2D Nanomaterials

Mosaic-Structured Cobalt Nickel Thiophosphate Nanosheets Incorporated N-doped Carbon for Efficient and Stable Electrocatalytic Water Splitting

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Engineering the nanostructures and compositions of 2D layered metal thiophosphates (MTPs) is significant for extending their applications. Here, a scalable and flexible strategy is presented to prepare single crystalline CoNiPS₃ incorporated with N-doped carbon (CoNiPS₃/C) nanosheets (≈16 nm thickness), which can be further processed into the mosaicstructured CoNiPS₃/C nanosheets (≈6 nm thickness) composed of randomly distributed crystalline nanodomains (≈15 nm diameter) and disordered boundaries (denoted as mosaic CoNiPS3/C nanosheets), and further into separated CoNiPS₃/C nanodots (≈4 nm diameter). The initial CoNiPS₃/C nanosheeets are prepared by using Co-Ni Prussian-blue analogue nanoplates as templating precursors. As compared to the initial CoNiPS₃/C nanosheets and nanodots, the mosaic CoNiPS₃/C nanosheets exhibit plenty of active edge sites, retained crystallinity, and good structural stability. Synergistically, density functional theory calculations reveal that the bimetallic composition results in higher intrinsic activity, better conductivity, and lower kinetic energy barriers for bifunctional oxygen/hydrogen evolution reactions. More importantly, a water-splitting electrolyzer constructed using the mosaic CoNiPS₃/C nanosheets as both cathode and anode achieves 30 mA cm⁻² at 1.62 V, which is better than the initial CoNiPS₃/C nanosheets (1.69 V) and is comparable to the discreted nanodots (1.58 V). Besides, the mosaic CoNiPS₃/C nanosheets show much better electrocatalytic stability than nanodots.

1. Introduction

Due to the high efficiency, simplicity, and environmental friendliness, electrocatalytic overall water splitting is being vigorously pursued as one of the most sustainable technologies through producing clean and renewable gaseous hydrogen

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and oxygen in large scale.^[1-7] In order to achieve high energy conversion efficiency, the state-of-the-art electrolyzer usually needs highly active electrocatalysts to simultaneously lower energetic barriers of hydrogen/oxygen evolution reaction (HER/OER). However, since overall water splitting process is an uphill reaction, the commercial electrolyzer still requires a much higher operating voltage (≈ 2.0 V) than theoretical value (≈1.23 V) even with the costly Pt and IrO₂ or RuO₂ as the benchmark HER and OER electrocatalysts, respectively.^[8-15] As such, developing highly efficient, stable, and cost-effective electrocatalysts for overall water splitting is of crucial importance to advance the prospects of this fascinating technology.

Recently, various cost-effective transition metal based electrocatalysts have received considerable attention for HER and OER because of their environmentally benign nature and easy availability.^[16–21] Particularly, lamellar metal thiophosphates (MTPs), a new family of ternary 2D nanomaterial, are emerging as highly attractive electrocatalysts due to the good activity, earth abundance, and compositional diversity.^[5,20,22–27] Despite advances in

individual metrics for HER or OER through various strategies,^[22,23,28,29] the performance of MTPs as bifunctional electrocatalysts for HER/OER is still far from satisfactory. According to the fundamental principles of HER/OER reactions, the electrocatalytic water-splitting activity is dependent on many other factors, such as the intrinsic electronic structure, electrical conductivity, accessible active sites, and reaction energy barriers, which are highly related to the internal chemical composition, external morphological features, exposed surface and edges, and interfacial modification. Hence, there are multiple effective strategies to improve water splitting performance of MTP electrocatalysts: 1) our density functional theory (DFT) calculations demonstrate that the single-phased MTPs with mixed metal cations show more favorable electronic structures, lower energy barriers, and higher intrinsic electrocatalytic activity for water splitting than the counterparts with single metal cation (see discussion below); 2) decreasing lateral size or thickness is an effective way to increase the number of exposed edges that has been identified as the active sites toward HER of MTP electrocatalysts^[26,30]; 3) introducing boundaries while maintaining original electron conjugated system is beneficial for exposing more accessible surface and accelerating mass transport as well as maintaining fast electron transfer along two-dimension plan for 2D electrocatalysts^[31–33]; 4) incorporating conductive carbon layer could further improve electron and mass transfer as well as structural stability of MTPs during long-term cycling process.

In consideration of the above merits, we here show an easy approach for realizing compositional, morphological, lattice structural, and interfacial engineering of MPTs. Particularly, mosaic structured CoNiPS3 nanosheets (~6 nm thickness) composed of numerous randomly distributed crystalline nanodomains (≈15 nm), which are connected by disordered boundaries embedded in N-doped carbon matrix (denoted as mosaic CoNiPS₃/C nanosheets) were designed for efficient and stable overall water splitting. The mosaic CoNiPS₃/C nanosheets were produced by an easy sonication of singlephased CoNiPS₃/C nanosheets in water, which were prepared by using the Co-Ni Prussian-blue analogues (PBA) templating precursors. The resultant mosaic CoNiPS₃/C nanosheets show an average thickness of ≈ 6 nm and a lateral size of ≈ 130 nm. Coupled with intrinsic electronic benefits and external structural advantages, the mosaic CoNiPS₃/C nanosheets were demonstrated to be an efficient bifunctional electrocatalyst for HER/OER in 1.0 M KOH with low overpotentials of 140 mV for HER and 262 mV for OER at 30 mA cm⁻², and Tafel slopes of 60 mV dec⁻¹ for HER and 56 mV dec⁻¹ for OER, respectively. More significantly, using the mosaic CoNiPS₃/C electrode as both cathode and anode, a two-electrode setup with 1.0 M KOH electrolyte for overall water splitting affords a current density of 30 mA cm⁻² at 1.62 V as well as good stability with 89.2% retention for 28 h. The generality and scalability of the preparation method coupled with the remarkable water splitting performance enable the mosaic CoNiPS₃/C nanosheets to be a promising candidate for future applications.

