

Supporting Information for

Metal-organic framework derived Os-doped Ni_xP/N-doped carbon composite nanosheet arrays toward boosting methanol oxidation into value-added chemicals coupled with hydrogen production.

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Experimental Section

Materials and chemicals

Potassium hexachloroosmate (K_2OsCl_6), ruthenium oxide (RuO_2), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), commercial Pt/C (20 wt%), N, N-dimethylformamide (DMF), Maleic acid, triethylenediamine (TED), 1,4-benzene dicarboxylic acid (BDC), and deuterated water (D_2O) were purchased from Aladdin. HCl and methanol (CH_3OH) were purchased from Xilong Scientific Co., Ltd.

Synthesis of the NiOs-MOF/NF

Prior to the reaction, the nickel foam was immersed in 3 M HCl for 15 min to remove the oxide layer and then washed with alcohol and water. The NiOs-MOF/NF was synthesized based on a previous study with slight modifications¹. In a typical synthesis, $Ni(NO_3)_2 \cdot 6H_2O$ (0.3 g), TED (0.033 g), and BDC (0.105 g) were dissolved in 30 mL of DMF. After that, 3 mL of K_2OsCl_6 aqueous solution (20 mM) was added with stirring to form a homogeneous solution. Finally, the above solution was transferred to a 50 mL Teflon-lined autoclave, and a piece of clean nickel foam was added. The hydrothermal treatment was conducted at 130 °C for 24 h. After the solvothermal reaction, the NiOs-MOF/NF was obtained by washing and drying. Meanwhile, Ni-MOF/NF was synthesized under otherwise identical conditions, except for replacing K_2OsCl_6 aqueous solution with same volume of deionized water.

Synthesis of the Os-Ni_xP/N-C/NF

In a typical synthesis, 200 mg of NaH_2PO_2 and a piece of NiOs-MOF/NF precursors were placed upstream and downstream of the tinfoil-sealed porcelain boat, respectively. Then, the porcelain vessel was heated from room temperature to 500 °C under N_2 atmosphere at 2 °C/min and held for 2

h. Once the sample was cooled to room temperature, it was obtained. The Ni_xP/N-C/NF was prepared by the same method, except that Ni-MOF was used as the precursor.

Characterizations:

TEM (JEM-2010) and SEM (ZEISS SUPRA 55) combined with EDS were used to describe the morphological and structural information of the catalyst. PXRD (D8 ADVANCE, BRUKER AXS) and XPS (ESCALAB MK II) were used to characterize the electronic structure information. The liquid products were analyzed by NMR spectrometer (Bruker Avance NEO 600).

Electrochemical measurements:

The HER, OER, and MOR electrochemical measurements were evaluated on a CHI660E electrochemical workstation using a conventional three-electrode system. The electrolyte solutions were purged with N₂ gas for 30 min prior to the electrochemical experiments. The Os-Ni_xP/N-C/NF (1 cm × 1 cm), graphite rod, and Ag/AgCl electrode were used as working electrode, a counter electrode, and reference electrode, respectively. As comparison samples, the amount of Pt/C (20 wt%) and RuO₂ on NF were both 1.0 mg cm⁻². Linear sweeping voltammograms (LSVs) curves were tested in 1.0 M KOH with and without methanol with a scan rate 5 mV s⁻¹ and 95% iR correction. All the potentials were converted into RHE according to the equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}}^{\theta} + E_{\text{Ag/AgCl}} + 0.059 \times \text{pH}$. Electrochemical impedance spectroscopy (EIS) was recorded in the range of 100 kHz to 1 mHz. Long-term stability measurement (V-t) was carried out at a current density of 10 mA cm⁻². In the HER-MOR two-electrode system, the Os-Ni_xP/N-C/NF was used as both anode and cathode. The generated amounts of H₂ and formate were quantified by the water drainage method and ¹H nuclear magnetic resonance (¹H NMR) spectroscopy. The faraday efficiency is calculated as follows:

$$FE(H_2) = \frac{N(H_2) * Z_1 * F}{Q_1} * 100\% \quad (1)$$

$$FE(formate) = \frac{N(formate) * Z_2 * F}{Q_2} * 100\% \quad (2)$$

Where N is the mole of product, F is the Faraday constant (96485 C mol⁻¹), Z represents the number of electron transfers (Z₁=2, Z₂=4), and Q is the total charges during HER and MOR.

