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Cobalt Phosphide Supported by Two-Dimensional Molybdenum Carbide (MXene) for Hydrogen Evolution Reaction, Oxygen Evolution Reaction, and Overall Water Splitting

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Developing low cost, high performance, and durable bifunctional catalyst to boost the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) for water splitting is a critical yet challenging task. Transition metal phosphides have been identified as promising dual functional catalysts recently. Herein, we report a facile strategy to construct a heterostructure catalyst by integrating cobalt phosphide with molybdenum carbide (MXene). The CoP/Mo₂CT_x (T is the surface terminal group) catalyst exhibited good HER activity with an overpotential of 78 mV at the current density of 10 mA cm⁻², close to the Pt/C benchmark, and its OER performance is markedly better than the RuO₂ benchmark, evidenced by a very small overpotential of 260 mV at 10 mA cm⁻² in 1 M KOH. Impressively, when employed for overall water splitting, CoP/Mo₂CT_x also outperformed the Pt/C+RuO₂ combination with a voltage of 1.56 V @ 10 mA cm⁻². Density functional theory (DFT) calculations revealed that CoP/Mo₂CT_x has appropriate water adsorption especially the optimal H* adsorption free energy (ΔG_{H^+}), and the Mo₂C MXene support can significantly increase the total density of states and downshift the d-band center for HER, while for OER, multiple characterizations of CoP/Mo₂CT_x post OER test show that, CoP in the catalyst can be transformed into Co-OOH during the electrocatalytic process. This study can pave a pathway for design and fabrication of MXene-supported noble-metal-free bifunctional catalysts toward practical water splitting and energy conversion.

1. Introduction

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The excessive dependence on fossil fuels has caused ubiquitous environmental pollution and global energy crisis, and the development and utilization of renewable energy hold great potentials to mitigate such issues.¹⁻⁵ Hydrogen is a clean, environmentally friendly, renewable energy source, and water splitting is an effective means to produce high-quality H₂.⁶ Water splitting includes two key electrochemical processes, hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), and currently Pt/C and Ir/RuO₂ are the best HER and OER catalysts.^{2, 7-9} However, the scarcity of metal resources and the associated skyrocketing high price have significantly hindered the large-scale applications of these catalysts. To that end, it is highly desirable to develop cost effective and high-performance bifunctional catalysts to realize practical water splitting. So far, extensive research efforts have been devoted to find alternative catalysts, such as transition metal sulfides, selenides, phosphides, nitrides, and heteroatomdoped carbons.¹⁰⁻¹⁴ Among them, transition metal phosphide has been attracting continuously increasing research attentions due to their unique two-dimensional structure, increased numbers of active sites, and promising electrocatalytic performance.¹⁵ For instance, in 2015, Sun group found that the as-prepared Co-P films exhibited remarkable catalytic performance for both HER and OER in alkaline media, and 100% Faradaic efficiency for overall water splitting, rivalling the integrated performance of Pt and IrO₂.¹⁶ In a recent report, Ji et al. documented the fabrication of CoP nanoframes with hollow structure, which enabled a highly efficient water electrolyzer with a current density of 10 mA cm⁻² driven by a cell voltage of 1.65 V.¹⁷ Even so, the electrocatalytic performance of CoP is still far from satisfactory mainly because of its poor conductivity.¹⁸ However, it can be coupled with some conductive substrate to enhance the conductivity and accelerate the electron

MXene is an emerging two-dimensional material made of metal carbides or nitrides (usually formulated as $M_n C_2 T_{x\prime},\ M$

transfer hence improve the activity and stability.

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represents an early transition metal), and its surface is rich in functional groups $(T_x = -OH, -O, -F)$.¹⁹⁻²² Thanks to the merits including high mechanical stability, excellent conductivity, and high specific surface area, MXene has attracted widespread attentions in the field of energy storage and conversion. The general precursor to prepare MXene is $M_{n\!+\!1}\!AX_n\!,$ where A is IIIA or IVA group element (e.g., Al or Ga), X represents the C or N element.^{23, 24} MXene can be prepared by selectively etching the A layer from a large MAX phase and substituted by -OH, -O, -F terminal groups, making MXene an ideal substrate for anchoring various active substances.²⁵⁻²⁷ Consequently, MXene has been employed to anchor other functional materials to form active electrocatalysts. For instance, using $Ti_3C_2T_x$ MXene as both the conductive support and the second metal precursor, Li et al. prepared intermetallic compound of Pt₃Ti on MXene for HER, which exhibited 4.4 and 13 times of mass activity and specific activity higher than Pt/Vulcan at an overpotential of 70 mV.28 In another report, Ramalingam and Varadhan groups constructed ruthenium single atoms supported by Ti_3C_2 MXene, which displayed an overpotential of 76 mV at a current density of 10 mA cm⁻² with a Tafel slope of 90 mV dec⁻¹ in 0.5 M H₂SO₄ toward HER. Lim et al. fabricated a 2H-MoS₂ on Mo₂C MXene nanohybrid, which showed exceptional durability, as less than 30 mV overpotential degradation was observed after 10 continuous days of electrolysis at a fixed -10 mA cm $^{-\,2}$ current density or 100,000 successive cyclic voltammetric cycles.²⁹ Muller and coworkers documented the synthesis of a solid solution of Mo₂CT_x:Co MXene phase with cobalt substitution on the molybdenum sites with impressive HER performance, while DFT calculations revealed that upon cobalt substitution, the thermodynamics of hydrogen binding on the MXene surface can be significantly improved to enhance the HER kinetics.³⁰ Despite the above progress achieved, for MXene/transition metal hybrid catalyst, there are still several critical questions remained to be resolved. For instance, the HER activity and stability in alkaline solution are not that desirable, the catalyst preparation process is rather tedious with low yield, and more importantly, the catalytic mechanism and related structure evolution of the catalyst during the catalytic process are still puzzling. These questions form the primary motivation and goal of our current study.