2. Results and Discussion

We intend to combine two or more different metal cations together to build the MTP compounds as multifunctional electrocatalysts due to the better electrical conductivity and richer redox reactions. To rational design such MTPs, we first performed theoretically calculations with density functional theory (DFT) using VASP software (Vienna ab initio simulation package).^[34,35] As shown in **Figure 1**a, all the total density of states (TDOS) calculated for CoPS₃, NiPS₃, CoNiPS₃ are discontinuous near the Fermi levels (E_f) , suggesting the semiconductor features of these compounds. Notably, the bimetallic CoNiPS₃ shows a smaller energy band of 1.47 eV than CoPS₃ (1.62 eV) and NiPS₃ (1.51 eV), suggesting a higher conductivity of CoNiPS₃. Moreover, the valence band edge of CoNiPS₃ is much closer to the $E_{\rm f}$ than that of CoPS₃ and NiPS₃, indicating the faster electron transfer of CoNiPS₃. To further confirm this, the projected density of states (PDOS) for Ni and Co near the $E_{\rm f}$ were compared in Figure 1b. The CoNiPS₃ shows higher PDOS intensity than CoPS₃ and NiPS₃ (insets in Figure 1b), suggesting more carriers available in CoNiPS₃ than that of CoPS₃ and NiPS₃.^[36] Moreover, an obviously different PDOS of Co or Ni after coupling in CoNiPS₃ also indicates the change of 3d e_g filling states of metals (blue rectangle in Figure 1b), resulting in greatly improved intrinsic activity due to the better electronic interaction with intermediates in electrocatalysis.^[31,37]

To verify this, DFT calculations were further conducted to estimate the kinetics energy barriers of key reactions for water splitting at atomic scale. We first simulated the hydrogen adsorption free energy (ΔG_{H*}) of CoPS₃, NiPS₃, and CoNiPS₃ electrocatalysts, which is directly related to the HER activity. The calculations of static absorption energy show that the hydrogen atom is preferable to be adsorbed on edge sites of CoNiPS₃ than on the basal surface (Figure 1c), according well with previous report.^[26] The optimized free energy diagram at equilibrium reveals that the smallest absolute ΔG_{H^*} values for each H* adsorption determined for CoPS₃, NiPS₃, and CoNiPS₃ are 0.12, 0.40, and 0.20 eV, respectively (Figure 1d). The smaller ΔG_{H^*} values of CoPS₃ and CoNiPS₃ than NiPS₃ indicate their lower energy barriers for H₂ formation during HER. Furthermore, as shown in Figure S1 (Supporting information) the adsorption energy calculations of H₂O molecular on the surface of CoPS₃, NiPS₃, and CoNiPS₃ reveal that CoNiPS₃ possesses a similar value as NiPS₃ (-0.19 eV). However, this value is lower than that for CoPS₃ (-0.16 eV), suggesting that the water adsorption on the surface of CoNiPS₃ is more energetically favored (Figure 1d). The smaller ΔG_{H^*} and lower water adsorption energy contribute to much faster mass and charge transfer of CoNiPS₃ than those of CoPS₃ and NiPS₃.^[9] These DFT calculation results confirm that CoNiPS₃ is a promising candidate with improved intrinsic electronic structure, better conductivity, and lower energy barriers than NiPS₃ and CoPS₃ for electrocatalytic water splitting.

The theoretical calculation results motivate us to develop the single-phased CoNiPS3 with bimetallic composition as electrocatalysts for overall water splitting. In our case, the CoNiPS3 was prepared by one-step simultaneous phosphorization and phosphorization of the Co-Ni Prussian-blue analogues (PBA) as templating precursor. Typically, the Co-Ni mixed PBA nanosheets were prepared in large scale by a citrate-mediated crystallization approach at room temperature (see detail in the Experimental Section and Figure S2 (Supporting information)).[38] The asprepared Co-Ni PBA nanosheets are uniform with an average size and thickness about 400 and 40 nm, respectively (Figure S3, Supporting information). Afterwards, the resultant Co-Ni PBA nanosheets were well placed separately with phosphor and sulfur inside an evacuated quartz tube sealed with Partulab MRVS-1002 system. After thermal treating process, the Co-Ni PBA nanosheets were chemically converted into CoNiPS3 as a result of the simultaneous phosphorization and sulfurization processes. Simultaneously, due to the uniform distribution of cyano groups in the Co-Ni PBA precursors, the derived CoNiPS3 are evenly incorporated with amorphous N-doped carbon.