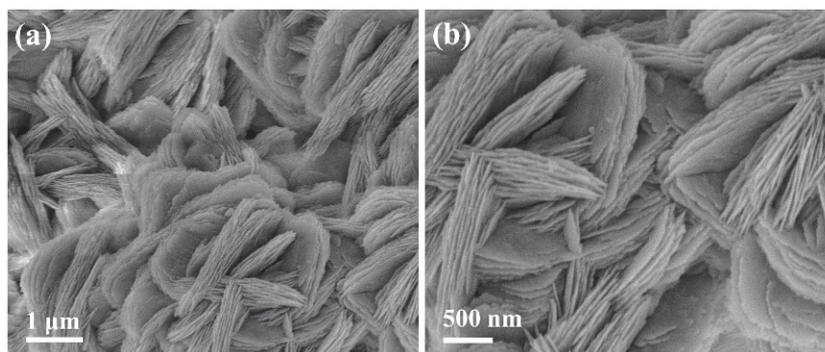


Fig. S1 SEM images of NiOs-MOF/NF.

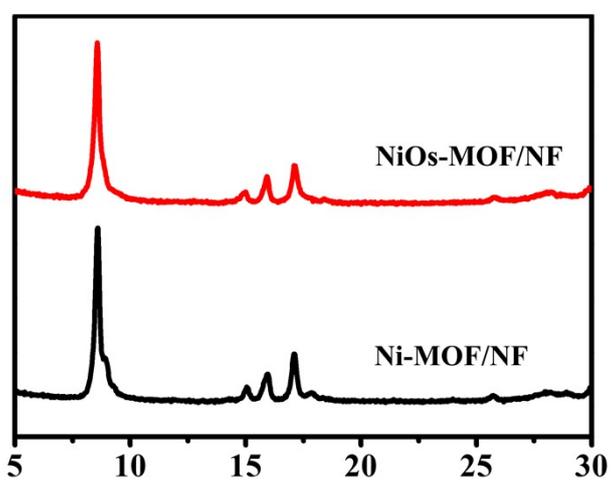


Fig. S2 XRD patterns of NiOs-MOF/NF and Ni-MOF/NF.

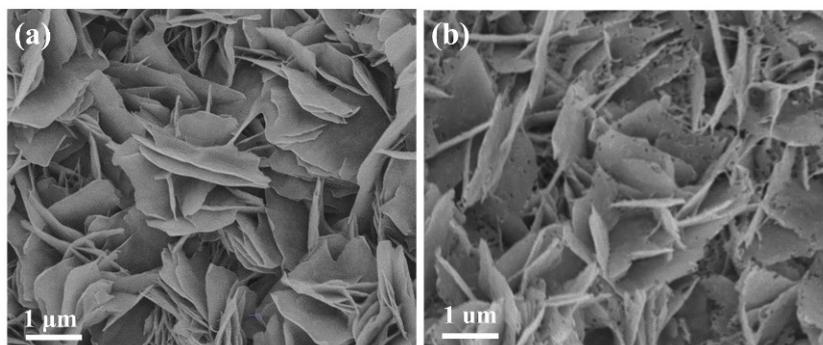


Fig. S3 SEM images of (a) Ni-MOF/NF and (b) Ni_xP/NF.