Herein, we developed a simple hydrothermal and calcination approach that can grow CoP nanoarrays onto the surface of Mo₂C MXene to form a heterostructure catalyst of CoP/Mo₂CT_x. CoP/Mo₂CT_x exhibited comparable activity but superior stability to the Pt/C catalyst for HER, and markedly outperformed activity and long-term durability than the RuO₂ benchmark for OER in alkaline solution. Notably, it showed much lower voltage to achieve the current density of 10 mA cm⁻² than the Pt/C+RuO₂ combined benchmark catalyst for overall water splitting, also better than most of the recently reported non-noble-metal based catalysts.³¹⁻³⁵ DFT calculations revealed that CoP/Mo₂CT_x has the optimal H* adsorption free energy (ΔG_{H^*}), and the Mo₂C MXene support can significantly increase the total density of states and downshift the d-band center for HER, while CoP in the catalyst can transform into Co-OOH during the OER process. DOI: 10.1039/D1TA05648D

2. Experimental section

2.1 Materials

Cobalt nitrate hexahydrate (Co(No₃)₂-6H₂O), ammonium fluoride (NH₄F), urea (CO(NH₂)₂) were supplied by Macklin biochemical company, China. Hydrofluoric acid was purchased from Damao Chemical Reagents, Tianjin, China. Ruthenium dioxide (RuO₂) and 20 wt.% Pt/C were obtained from Alfa Aesar. Deionized water with a resistivity of 180.2 M Ω ·cm⁻¹ was prepared by the Barnstead Nanopure water system. All chemical reagents were directly used as received without further purification.

2.2 Synthesis of Mo₂C MXene

 Mo_2Ga_2C powders were synthesized from $\beta\text{-}Mo_2C$ and Ga according to a previously reported method.^{36} The Mo_2C MXene nanosheets were produced by etching Mo_2Ga_2C powders in 14 M HF. Briefly, Mo_2Ga_2C powders (2.0 g) were added into the HF solution (14 M, 20 mL) under magnetic stirring. Afterward, the reaction temperature was raised to 55 °C for 160 h. The resulting product was thoroughly washed with deionized water until it reached a pH approximately neutral. The product of MXene was then vacuum dried at 60 °C for 12 h and sealed for preservation.

2.3 Synthesis of Co(OH)F and Co(OH)F/Mo₂CT_x

First of all, $Co(NO_3)_2 \cdot GH_2O$ (291 mg), NH_4F (296 mg), and urea (600 mg) were co-dissolved in deionized water (30 mL) under sonication, and kept stirring for 10 mins. Mo_2C MXene powders were then added into the solution and the mixture was kept stirring for 20 mins. Subsequently, the solution was transferred into a Teflon autoclave (45 mL) and heated at 120 °C for 10 h. The asobtained Co(OH)F/Mo_2CT_x was washed several times with deionized water and dried in a vacuum oven at 60 °C. Co(OH)F was produced by the same manner without adding MXene.

2.4 Synthesis of CoP and CoP/Mo₂CT_x

For preparing CoP/Mo₂CT_x, Co(OH)F/Mo₂CT_x (30 mg), and NaH₂PO₂ (300 mg) were placed at the different sides of the tube furnace. NaH₂PO₂ was loaded at the upstream side, while Co(OH)F/MXene was at the other side. Subsequently, the temperature was increased to 350 °C at the rate of 2 °C min⁻¹ in Ar gas and maintained for 2 h to acquire the final product of CoP/Mo₂CT_x. CoP was prepared in a similar manner with the precursor of Co(OH)F employed instead.