The phase of the as-obtained $CoNiPS_3$ was first characterized by X-ray diffraction (XRD). As shown in **Figure 2**, there are numerous strong diffraction peaks accompanied with a weak bump centered at about 25° in the XRD pattern. In order to index these strong diffraction peaks, Rietveld refinement was







Figure 1. a) The calculated TDOS for the CoNiPS₃, CoPS₃, and NiPS₃. b) The PDOS for Ni and Co obtained from DFT + U calculations of CoPS₃, NiPS₃, and CoNiPS₃. c) Atomic models for hydrogen atoms absorbed on the edge of CoPS₃, NiPS₃, and CoNiPS₃. d) The DFT calculated absolute ΔG_{H^*} and H₂O molecular absorption energies of CoPS₃, NiPS₃, and CoNiPS₃. The insets in inset (b) are the enlarged projected DOS near Fermi level. The mainly exposed (001) facets was used for calculating the water absorption energy. The most stable (110) facets were used for calculating the edge models.

performed by using the monoclinic NiPS₃ with C12/m1 space group as the initial crystal structural model. As expected, the sample preserves the structural framework of monoclinic NiPS₃ with layered structure, but with uniformly distributed Co and Ni cations (inset in Figure 2). The extracted lattice parameters are a = 5.7346(6) Å, b = 9.9305(3) Å, c = 6.5289(6)Å, and $\beta = 107.155(2)^{\circ}$. The final refined reliability factors are $R_{\rm p}$ = 2.07%, $R_{\rm wp}$ = 2.85%, and $R_{\rm exp}$ = 1.73%, indicating the formation of single-phased CoNiPS₃ without any other crystalline impurity. Noted that the broad hump at about 25° comes from amorphous carbon. To further verify the generality of this preparation strategy, the single-phased FeNiPS₃ and MnNiPS₃ were prepared by a similar process using the bimetallic Fe-Ni and Mn-Ni PBA as precursors, respectively. As demonstrated by the XRD patterns (Figure S4, Supporting information), the as-obtained FeNiPS₃ and MnNiPS₃ also retain monoclinic structures without any other detectable impurity. In order to make more concise, the CoNiPS₃/C was typically studied as in this work unless otherwise specified.

X-ray photoelectron spectroscopy (XPS) was performed to reveal the chemical composition and bonding configurations of the resultant CoNiPS₃/C. The survey XPS profile shows the presence of Co, Ni, P, S, C, N, and O elements in the CoNiPS₃/C (Figure S5, Supporting information). The atomic ratio of Co:Ni is ≈0.98, which is close to that of the Co-Ni PBA precursor (≈1.0), indicating a complete transformation of Co-Ni PBA to CoNiPS₃ after reaction. The atomic percentage of C is about 6.2%. The high-resolution Ni 2p XPS spectrum can be deconvoluted into six typical components at 881.5, 876.5, 872.6, 863.0, 858.1, and 845.8 eV (Figure 3a), corresponding to the spin-orbit doublets of 2p1/2 and 2p3/2 and their shakeup satellites from Ni²⁺ species, respectively.^[39] The high-resolution Co 2p XPS profile can also be fitted into six typical peaks at 803.5, 800.5, 797.7, 786.0, 782.9, and 780.7 eV (Figure 3b), attributing to the spin-orbit doublets of 2p1/2 and 2p3/2 and the corresponding shakeup satellites from Co2+ species, respectively.[40-42] The P 2p XPS spectrum can be resolved into two peaks at 133.2 and 132.3 eV (Figure 3c), ascribing to the 2p1/2 and 2p3/2 species







Figure 2. XRD pattern and the Riteveld refinements of the $CoNiPS_3/C$ nanosheets. The inset is the corresponding crystal structure of bimetallic $CoNiPS_3$.

of P4-.[43,44] The high-resolution S 2p XPS profile shows two components at 163.6 and 162.4 eV (Figure 3d), corresponding to the 2p1/2 and 2p3/2 species of S2-.[40,45-47] Besides, the C 1s XPS spectrum contains three peaks at 289.2, 286.2, and 285.0 eV (Figure 3e), which can be attributed to the C-C, C-N, and C-O species, respectively.^[48,49] This is also confirmed by the high-resolution N 1s XPS profile with one fitting peak at 401.8 eV (Figure 3f).^[50,51] The incorporation of carbon in the CoNiPS₃/C is further verified by Raman test. As shown in Figure 3e, the Raman spectrum of the CoNiPS₃/C contains several small sharp peaks below 600 cm⁻¹, corresponding to the characteristic E_{g} and A_{1g} bands due to the different vibrations of PS3 ligands (insets in Figure 3g).^[52] Two strong broad peaks centered at 1350 (D-band) and 1460 cm⁻¹ (G-band) of the Raman spectrum confirm the presence of carbon species.^[48] Notably, the much stronger intensity of D band than that of G band can be explained by the numerous defects in the amorphous carbon because of the N-doping of C sp² scaffold,^[48] agreeing well with the XPS results. The XRD test coupled with XPS and Raman measurements confirm the sample is singlephased CoNiPS3 incorporated with N-doped carbon.