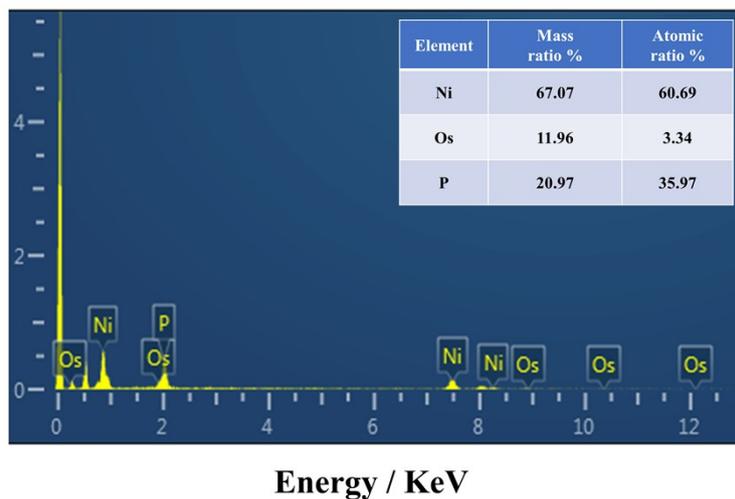


Fig. S4 EDX spectrum of the Os-Ni_xP/N-C/NF.

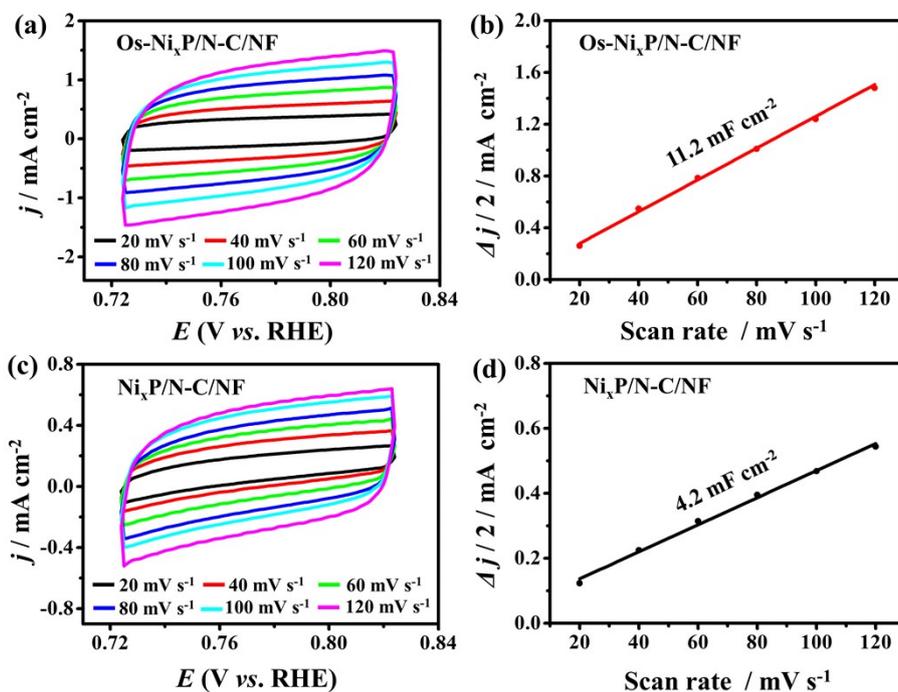


Fig. S5 CV curves at different scan rates and capacitive current densities of (a, b) Os-Ni_xP/N-C/NF, and (c, d) Ni_xP/N-C/NF.

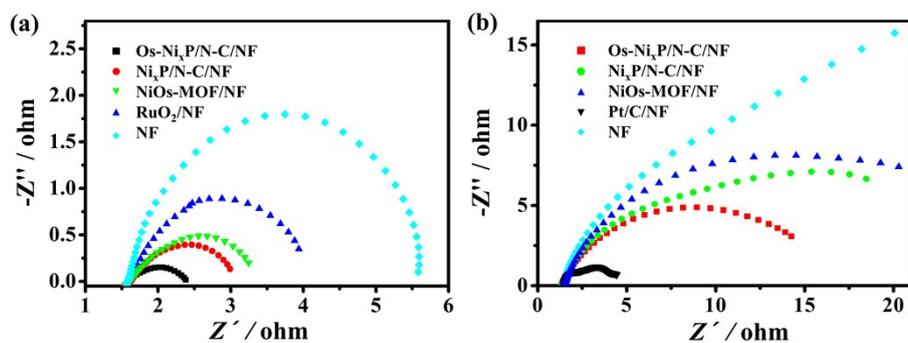


Fig. S6 Electrochemical impedance spectra of various catalysts in 1.0 M KOH with 1.0 M methanol (a) and (b) without 1.0 M methanol.