2.5 Electrochemical measurements

Firstly, 450 μ L deionized water, 5 wt.% Nafion solution (50 μ L), and 500 μ L ethanol were mixed following by sonicating for 1 h to form a uniform suspension as the catalyst ink. The HER measurements were performed in a glassy carbon electrode (GCE, 0.07 cm²). In a typical test, 20 μ L of the catalyst ink (5 mg/mL) was dropwise cast onto the GCE with a loading of 1.428 mg cm⁻². Linear

sweep voltammetry (LSV) was conducted between -1.6 V and -0.8 V with a scan rate of 5 mV s⁻¹. In addition, the cyclic voltammetric (CV) measurements were conducted at a potential range of -1.2 V to -0.9 V, and the scan rate was 20-200 mVs⁻¹. The OER tests were performed in a carbon cloth (0.25 cm²) with a catalyst loading of 0.4 mg cm⁻². LSV was performed within the potential range of 0 to 1 V (vs. Ag/AgCl) at a scan rate of 10 mV s⁻¹, while CV was conducted in the potential range between 0 and 0.5 V at a scan rate of 10 mV s⁻¹. Water splitting measurements were performed using CoP/Mo₂CT_x on carbon cloth with a loading of 0.4 mg $\rm cm^{-2}$ as both cathode and anode catalysts in 1 M KOH. The potential was calculated via the following equations. The electrochemical performance was carried out with an electrochemical workstation (CHI750E). HER and OER tests were conducted by a conventional three-electrode cell in 1 M KOH. In all electrochemical tests, graphite rod (in saturated KCl) was used as counter electrode. Hg/HgO was employed as reference electrode for HER, OER, and water splitting long-time i-t test, and besides that, Ag/AgCl (in saturated KCl) was used as reference electrode for other electrochemical tests.

 $E_{\text{RHE}} = E_{\text{Ag/AgCI}} + 0.197 + 0.0591^{*} \text{pH}$

HER potential $\eta(V) = E_{RHE} - 0 V$

OER potential $\eta(V) = E_{RHE} - 1.23 V$

2.6 Material characterization

The morphology and surface structure of the samples were analyzed on field emission scanning electron microscopy (FE-SEM, Merlin) and transmission electron microscopy (TEM, JEOL-2010). Xray diffraction (XRD, Empyrean) measurements were performed to identify the crystal structural feature of the catalysts. X-ray photoelectron spectroscopy (XPS) tests were conducted using Phi Xtool instrument with an Al K_{α} radiation. The composition and content of the elements in the catalysts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Specific surface areas and pore diameter distributions of the samples were estimated using Micromeritics ASAP2460 by Brunauer-Emmett-Teller (BET).

2.7 Computational method

The DFT computations were performed using Vienna ab initio simulation package (VASP). Projector augmented wave (PAW) and the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) function were used to describe the ionelectron interaction and the exchange-correlation potential. 400 eV cutoff was employed while the convergence threshold for the selfconsistent field (SCF) and ion steps was set to be 1×10^{-5} eV and 0.01 eV Å⁻¹. Van der Waals interaction was considered by the DFT-D3 method. The dipolar correction was included and the symmetrisation was switched off. The vacuum space of all investigated slab models was 15 Å. The Brillouin zones were sampled by Monkhorst-Pack 3*3*1 for all slab models. The barrier of water dissociation was estimated by nudged elastic band (NEB) method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data of the method. The adsorption Gibbs free energy (ΔG) was very large data

$\Delta G = \Delta E + \Delta Z P E - T \Delta S$

Where ΔE is the DFT-derived adsorption free energy, which is the energy difference of configuration after and before adsorbing a reaction species. ΔZPE , T, and ΔS are the zero-point energy, temperature, and the difference of entropy, respectively.

3 Results and discussion

3.1. Structural characterizations

The CoP/Mo₂CT_x composite was firstly prepared by following the previously reported method with some modifications.³⁷ **Scheme 1** presents the synthetic route for CoP/Mo₂CT_x. Firstly, HF as the selective etchant was employed to produce irregular MXene nanosheets from the Mo₂Ga₂C phase according to a recently reported procedure,³⁸ whereas few-layered MXene sheets were collected. Subsequently, cobaltous nitrate hexahydrate was added into the above MXene suspension with NH₄F and urea under ultrasonication and mild stirring. As the surface of MXene is negatively charged, Co²⁺ ions can be electrostatically assembled onto the MXene. Upon hydrothermal treatment, the anchored Co²⁺ ions began to grow vertically onto the MXene. Finally, Co(OH)F/Mo₂CT_x was subjected to phosphorization to form the CoP/Mo₂CT_x composite.