The field-emission scanning electron microscope (FESEM) image in low magnification shows that the CoNiPS₃/C is nanosheet structure with the lateral size of 50–200 nm (**Figure 4**a). The magnified FESEM image reveals that the average thickness of the CoNiPS₃/C nanosheets is about 16 nm (inset in Figure 4b). Note that both the lateral size and the thickness of the Co-NiPS₃/C nanosheets are much smaller than those of the Co-Ni PBA precursors (Figure S3, Supporting information). This is attributed to the obvious volume shrinkage caused by the chemical conversion reaction accompanied with the carbonization of cyano groups. The corresponding energy dispersive X-ray (EDX) pattern shows the presence of C, N, Co, Co, P, S, and O elements of the CoNiPS₃/C nanosheets with the XPS results.

The panoramic transmission electron microscope (TEM) image clearly shows the lamellar structure of the CoNiPS₃/C nanosheets with the average lateral size of ≈ 130 nm (Figure 4c). The EDX elemental mapping took from the high angle annular dark field scanning TEM images indicate the uniform distribution of Ni, Co, P, and S throughout the CoNiPS₃/C nanosheets (Figure S7, Supporting information). Moreover, as shown in Figure 4d, the high-resolution TEM (HRTEM) image clearly shows two sets of lattice fringe with distances about 0.51 and 0.49 nm, corresponding to the *d*-spacing of the (020) and (110)atomic planes, respectively. This is also consistent with the characterization by the affiliated selected area electron diffraction (SAED) of one single CoNiPS3/C nanosheet, showing regular bright spots with hexagonal symmetry (Figure 4e). The HRTEM image and SAED pattern also indicates the CoNiPS₃ nanosheets are single-crystalline structure exposed with (001) facets along their primary surfaces. Besides, the HRTEM image of the edge reveals that the CoNiPS3 nanosheets are tightly covered by amorphous carbon layer of about 2 nm in thickness (Figure 4f). Such an incorporation of carbon layer is very helpful for improving the charge transfer efficiency retarded by the semiconductive feature of the CoNiPS₃ during electrocatalytic process. More importantly, the carbon layer enables the CoNiPS₃ nanosheets to be very stable without decomposition even placing in water for over longer than six month (Figure S8, Supporting information).

Since the electrocalytic activity is highly correlates with the number of active sites, the exposure of more surface and edges by decreasing the lateral size or thickness and introducing subtle distortion of atomic arrangement and grain boundaries could further improve the electrocatalytic performance of the CoNiPS₃/C nanosheets. On this consideration, we tried to process the CoNiPS₃/C nanosheets with sonication in water. As shown in **Figure 5**, depends on process time, we obtained ultrathin nanosheets (≈ 6 nm thickness) and ultrasmall



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Figure 3. a) High-resolution Ni 2p, b) Co 2p, c) P 2p, d) S 2p, e) C 1s, and f) N 1s XPS spectra and d) Raman spectrum of the CoNiPS₃/C nanosheets. The insets in inset (g) show three different kinds of vibrational amplitudes in A_{1g} modes of CoNiPS₃.

nanodots (\approx 4 nm diameter). After sonication, the as-produced thinner nanosheets still show incorporation of carbon layer (\approx 2 nm thickness) and the retained monoclinic crystal structure of CoNiPS₃ (Figure 5a; Figure S9, Supporting information), confirming the good stability of CoNiPS₃/C nanosheets in water. Notably, the HRTEM images (Figure 5b) and corresponding fast Fourier transform patterns (Figure S10, Supporting information) reveal that the as-derived thinner CoNiPS₃

nanosheets show a mosaic structure. The mosaic-structured CoNiPS₃/C nanosheets (denoted as mosaic CoNiPS₃/C nanosheets) are composed with numerous randomly distributed crystalline nanodomains (\approx 15 nm diameter), which are connected by disordered boundary regions in the basal plane. Notably, the disordered regions cause subtle lattice distortion of the adjacent crystalline domains, as reflected by an obviously different lattice spacing of (020) plane between the near and







Figure 4. a,b) SEM, c) TEM, d) HRTEM images, and e) SAED pattern of the CoNiPS₃/C nanosheets, and f) HRTEM image of the amorphous carbon layer. The inset in inset (b) is the enlarged SEM image of one standing nanosheet with the thickness of \approx 16 nm.

far from disordered boundaries (Figure 5c). The formation of the mosaic structures could be attributed to the following two reasons. On one hand, the mismatch in the degree of Jahn-Teller distortion between Co-S and Ni-S coordination could possibly cause internal strain.^[53] As such, some coordinatively unsaturated Co or Ni metal centers will be produced as a result of disordered atomic arrangements under external force. On the other hand, the strong shear stress of the high-energy sonication could cause the partial cracking of crystal lattices and the fracture of covalent chemical bonds of the ultrathin CoNiPS3 nanosheets, as previously demonstrated in preparation nanodots of graphene oxide, MoS₂, and black phosphorus.^[54-58] As shown in Figure 5d, we also obtained ultrasmall nanodots (≈4 nm average) with similar composition after sonication for more than 6 h and followed with a density gradient centrifugation process (Figure S11, Supporting information). The HRTEM image and SAED pattern confirm that these nanodots also retain the crystal structure of CoNiPS₃ (Figure 5e,f). Notably, the ultrathin nanostructures, disordered boundaries, subtle lattice distortion, and carbon incorporation enable the mosaic CoNiPS3 nanosheets with abundant exposed surfaces and active edge sites, original 2D electronic system, retained crystallinity, and good structural stability.