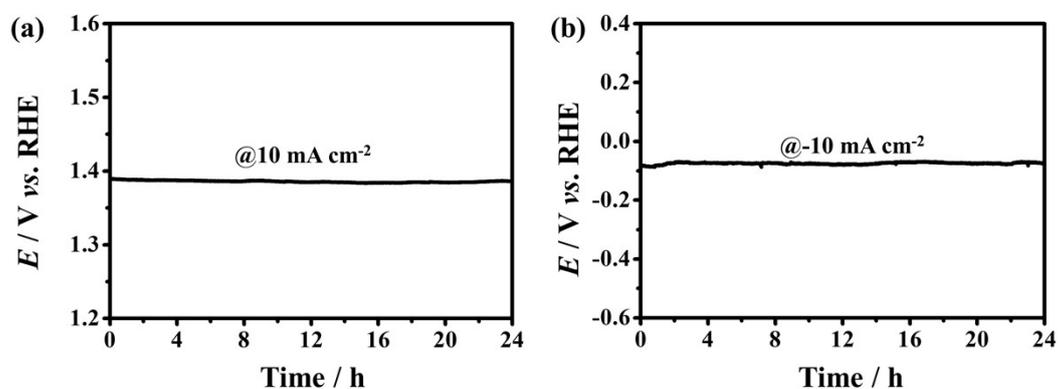


Fig. S7 The chronopotentiometry (V-t) curve (without iR compensation) of Os-Ni_xP/N-C/NF in 1.0 M KOH with 1.0 M methanol (a) and (b) without 1.0 M methanol.

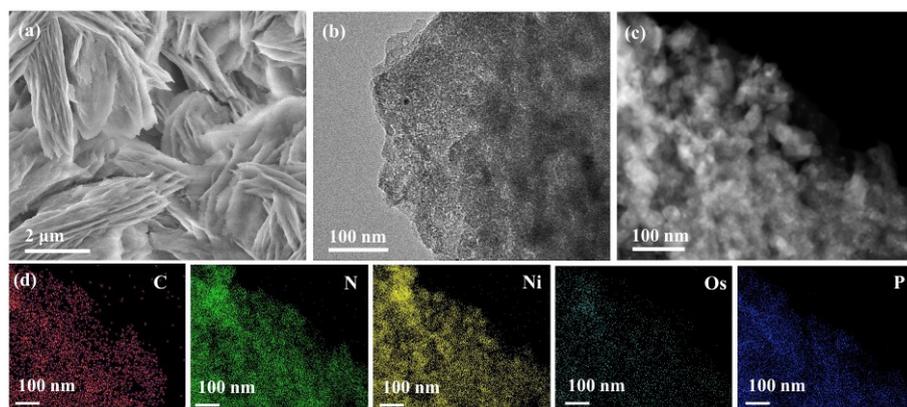


Fig. S8 (a) SEM image of the post-MOR Os-Ni_xP/N-C/NF. (b) TEM image and (c) HAADF-STEM and (d) elemental mapping images of the post-MOR Os-Ni_xP/N-C nanosheets.