Subsequently, the morphology and structure during the preparation of MXene, CoP, and the CoP/Mo₂CT_x catalyst were characterized by scanning electron microscopy. As shown in Figure S1, stacked layers are clearly observed in the MAX precursor, where some are clustered together. Fig. 1a shows the typical SEM image of Mo₂C MXene, which maintained the feature of the MAX precursor. The SEM image of the Co(OH)F and Co(OH)F/Mo₂CT_x precursors can be found in Figure S2. Numerous nanoarrays can be observed in Co(OH)F, and such well-defined arrays can be clearly visualized in CoP (Fig. 1b). It indicates that, the structure and morphology can be well maintained upon phosphorization, and such phenomenon also occurred in the Co(OH)F/Mo₂CT_x and CoP/Mo₂CT_x composites. As shown in Fig. 1c, CoP nanoarrays grow densely onto the MXene surface for CoP/Mo₂CT_x, inheriting the pattern of Co(OH)F/Mo₂CT_x (Figure S2). Further TEM test (Figs. 1d, 1e) shows that, with CoP grown onto the MXene surface, the heterostructure is clearly visible. As depicted in the high-resolution TEM image in Fig. 1e, the legible lattice spacing of 0.282 nm can be attributed to the (011) plane of crystalline CoP. The corresponding fast fourier transform (FFT) pattern verified the presence of the (011), (112), and (211) crystal planes of CoP in the heterostructure. The HAADF-STEM image of CoP/Mo_2CT_x is presented in Fig. 1f, and the corresponding energy dispersive X-ray (EDX) elemental mapping (Figs. 1g-I) clearly shows that, all the Co, P, Mo, C, and O elements are uniformly distributed in the sample. Then, the amount of each element was quantitatively determined by ICP-OES, as summarized in Table S1. It is worth noting that, the content of Co element is

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much higher than the value obtained from EDX, probably due to that, the MXene surface is covered by CoP while EDX only detects the surface atoms with a few nanometer depth.

Next, the XRD patterns of the samples were probed. Compared with the Mo₂Ga₂C precursor, the XRD pattern remained almost unchanged for the Mo₂C MXene, except a new broad peak appeared at 7.3° after HF etching (Figure S3).³⁶ It is probably due to that, the removal of Ga caused the increase of the layer spacing in the Mo₂C MXene. As shown in Fig. 2a, for CoP/Mo₂CT_x, the peaks with 20 positioned at 39.4°, 42.8° match well with the Mo₂C MXene planes, while the peaks located at 31.5°, 36.4°, 46.2°, 48.0°, 52.3°, and 56.9° can be attributed to the crystal planes of (011), (111), (112), (211), (103), and (301) for CoP (Standard card: JCPDS No. 29-0497), respectively.³⁹ In addition, the XRD pattern of $Co(OH)F/Mo_2CT_x$ can be found in Figure S4, which is also in good accord with the standard card. The composition and valence state of CoP/Mo_2CT_x were then analyzed by XPS measurements. Fig. 2b shows the high-resolution XPS spectrum of the Co element, where the peaks with binding energy at 778.4 eV and 793.5 eV can be assigned to Co-P, and the peaks at 782.2 eV and 798.2 eV are attributed to Co(II)-O (Inevitable oxidation occurs on the surface of CoP). As illustrated in Fig. 2c, the broad peak for the O1s electrons can be deconvoluted into two peaks with binding energy at 531.5 and 533.0 eV, which are attributable to the hydroxide species and adsorbed O, respectively. Fig. 2d presents the core-level XPS spectrum of the P element, and the peaks with binding energy at 129.1 eV and 129.9 eV can be attributed to the Co-P and PO_x species, respectively.⁴⁰ Figure S5a shows the high-resolution Mo3d XPS spectrum, which can be deconvoluted into six peaks. The peaks with binding energy at 228.8 and 231.9 eV, 229.4 and 232.6 eV, 233.5 and 235.5 eV are attributed to Mo^{2+} , Mo^{4+} , and Mo^{6+} , respectively. The high-resolution C1s XPS spectrum (Figure S5b) shows a broad peak which is deconvoluted into three peaks, where the peak at 286 eV is attributable to C-O bond, the peak at 283.7 eV relates to C-Mo bond, and the peak at 284. 7 eV is ascribed to C-C bond.

Furthermore, as the surface area and porosity characteristics are critical to the electrocatalytic performance, we also conducted the Brunauer-Emmett-Teller (BET) test, in which the surface area was estimated by N₂ adsorption/desorption measurements and the pore size distribution was determined by Barrett-Joyner-Halenda method. As shown in Figure S6, the specific surface area of CoP/Mo_2CT_x is calculated as 46.49 m² g⁻¹, much higher than CoP (7.96 m²g⁻¹), indicating that Mo₂C MXene can significantly boost the surface area for the heterostructure. In addition, the isotherm curve exhibited type IV pattern, suggesting that there are both mesopores and macropores in CoP/Mo₂CT_x. The inset graph of pore size distribution in Figure S6 shows that, the average pore size of CoP/Mo₂CT_x is 1.7-11.8 nm. Such high surface area and well-defined pore structure might be beneficial for the ion and mass transport during the electrochemical reaction.