Subsequently, the electrocatalytic activity of the mosaic CoNiPS₃/C nanosheets was evaluated by a standard

three-electrode system in an alkaline electrolyte (1.0 M KOH). The samples deposited on glass carbon electrodes and a high-purity graphite rod were used as the working and counter electrodes, respectively. For comparison, the initial CoNiPS₃/C nanosheets, the ultrasmall nanodots, and the NiPS₃/C nanosheets prepared by a similar method were also tested as well. Figure 6a shows the typical HER polarization curves obtained by steadystate linear sweep voltammetry (LSV) measurements. Among them, the NiPS3/C shows poor HER performance with a very high onset potential over 330 mV versus RHE, agreeing well with above DFT calculations. In comparison, other samples show much lower onset potentials and overpotentials. Particularly, to afford a Cathodic current density of 30 mA cm⁻², the applied potentials required for the mosaic CoNiPS₃/C nanosheets, nanodots, and the CoNiPS₃/C nanosheets, are 140, 136, and 216 mV (versus RHE). Notably, as shown in Figure 6b, the Tafel slopes obtained by Tafel equation unravel that the mosaic CoNiPS3 nanosheets show the fastest HER kinetics with a smaller Tafel slope of 60 mV dec⁻¹ than the nanodots (98 mV dec⁻¹), CoNiPS₃/C nanosheets (66 mV dec⁻¹), and NiPS₃/C nanosheets (76 mV dec⁻¹). This indicates the much better charge transfer of the mosaic CoNiPS₃/C nanosheets, agreeing well with the electrochemical impedance spectroscopy tests that show the lowest reaction resistance of the mosaic CoNiPS₃/C electrode (Figure S12, Supporting information).







Figure 5. a) TEM and b,c) HRTEM images of the mosaic $CoNiPS_3/C$ nanosheets. d) TEM, e) HRTEM images, f) SAED pattern of the $CoNiPS_3/C$ nanodots. The circles marked in inset (b) show the disordered region. The insets in inset (c) show subtle lattice distortion reflected by the different spacing of (020) facets near and far from disordered boundaries.

More importantly, the potentiostatic test shows that a more stable current density is obtained for the mosaic CoNiPS₃/C nanosheets than the CoNiPS₃/C nanodots (Figure S13, Supporting information). The SEM, HRTEM, and EDS characterizations reveal that the mosaic CoNiPS₃/C nanosheets still maintain the original phase and structure after long-term HER testing (Figures S14–S16, Supporting information), suggesting the good structural stability during the electrocatalytic HER process. Besides, the mosaic CoNiPS₃/C nanosheets also show better HER performance than CoPS₃/C sample (Figure S17, Supporting information).

In addition to the efficient and stable HER performance, the mosaic CoNiPS₃/C nanosheets also show good performance for OER in alkaline electrolyte. We further evaluated the OER performance of these samples in the same electrolyte. As shown in Figure 6c, an obvious anodic peak around 1.40 V (versus RHE) assigned to the Ni²⁺/Ni³⁺ redox reaction can be clearly observed in the LSV profiles of all samples.^[22,59] Specifically, the mosaic CoNiPS₃/C nanosheets also show much better OER

activity with a smaller overpotential of 262 mV at 30 mA cm⁻² than the NiPS₃/C (330 mV) and CoNiPS₃/C nanosheets (285 mV), and comparative performance as the nanodots (250 mV). As shown in Figure 6d, the OER Tafel slope of the mosaic CoNiPS₃/C nanosheets (56 mV dec⁻¹) is close to that of the initial CoNiPS₃/C nanosheets (60 mV dec⁻¹) and nanodots (53 mV dec⁻¹), and is much smaller than that for the NiPS₃/C nanosheets (70 mV dec⁻¹), indicating the faster OER kinetics of the mosaic $CoNiPS_3/C$ nanosheets and nanodots that have both bimetallic composition and more active sites. The electrochemically active surface area (ECSA) tests reveal that the mosaic CoNiPS₃/C nanosheet (12.3 mF cm⁻²) and nanodots (14.2 mF cm⁻²) show much larger EASAs than the CoNiPS₃/C (4.2 mF cm⁻²) and NiPS₃/C nanosheets (3.3 mF cm⁻²), as shown in Figure S18 in the Supporting information. The normalized current densities to the ECSA show a higher value in the mosaic CoNiPS3/C nanosheets. This also verifies that the much higher density of active sites in the mosaic CoNiPS₃/C nanosheet contributes to the high electrocatalytic





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Figure 6. a) HER polarization curves, b) corresponding Tafel plots, c) OER polarization curves, d) corresponding Tafel plots, and e) polarization curves for water splitting of NiPS₃/C, CoNiPS₃/C, the mosaic CoNiPS₃/C nanosheets, and nanodots. The inset in (e) is the optical image of water electrolysis using the mosaic CoNiPS₃/C nanosheets both as cathode and anode. f) The chronoamperometric curves of the mosaic CoNiPS₃/C nanosheets and nanodots for electrocatalytic water splitting.

activity. Notably, the potentiostatic tests also indicate that the mosaic CoNiPS₃/C nanosheets show much better stable OER performance than the nanodots (Figure S19, Supporting information), suggesting that the better structural stability of the mosaic CoNiPS₃/C nanosheets than nanodots during long-term OER process in alkaline electrolyte. The SEM and TEM observations also confirm the morphology and structure of the mosaic CoNiPS₃/C nanosheets retained after long-term OER potentiostatic test (Figure S14, Supporting information). Besides, the HRTEM image verifies the still existence of mosaic microstructure accompanied with possible formation of thin

layer of nickel (cobalt) hydroxides on the surface after the OER test (Figure S16, Supporting information). In comparison, the CoNiPS₃/C nanodots became amorphous after long-term OER test (Figure S20, Supporting information), suggesting that the poor crystallinity results in serious corrosion and oxidation of the nanodots during the long-term OER test. More indicatively, the much larger ECSA of the mosaic CoNiPS₃/C nanosheets (11.2 mF cm⁻²) than that of nanodots (5.6 mF cm⁻²) after long-term electrolysis suggests the robust ECSA of the mosaic CoNiPS₃/C nanosheets in alkaline solution, accounting for the stable electrocatalytic performance.



