure S29. (a) Infrared spectra and (b) Raman spectra of **2D-CoNi-single-layer** before and after OER testing.

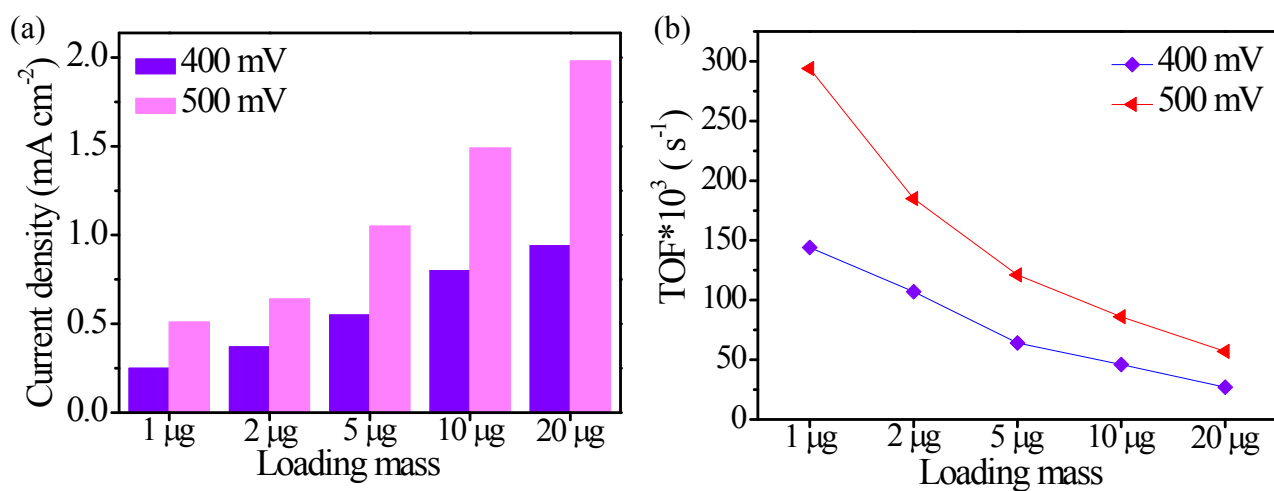


Figure S30. (a) Current density of **2D-CoNi-single-layer** with different loading mass calculated from LSV curves at the overpotentials of 400 mV and 500 mV, respectively. (b) TOF values of **2D-CoNi-single-layer** with different loading mass calculated from LSV curves at the overpotentials of 400 mV and 500 mV, respectively.

Table S1 Comparison of catalytic OER performance for well-developed metal-based electrocatalysts in PB solution.

Catalysts	Mass loading (mg cm ⁻²)	Overpotential (mV)	Tafel slope (mVdec ⁻¹)	<i>J</i> @1.8 V (mA·cm ⁻²)	TOF (s ⁻¹)@ Overpotential	Reference
2D-Co-single-layer	0.2	425 ^a 667 ^b	175	2.9	0.0025@400 mV 0.0044@500 mV	<i>This work</i>
2D-Ni-single-layer	0.2	581 ^a 749 ^b	182	0.9	0.0004@400 mV 0.001@500 mV	
2D-CoNi-single-layer	0.2	344 ^a 527 ^b	171	17.6	0.0052@400 mV 0.021@500 mV	
	0.01	584 ^a 825 ^b	249	0.85	0.144@400 mV 0.294@500 mV	
Co4Mo or MAF-69-Mo	0.2	490 ^b	144	22.0	0.03@490 mV	<i>Angew. Chem. Int. Ed.</i> 2019 , 58, 139
Ru-RuO ₂ -CNT	NA	270 ^b	97	NA	0.013@400 mV	<i>Nano Energy</i> 2019 , 61, 576
atomically-thin Co ₃ S ₄ nanosheets	0.28	650 (3.27 mA cm ⁻²)	151	NA	0.00605@500 mV	<i>Angew. Chem. Int. Ed.</i> 2015 , 127, 11383
Co(PO ₃) ₂ nanoparticles	> 0.6	440 (8.01 mA cm ⁻²)	74.1	NA	0.10~0.21@440 mV	<i>Adv. Funct. Mater.</i> 2013 , 23, 227
Co ₃ O ₄ QDs	0.05	400 ^a	80	NA	0.07@420 mV	<i>Ind. Eng. Chem. Res.</i> 2018 , 57, 1441
Co-Pi NA/Ti	0.96	380 ^b	187	NA	0.065@420 mV	<i>Angew. Chem. Int. Ed.</i> 2017 , 56, 1064
CCH@Co-Pi NA/Ti	2	460 ^b	284	NA	0.0015@410 mV	<i>Nanoscale</i> 2017 , 9, 3752
Ti@Co ₃ O ₄	0.147	550 ^b	88	NA	0.23@410 mV	<i>ChemSusChem</i> 2017 , 10, 2875
HEPES (Fe)	12.3 nmol/cm ²	473 ^a (NHE)	47	NA	0.42 (1.45 V, NHE)	<i>ACS Appl. Mater. Interfaces</i> 2015 , 7, 21852
Fe-based film	10.2 nmol/cm ²	480 ^a (NHE)	52	NA	0.21@530 mV	<i>Angew. Chem. Int. Ed.</i> 2015 , 54, 4870
MnCat	98 nmol/cm ²	590 ^a (NHE)	76	NA	0.01 (1.35 V, NHE)	<i>Energy Environ. Sci.</i> 2012 , 5, 7801

^a 1 mA cm⁻², ^b 10 mA cm⁻².