3.2. Electrocatalytic performance

The HER performance of CoP/Mo₂CT_x was first evaluated through a standard three-electrode system $\mathsf{P}^{1}\mathsf{in}^{10}1.03\,\mathsf{WP}^{1}\mathsf{KOH}_{5}.6\,\mathsf{FO}$ comparison, the various catalysts of CoP, Co(OH)F/Mo₂CT_x, Mo₂C MXene and commercial Pt/C were also investigated under the same conditions. Fig. 3a shows the HER polarization curves, where Pt/C has excellent activity with the lowest overpotential of 23 mV to reach the current density of 10 mA cm⁻². Notably, CoP also exhibits acceptable HER activity, however, CoP/Mo₂CT_x possesses superior HER activity with an overpotential of 78 mV @ 10 mA cm⁻², much lower than that of CoP and the Co(OH)F/Mo₂CT_x precursor. It indicates that, the phosphorization can significantly promote the HER activity and there is synergistic catalytic effect between CoP and the Mo₂C MXene. The reaction kinetic and the rate determining step in the electrocatalytic process can be revealed by Tafel plots, and the Tafel slope can be calculated by linear fitting of the LSV curves according to the Tafel equation: η = b*log j + a.⁴¹ As illustrated in Fig. 3b, the Tafel slope of CoP/Mo₂CT_x is calculated as 66 mV dec⁻¹, lower than that of CoP (95 mV dec⁻¹), Co(OH)F/Mo₂CT_x (158 mV dec⁻¹), and Mo₂C MXene (192 mV dec⁻¹), slightly higher than Pt/C (40 mV dec⁻¹). It indicates CoP/Mo_2CT_x had an enhanced HER kinetics, and the HER process followed the Volmer-Heyrovsky mechanism. The close Tafel slope value with Pt/C suggests that, they probably have the identical reaction pathway, that is, the rate limiting step is the desorption of H₂. The lower overpotential at 10 mA cm⁻² and Tafel slope value of CoP/Mo₂CT_x for HER outperformed the other samples in the series (Fig. 3c), also superior to the recently reported top-level electrocatalysts (Table S2). The exchange current density (j_0) is also an important indicator to evaluate the intrinsic HER activity of the electrocatalyst, and the j_0 value can be obtained by extrapolating the Tafel plot to an overpotential of 0 V (Figure S7). Besides Pt/C, CoP/Mo₂CT_x exhibits the highest j_0 value among these catalysts, indicating that CoP/Mo₂CTx has fast electron-transfer rate and displays favorable HER reaction kinetics. The charge transfer resistance and electronic conductivity can be used to unravel the HER mechanism. EIS analysis was conducted at the same HER experimental condition and the Nyquist plot was fitted via a simplified equivalent circuit model (Fig. 3d). All the fitting parameters in the EIS spectra can be found in Table S3. Note that, the R_{ct} value represents the charge transfer resistance at the electrocatalyst/electrolyte interface. As expected, CoP/Mo_2CT_x exhibited the smallest R_{ct} value and semicircle than those of CoP, Co(OH)F/Mo₂CT_x, and Mo₂C MXene, reflecting a superior kinetic process and enhanced electronic conductivity. Stability is another important parameter to evaluate the performance of the electrocatalyst for long-term test. Fig. 3e shows the chronoamperometric curves tested under the current density of 10 mA cm⁻² for CoP/Mo₂CT_x and Pt/C. According to the *i*-t curve, 89% of the initial current was maintained after a continuous operation of 50 h, while in sharp contrast, Pt/C could only retain 68% of the initial value. Moreover, in the accelerated durability test (ADT, Fig. 3f), CoP/Mo₂CT_x exhibited an extremely small potential shift (10 mV) after 3000 CV cycles of potential scan, superior than that of Pt/C (Inset in Fig. 3f, 15 mV) at the same conditions, implying remarkably excellent long-term durability for HER.

Notably, the feature of the Raman spectra before and after the HER test for CoP/Mo₂CT_x remained almost unchanged (Figure S8), further confirming the robust durability of CoP/Mo₂CT_x for prolonged operation. The SEM and TEM images of CoP/Mo₂CT_x after the HER stability test also reveal negligible morphology and structure change (Figure S9).