Based on above electrocatalytic results, the remarkable bifunctional activity of the mosaic CoNiPS3/C nanosheets can be rationalized as follows: 1) the bimetallic composition enables the CoNiPS₃ with higher intrinsic activity, better conductivity, and lower energy barriers; 2) the unique mosaic and ultrathin nanostructures provide more active edge sites and larger ECSA that are helpful for fast mass transfer; 3) the interconnected crystalline domains maintain the original electronic structure and structural stability of the 2D plane, which can facilitate the electron transfer and improve electrocatalytic stability; 4) the incorporation of N-doped carbon not only increases the electronic conductivity but also improve the charge transfer and structural stability for the interfacial electrocatalytic reaction in alkaline electrolyte. Overall, these combined factors synergistically contribute to efficient and stable electrocatalytic water splitting performance of the mosaic CoNiPS₃/C nanosheets.

Motivated by the extraordinary bifunctional electrocatalytic performance of the mosaic CoNiPS3/C nanosheets for HER/ OER, we further constructed an alkaline electrolyzer to evaluate the electrocatalytic performance for overall water splitting. The electrocatalyst loaded on clean Ni foam support was explored as both cathode and anode. Pure Ni foam was tested for comparison. As shown in Figure 6e, the mosaic CoNiPS₃/C nanosheets achieve a current density of 30 mA cm⁻² at a voltage of 1.62 V. This value is very close to that of the nanodots (1.56 V) and is much smaller than that of the initial CoNiPS₃/C nanosheets (1.70 V), NiPS₃/C nanosheets (1.83 V), and Ni foam (1.96 V). The mosaic CoNiPS₃/C nanosheets also outperforms many newly developed electrocatalysts for overall water splitting (Tables S1, Supporting information). A further increase of the applied voltage is accompanied by the significant increase of the current density, as demonstrated by releasing of abundant oxygen and hydrogen bubbles from the electrode surfaces (inset in Figure 6e and Movie, Supporting information). More importantly, the durability of water electrolysis revealed by long-term potentiostatic tests shows a much more stable performance of the mosaic CoNiPS₃/C nanosheets than the nanodots. Typically, 89.2% retention of current density is obtained of the mosaic CoNiPS₃/C nanosheets at 30 mA cm⁻² for 28 h (Figure 6f). While the current density of the nanodot electrodes decreased continuously to a retention of 48.3% after 28 h. This is caused by the continually decreased HER/OER performance of the nanodots during the chronoamperometric test. Such efficient and stable overall water-splitting performance enables the mosaic CoNiPS₃/C nanosheets to be promising electrocatalysts for the practical and long-term applications.

3. Conclusions

In conclusion, we have developed an easy approach for engineering the nanostructures and chemical compositions of 2D ternary MTPs to simultaneously meet the electrocatalytic performance and stability for water splitting. Exemplified by the mosaic CoNiPS₃/C nanosheets, the bimetallic composition contributes to the improved intrinsic activity, better conductivity, and lower energy barriers for electrocatalytic HER/OER, as demonstrated by DFT calculations. The mosaic structure composed of numerous crystalline nanodomains connected by

disordered boundaries, as revealed by HRTEM, provides abundant active edge sites and highly exposed surfaces, ensuring of fast HER/OER kinetics. Furthermore, the in situ formed carbon incorporation enables the mosaic CoNiPS₃ nanosheets with better conductivity as well as remarkable structural stability. As expected, when explored as electrocatalyst for overall water splitting, the mosaic CoNiPS₃/C nanosheets deliver a durable current density of 30 mA cm⁻² at 1.62 V. This work demonstrates further inspiration for developing MTPs with tunable compositions and nanostructures for achieving high electrocatalytic activity towards overall water splitting.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D nanosheets, DFT calculations, metal thiophosphates, nanodots, water splitting