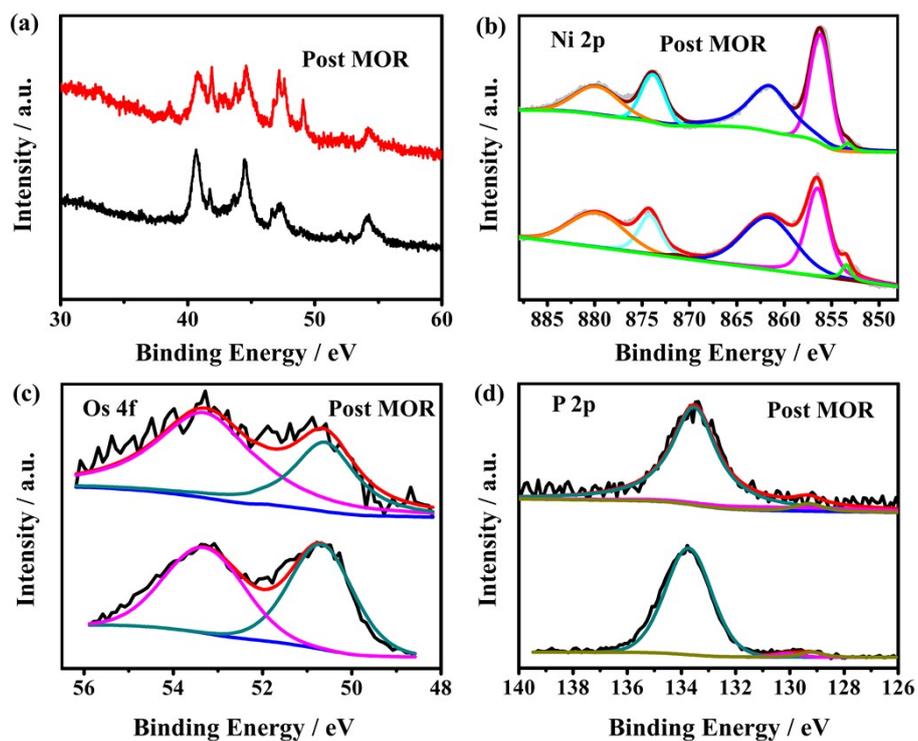


Fig S9 (a) XRD patterns, (b) Ni 2p spectra, (c) Os 4f spectra, and (d) P 2p spectra of Os-Ni_xP/N-C before and after MOR testing.

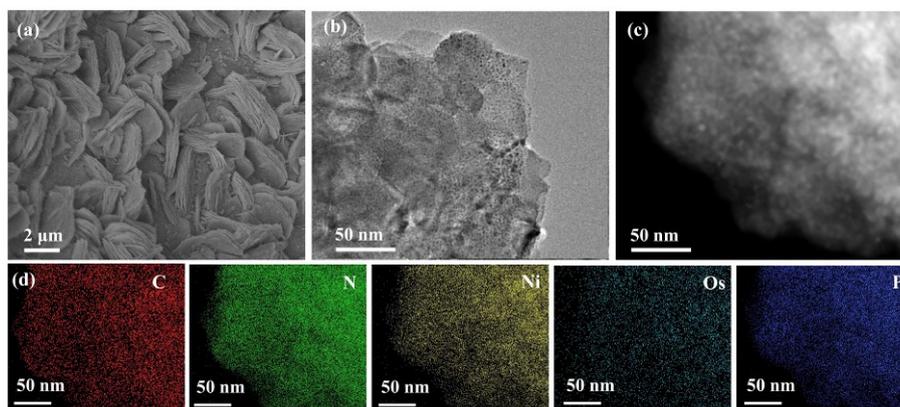


Fig. S10 (a) SEM image of the post-HER Os-Ni_xP/N-C/NF. (b) TEM image and (c) HAADF-STEM and (d) elemental mapping images of the post-HER Os-Ni_xP/N-C nanosheets.