The OER performance was also examined in alkaline medium. As shown in the polarization curves in Fig. 4a, the benchmark RuO₂ catalyst demonstrated preferable OER activity, but it was still inferior to that of CoP and CoP/Mo₂CT_x. To afford a current density of 10 mA cm⁻², CoP/Mo₂CT_x only needs an overpotential of 260 mV, lower than that of CoP (290 mV) and RuO₂ (310 mV). Meanwhile, from Fig. 4b, it can be seen that, CoP/Mo_2CT_x also exhibits the lowest Tafel slope (51 mV dec⁻¹), in comparison with CoP (121 mV dec⁻¹), RuO₂ (137 mV dec⁻¹), Co(OH)F/Mo₂CT_x (218 mV dec⁻¹), and Mo₂C MXene (340 mV dec⁻¹), indicating the favourable OER reaction kinetics. Note that, the smallest overpotential and Tafel slope of CoP/Mo₂CT_x for OER is lower than that of recently reported transition metal-based high-performance electrocatalysts (Summarized in Table S4). The turnover frequency (TOF) is an important intrinsic activity and kinetic parameter in OER, and the TOF value of various catalysts at different overpotentials was then caluclated.⁴² As demonstrated in Fig. 4c, the TOF value of CoP/Mo_2CT_x is higher than the other samples at the same overpotentials, suggesting remarkably enhanced OER activity. EIS measurement was then conducted (Fig. 4d), and the fitted results are compiled in Table S5. CoP/Mo_2CT_x exhibited the smallest semicircle, suggesting that the lowest charge transfer impedance. At last, the stability of CoP/Mo_2CT_x for OER was evaluated and compared with the RuO₂ benchmark catalyst. As shown in the chronoamperometric test (Fig. 4e), after about 50 h's measurement, CoP/Mo₂CT_x can preserve much higher initial current density than that of RuO_2 (87% vs. 65%). Such markedly outperformed long-term durability was further validated by the ADT test, as CoP/Mo₂CT_x exhibited an overpotential degradation of 18 mV after 3000 cycles of potential scans, smaller than that of RuO₂ (25 mV) at the same conditions (Fig. 4f). In addition, SEM and TEM images after the OER stability test (Figure S10) disclose that, the structure and morphology of CoP/Mo_2CT_x remained almost unchanged, further confirming the robust stability.

To elucidate the physical origin of the excellent HER and OER activity of CoP/Mo₂CT_x, the specific capacitance (C_{dl}) and electrochemically active surface area values were calculated. As presented in Figure S11 and Figure S12, from the cyclic voltammograms of Mo₂C MXene, CoP, and CoP/Mo₂CT_x in either HER and OER, the current density as a function of scan rate showed a rather linear regression relationship. In either HER or OER test, CoP/Mo₂CT_x possessed much higher C_{dl} values than that of Mo₂C MXene and CoP. As the ECSA value holds a direct proportional relationship with the C_{dl} value, consequently, CoP/Mo₂CT_x had much higher ECSA values for both HER and OER than Mo₂C MXene and CoP, as compiled in Figure S13. To disclose the intrinsic activity

of the catalysts, the mass activity of the samples for $MER_{ARC} OER$ was calculated. As illustrated in Figure S14, COP/MO2CTQ Had field higher mass activity than CoP, Mo₂C MXene, and the Co(OH)F/Mo₂CT_x precursor, also superior to Pt/C for HER and RuO₂ for OER, indicating that Mo₂C MXene as the conducive support can significantly promote both the HER and OER activity.

Inspired by the outstanding HER and OER properties, we constructed a two-electrode water splitting device in alkaline electrolyte using CoP/Mo_2CT_x as both anode and cathode catalysts, which was compared with the benchmark combination of Pt/C deposited on carbon cloth cathode and RuO₂ on anode. Fig. 5a shows the overall water splitting polarization curves of CoP/Mo₂T_x and Pt/C+RuO₂ in 1 M KOH solution with the reacting electrode graph inserted. The bubbles on the two electrodes are H₂ and O₂ generated simultaneously. To reach the current density of 10 mA cm⁻², the cell voltage of CoP/Mo₂CT_x was 1.56 V, which is impressively lower than the precious metal-based catalyst assembled by Pt/C and RuO₂ (1.62 V) and most of the reported toplevel catalysts (Table S6).^{33, 43} In addition to excellent catalytic activity, CoP/Mo₂CT_x showed high stability during a 50 h test at 10 mA cm⁻² in the *i*-t curve (Fig. 5b). CoP/Mo₂CT_x maintained 89% of the initial current, higher than that of the combined Pt/C and RuO₂ catalyst (83%). Finally, in the ADT test in Fig. 5c, the LSV curve shows that only a slight potential shift of 30 mV after continuous operation of 10 h, indicating that CoP/Mo₂CT_x has advantageous durability and stability in alkaline medium. The above results demonstrate that CoP/Mo₂CT_x could be a potent bifunctional catalyst toward practical water splitting.