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- W. Li, X. Gao, D. Xiong, F. Wei, W.-G. Song, J. Xu, L. Liu, Adv. Energy Mater. 2017, 7, 1602579.
- [2] Y. Xu, M. Kraft, R. Xu, Chem. Soc. Rev. 2016, 45, 3039.
- [3] S. Dou, C.-L. Dong, Z. Hu, Y.-C. Huang, J.-I. Chen, L. Tao, D. Yan, D. Chen, S. Shen, S. Chou, S. Wang, *Adv. Funct. Mater.* **2017**, *27*, 1702546.
- [4] Y. Wu, X. Liu, D. Han, X. Song, L. Shi, Y. Song, S. Niu, Y. Xie, J. Cai, S. Wu, J. Kang, J. Zhou, Z. Chen, X. Zheng, X. Xiao, G. Wang, *Nat. Commun.* **2018**, *9*, 1425.
- [5] T. Tang, W.-J. Jiang, S. Niu, N. Liu, H. Luo, Q. Zhang, W. Wen, Y.-Y. Chen, L.-B. Huang, F. Gao, J.-S. Hu, *Adv. Funct. Mater.* **2018**, 28, 1704594.
- [6] T.-Q. Zhang, J. Liu, L.-B. Huang, X.-D. Zhang, Y.-G. Sun, X.-C. Liu, D.-S. Bin, X. Chen, A.-M. Cao, J.-S. Hu, L.-J. Wan, J. Am. Chem. Soc. 2017, 139, 11248.
- [7] H. Cheng, M.-L. Li, C.-Y. Su, N. Li, Z.-Q. Liu, Adv. Funct. Mater. 2017, 27, 1701833.

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- [8] T. Tang, W.-J. Jiang, S. Niu, N. Liu, H. Luo, Y.-Y. Chen, S.-F. Jin, F. Gao, L.-J. Wan, J.-S. Hu, J. Am. Chem. Soc. 2017, 139, 8320.
- [9] Y. Zhao, C. Chang, F. Teng, Y. Zhao, G. Chen, R. Shi, G. I. N. Waterhouse, W. Huang, T. Zhang, *Adv. Energy Mater.* 2017, 7, 1700005.
- [10] X. Wang, W. Li, D. Xiong, D. Y. Petrovykh, L. Liu, Adv. Funct. Mater. 2016, 26, 4067.
- [11] Y. Hou, M. Qiu, T. Zhang, X. Zhuang, C.-S. Kim, C. Yuan, X. Feng, Adv. Mater. 2017, 29, 1701589.
- [12] J. Yin, Y. Li, F. Lv, M. Lu, K. Sun, W. Wang, L. Wang, F. Cheng, Y. Li, P. Xi, S. Guo, Adv. Mater. 2017, 29, 1704681.
- [13] Y. Hou, M. R. Lohe, J. Zhang, S. Liu, X. Zhuang, X. Feng, Energy Environ. Sci. 2016, 9, 478.
- [14] H. Duan, D. Li, Y. Tang, Y. He, S. Ji, R. Wang, H. Lv, P. P. Lopes,
 A. P. Paulikas, H. Li, S. X. Mao, C. Wang, N. M. Markovic, J. Li,
 V. R. Stamenkovic, Y. Li, J. Am. Chem. Soc. 2017, 139, 5494.
- [15] C. Huang, T. Ouyang, Y. Zou, N. Li, Z.-Q. Liu, J. Mater. Chem. A 2018, 6, 7420.
- [16] G. Yilmaz, K. M. Yam, C. Zhang, H. J. Fan, G. W. Ho, Adv. Mater. 2017, 29, 1606814.
- [17] K. Chang, X. Hai, J. Ye, Adv. Energy Mater. 2016, 6, 1502555.
- [18] Y. Zhong, X. Xia, F. Shi, J. Zhan, J. Tu, H. J. Fan, Adv. Sci. 2016, 3, 1500286.
- [19] Y. Shi, B. Zhang, Chem. Soc. Rev. 2016, 45, 1529.
- [20] K. Li, D. Rakov, W. Zhang, P. Xu, Chem. Commun. 2017, 53, 8199.
- [21] C.-Y. Su, H. Cheng, W. Li, Z.-Q. Liu, N. Li, Z. Hou, F.-Q. Bai, H.-X. Zhang, T.-Y. Ma, Adv. Energy Mater. 2017, 7, 1602420.
- [22] B. Konkena, J. Masa, A. J. R. Botz, I. Sinev, W. Xia, J. Koßmann, R. Drautz, M. Muhler, W. Schuhmann, ACS Catal. 2017, 7, 229.
- [23] D. Mukherjee, P. M. Austeria, S. Sampath, ACS Energy Lett. 2016, 1, 367.
- [24] C. C. Mayorga-Martinez, Z. Sofer, D. Sedmidubský, Š. Huber, A. Y. S. Eng, M. Pumera, ACS Appl. Mater. Interfaces 2017, 9, 12563.
- [25] M. A. Susner, M. Chyasnavichyus, M. A. McGuire, P. Ganesh, P. Maksymovych, *Adv. Mater.* 2017, 29, 1602852.
- [26] B. Song, K. Li, Y. Yin, T. Wu, L. Dang, M. Cabán-Acevedo, J. Han, T. Gao, X. Wang, Z. Zhang, J. R. Schmidt, P. Xu, S. Jin, ACS Catal. 2017, 7, 8549.
- [27] R. N. Jenjeti, M. P. Austeria, S. Sampath, ChemElectroChem 2016, 3, 1392.
- [28] Q. Liang, L. Zhong, C. Du, Y. Luo, Y. Zheng, S. Li, Q. Yan, Nano Energy 2018, 47, 257.
- [29] S. Xue, L. Chen, Z. Liu, H.-M. Cheng, W. Ren, ACS Nano 2018, 12, 5297.
- [30] T. Ouyang, A.-N. Chen, Z.-Z. He, Z.-Q. Liu, Y. Tong, Chem. Commun. 2018, 54, 9901.
- [31] J. Xie, H. Zhang, S. Li, R. Wang, X. Sun, M. Zhou, J. Zhou, X. W. Lou, Y. Xie, Adv. Mater. 2013, 25, 5807.
- [32] Y. Liu, C. Xiao, P. Huang, M. Cheng, Y. Xie, Chem 2018, 4, 1263.
- [33] M. Xiao, B. Luo, M. Lyu, S. Wang, L. Wang, Adv. Energy Mater. 2018, 8, 1701605.
- [34] G. Kresse, J. Furthmüller, Phys. Rev. B 1996, 54, 11169.