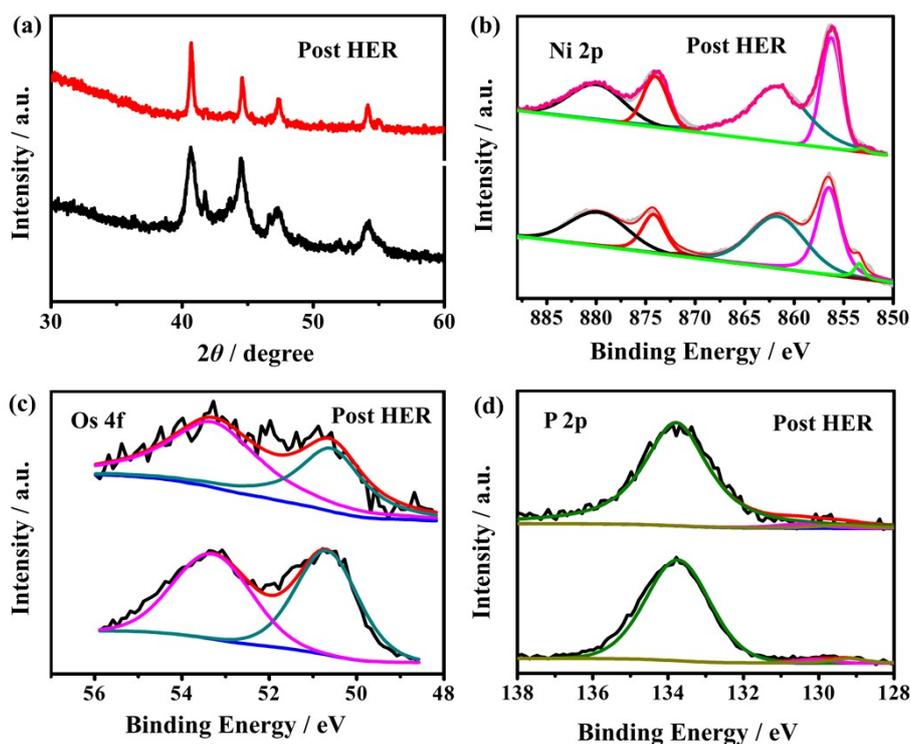


Fig. S11 (a) XRD patterns, (b) Ni 2p spectra, (c) Os 4f spectra, and (d) P 2p spectra of Os-Ni_xP/N-C before and after HER testing.

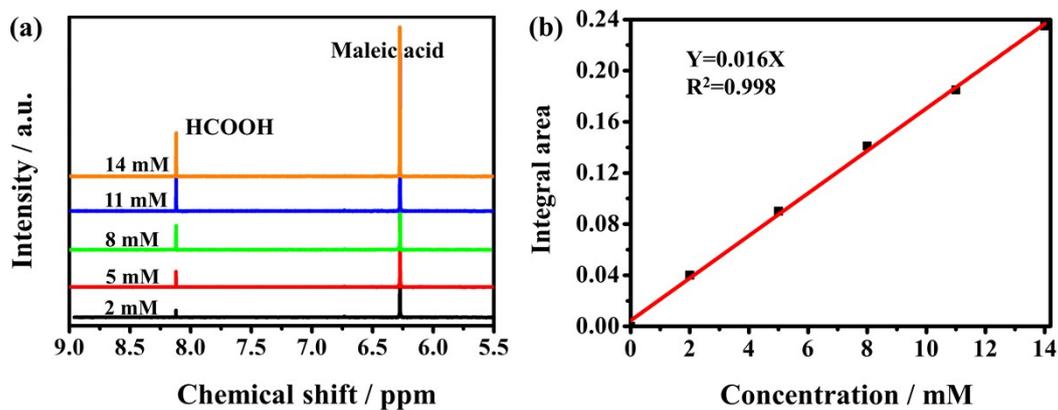


Fig. S12 The ¹H NMR spectra of HCOOH with different concentrations. Maleic acid is used as an internal standard for the quantification of HCOOH. (b) The corresponding calibration curve was used to quantify the concentrations of the produced HCOOH in the electrolyte.

Table S1. Comparison of the chemical-assisted hydrogen evolution reaction performance by alcohol of selective oxidation.

Catalyst	Electrolyte	Main anode product	Cell voltage at 10 mA cm ⁻² (V)	Ref.
This work	1.0 M KOH+ 1.0 M methanol	formate	1.43	This work
Ni(OH) ₂ /NF	1.0 M KOH+ 0.5 M methanol	formate	1.52	2
Ni _{0.33} Co _{0.67} (OH) ₂ /NF	1.0 M KOH+ 0.5 M methanol	formate	1.50	3
Co(OH) ₂ @HOS/CP	1.0 M KOH+ 3.0 M methanol	formate	1.50	4
Co _x P@NiCo-LDH/NF	1.0 M KOH+ 3.0 M methanol	formate	1.43	5
Co ₃ S ₄ -NSs/Ni-F	1.0 M KOH+ 0.5 M ethanol	potassium acetate	1.48	6
NC@CuCo ₂ N _x /CF	1.0 M KOH +0.015 M benzylalcohol	benzaldehyde	1.55	7

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