3.3. Investigation of catalytic mechanism

To obtain the comprehensive mechanistic insights on the excellent catalytic performance, we first conducted DFT calculation to disclose the HER mechanism. The H₂O adsorption, adsorbed water dissociation, and H^* adsorption free energies (ΔG_{H^*}) were performed by employing some simplified models (Figure S15). It is well known that, for HER occurring in alkaline medium, either Volmer-Heyrovsky or Volmer-Tafel mechanism is adopted.44 Nevertheless, the Volmer process takes place in the first step, that is, water molecules are adsorbed onto the catalyst surface with H_{ad} and OH⁻ formed. For the Heyrovsky process: H_{ad} and adsorbed H₂O can react to generate H_2 , while for the Tafel process: two H_{ad} react with each other to form H₂. During the HER process, the adsorption of water molecule, the dissociation of adsorbed water molecule, the adsorption of ${\rm H}_{\rm ad}$ and the desorption of the product are involved. Notably, the water adsorption free energy, the dissociation energy barrier of absorbed water, especially the Gibbs free energy of H_{ad} are directly related to the HER activity of the catalyst. Figs. 6a-c show the Gibbs free energy change of water adsorption and the dissociation of adsorbed water on the surface of CoP, Mo₂C MXene, and CoP/Mo₂CT_x. It can be noted that, CoP/Mo₂CT_x possesses a much lower Gibbs free energy for water adsorption, indicating the heterostructure has a strong affinity to H₂O molecule. Meanwhile, CoP/Mo₂CT_x has a much smaller

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dissociation energy barrier (1.06 eV) than CoP (1.18 eV), suggesting that CoP/Mo₂CT_x is more favourable for the dissociation of the adsorbed water. The Gibbs free energy of H_{ad} of the catalysts is presented in **Fig. 6d**. It can be observed that, CoP/Mo₂CT_x has a Δ G_{H*} value of -0.037 eV, quite close to zero, and the absolute value is much lower than that of Mo₂C MXene and CoP. The above findings demonstrate that, CoP/Mo₂CT_x has enhanced water adsorption, lower water dissociation energy barrier, and especially the optimized H* adsorption free energy, which can drastically promote the Volmer and Heyrovsky process hence boost the HER performance. These calculated results are also in good agreement with the experimental findings.

To further unravel the promoting effect from the MXene support, we also investigated the electron density of states and dband center of CoP/Mo₂CT_x, as compared with CoP. Previous study has disclosed that the DOS intensity of Fermi level is intimately connected with the electrical conductivity.⁴⁵ **Fig. 6e** shows that, the total density of states for CoP/Mo₂CT_x increased significantly, especially in the region near Fermi level. Such enhanced electrical conductivity from CoP/Mo₂CT_x is conducive to rapid electron transfer. Notably, the d-band center (ϵ_d) of CoP and CoP/Mo₂CT_x relative to E_f was calculated as -1.09 eV and -1.23 eV, respectively (**Fig. 6f**), manifesting that the d-band center of CoP/Mo₂CT_x is shifted negatively upon the integration of the MXene support. Such d-band center downshift can result in increased electron filling of the antibonding states, leading to optimized H* adsorption eventually.⁴⁶

We next explored the OER mechanism, where the proposed OER mechanism on the CoP/Mo₂CTx surface is schematically depicted in Fig. 7a. To scrutinize the compositional change of the catalyst, Raman, XPS, IR, XRD, and EDX measurements were conducted after the OER test. As shown in Fig. 7b, in the Raman spectrum, the 508, 608 peaks of Co-O bond can be assigned to Co-OOH.⁴⁷ Meanwhile, spin-orbit splitting in Fig. 7c shows that, the Co-P peak disappeared after oxidation, and two new peaks appeared, which can be deconvoluted with four sub-peaks at 780.2, 781.5, 795.4, and 796.5 eV. It further confirms the presence of the Co-OOH species after OER. As presented in Fig. 7d in the highresolution O1s XPS spectrum, the peaks with binding energy at 531.5 eV and 533 eV are from hydroxides and adsorbed oxygen, and a new peak appeared at 529.3 eV, which is the characteristic feature of Co-O. In contrast, the anionic components changed dramatically, and the characteristic peak of Co-P (Fig. 7e) disappeared after the OER test, whereas only the peak at 133.5 eV attributed to P-O_x remained.⁴⁰ The IR spectra of the CoP/Mo₂CT_x sample after OER can be found in Figure S16, where the peaks at 3420, 3646, 1629, and 590 cm⁻¹ are from -OH, O-H, Co-O, and Co-O₂ in CoOOH, respectively.⁴⁸ All the above results clearly show that Co hydroxide is gradually formed during the prolonged OER process, and PO_x is also formed on the surface of the catalyst. Notably, several recent reports have documented that, CoP can be reconstructed into Co-OOH during the OER catalysis.49, 50 We

further tested the catalyst after OER through XRD measurement As depicted in Figure S17, the peaks with 20 positioned are 20°7 39% and 51° belong to the (003), (012), (015) crystal plane of β -CoOOH, verifying the formation of CoOOH. The element content of the catalyst before and after the OER test was studied by EDS mapping (Figure S18 and Figure S19). It can be noted that, after the OER test (Table S1), the content of P decreased from 25.02% to 4.48%, the content of oxygen increased from 17.45% to 30.04%, and the anionic component also decreased significantly, which are in good consistence with the above finding.