- [35] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 1996, 6, 15.
- [36] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865.
- [37] S. Zhao, Y. Wang, J. Dong, C.-T. He, H. Yin, P. An, K. Zhao, X. Zhang, C. Gao, L. Zhang, J. Lv, J. Wang, J. Zhang, A. M. Khattak, N. A. Khan, Z. Wei, J. Zhang, S. Liu, H. Zhao, Z. Tang, *Nat. Energy* **2016**, *1*, 16184.
- [38] M. Hu, S. Ishihara, Y. Yamauchi, Angew. Chem., Int. Ed. 2013, 52, 1235.
- [39] Q. Liang, Y. Zheng, C. Du, Y. Luo, J. Zhang, B. Li, Y. Zong, Q. Yan, Small Methods 2017, 1, 1700304.
- [40] J. Yu, Q. Li, Y. Li, C.-Y. Xu, L. Zhen, V. P. Dravid, J. Wu, Adv. Funct. Mater. 2016, 26, 7644.
- [41] W. Zhou, J. Lu, K. Zhou, L. Yang, Y. Ke, Z. Tang, S. Chen, Nano Energy 2016, 28, 143.
- [42] J.-Y. Wang, T. Ouyang, N. Li, T. Ma, Z.-Q. Liu, Sci. Bull. 2018, 63, 1130.
- [43] P. Cai, J. Huang, J. Chen, Z. Wen, Angew. Chem., Int. Ed. 2017, 56, 4858.
- [44] X. Long, G. Li, Z. Wang, H. Zhu, T. Zhang, S. Xiao, W. Guo, S. Yang, J. Am. Chem. Soc. 2015, 137, 11900.
- [45] L. Yan, L. Cao, P. Dai, X. Gu, D. Liu, L. Li, Y. Wang, X. Zhao, Adv. Funct. Mater. 2017, 27, 1703455.
- [46] Y.-P. Zhu, Y.-P. Liu, T.-Z. Ren, Z.-Y. Yuan, Adv. Funct. Mater. 2015, 25, 7337.
- [47] X. Wang, P. Xiao, L. Thia, M. Alam Sk, R. J. Lim, X. Ge, J.-Y. Wang, K. H. Lim, *Energy Environ. Sci.* 2014, *7*, 2624.
- [48] Q. Liang, L. Ye, Q. Xu, Z.-H. Huang, F. Kang, Q.-H. Yang, Carbon 2015, 94, 342.
- [49] L. Yiling, C. Fengjiao, Y. Wen, Z. Min, H. Na, Z. Feipeng, W. Xinxia, L. Yanguang, *Adv. Funct. Mater.* **2017**, *27*, 1606034.
- [50] Q. Liang, Z. Li, X. Yu, Z.-H. Huang, F. Kang, Q.-H. Yang, Adv. Mater. 2015, 27, 4634.
- [51] L. Qinghua, L. Zhi, B. Yu, H. Zheng-Hong, K. Feiyu, Y. Quan-Hong, Sci. China Mater. 2017, 2, 108.
- [52] C.-T. Kuo, M. Neumann, K. Balamurugan, H. J. Park, S. Kang, H. W. Shiu, J. H. Kang, B. H. Hong, M. Han, T. W. Noh, J.-G. Park, *Sci. Rep.* **2016**, *6*, 20904.
- [53] C. Xia, H. Liang, J. Zhu, U. Schwingenschlögl, H. N. Alshareef, *Adv. Energy Mater.* 2017, 7, 1602089.
- [54] X. Zhang, H. Xie, Z. Liu, C. Tan, Z. Luo, H. Li, J. Lin, L. Sun, W. Chen, Z. Xu, L. Xie, W. Huang, H. Zhang, *Angew. Chem., Int. Ed.* 2015, 544, 3653.
- [55] W. John, A. M. J., S. C. K., P. D. V., C. Jonathan, A. L. M., H. D. L., Small 2018, 14, 1703615.
- [56] D. Gopalakrishnan, D. Damien, M. M. Shaijumon, ACS Nano 2014, 8, 5297.
- [57] A. Ciesielski, S. Haar, A. Aliprandi, M. El Garah, G. Tregnago, G. F. Cotella, M. El Gemayel, F. Richard, H. Sun, F. Cacialli, F. Bonaccorso, P. Samorì, ACS Nano 2016, 10, 10768.
- [58] X. Zhang, Z. Lai, Z. Liu, C. Tan, Y. Huang, B. Li, M. Zhao, L. Xie,
 W. Huang, H. Zhang, Angew. Chem. 2015, 127, 5515.
- [59] K. Xu, P. Chen, X. Li, Y. Tong, H. Ding, X. Wu, W. Chu, Z. Peng, C. Wu, Y. Xie, J. Am. Chem. Soc. 2015, 137, 4119.