4 Conclusions

In summary, a facile and straightforward method is developed to grow CoP nanoarrays onto the surface of MXene and the obtained CoP/Mo₂CT_x catalyst has excellent HER, OER, and overall water splitting properties, outperforming the Pt/C+RuO₂ combined benchmark catalyst. For HER, DFT calculations disclosed that, CoP/Mo₂CT_x has the appropriate water adsorption especially the optimal H* adsorption free energy (ΔG_{H^*}). Particularly, the Mo₂C MXene support can significantly increase the surface area and boost the electronic conductivity of the CoP/Mo₂CT_x catalyst hence dramatically increase the total density of states and downshift the d-band center. For OER, it was found that, CoP in the catalyst is transformed into Co-OOH during the electrocatalytic process. This study can pave a pathway for preparing MXene-supported noblemetal-free bifunctional catalyst toward practical water splitting and energy conversion.

Conflicts of interest

There are no conflicts to declare.

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Scheme 1. The schematic illustration for preparing the CoP/Mo_2CT_x catalyst.

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Fig. 1. (a)-(c) Representative SEM images of Mo_2C MXene, CoP, and CoP/ Mo_2CT_x . (d) and (e) Representative TEM image of CoP/ Mo_2CT_x with different magnifications. (f) HR-TEM image of CoP and (f, inset) corresponding FFT pattern of CoP, displaying lattice fringes and diffraction spots for CoP. (g) HAADF-STEM and (h)-(l) corresponding elemental mapping of Co, P, Mo, C, and O in CoP/ Mo_2CT_x .



Fig. 2. (a) XRD patterns of the Mo₂C MXene, and CoP/Mo₂CT_x. (b)-(d) High resolution XPS spectra of the Co 2p, O 1s, and P 2p electrons for CoP/Mo₂CT_x.



Fig. 3. (a) LSV curves, (b) Tafel plots, (c) The Tafel slope and overpotential @10 mA cm⁻² for Pt/C, CoP/Mo₂CT_x, CoP, Co(OH)F/Mo₂CT_x, Mo₂C MXene in 1 M KOH. (d) The electrochemical impedance spectra (EIS), (e) Chronoamperometric curves of CoP/Mo₂CT_x and Pt/C at the current density of 10 mA cm⁻² for 50 h. (f) LSV curves of CoP/Mo₂CT_x catalyst before and after 3000 CV cycles and inset is the corresponding LSV curves before and after 3000 CV cycles for Pt/C.

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Fig. 4. (a) LSV polarization curves and corresponding Tafel plots (b) of CoP/Mo₂CT_x, CoP, RuO₂, Co(OH)F/Mo₂CT_x, and Mo₂C MXene in 1 M KOH. (c) The turnover frequency (TOF) per surface site for different catalysts in 1 M KOH at various overpotentials. (d) The electrochemical impedance spectra (EIS), (e) Stability test at a current density of 10 mA cm⁻² for 50 h. And (f) corresponding LSV curves of CoP/Mo₂CT_x catalyst before and after 3000 CV cycles and inset is corresponding LSV curves before and after 3000 CV cycles for RuO₂.



Fig. 5. (a) LSV curves for water splitting cell consisting of CoP/Mo_2CT_x (+,-) and RuO_2 (+)||Pt/C(-) in 1 M KOH, the inset is the device photograph of the electrolyzer using CoP/Mo_2CT_x for both the anode and cathode catalyst. (b) Chronoamperometric analysis for water electrolysis catalyzed by CoP/Mo_2CT_x and RuO_2+Pt/C at 1.56 V. (c) LSV curves for CoP/Mo_2CT_x before and after the electrolysis test.

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Fig. 6. The energy barriers for water dissociation on the surface of (a) CoP (011), (b) $Mo_2C MXene and (c) CoP/Mo_2CT_x$, the inside are the views of the structures of initial states (IS), transition states (TS), and final states (FS), (d) ΔG_{H^*} calculated at the equilibrium potential of different models, (e) TDOS of CoP and CoP/Mo₂CT_x, (f) pDOS of d-state (the white bar shows d-band center, ϵ_d) of CoP and CoP/Mo₂CT_x.



Fig. 7. (a) Formation of the active layer reconstruction on CoP/Mo_2CT_x during OER. (b) Raman spectra of CoP/Mo_2CT_x after OER test. (c)-(e) High resolution XPS spectra of the Co 2p, O 1s, and P 2p electrons for CoP/Mo_2CT_x after the OER test.