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Introduction

Sustainable and clean energy sources have attracted widespread attention around the world due to the increasing global warming and pollution caused by traditional fossil fuels. Hydrogen (H_2) can be considered to be a potential alternative to traditional fossil fuels owing to the advantages of environmental friendliness and high energy density.1-3 Electrochemical water splitting is an attractive method for hydrogen generation through the cathodic hydrogen evolution reaction (HER).⁴⁻⁶ To achieve large-scale hydrogen generation, it is urgently necessary to design and develop high-efficiency electrocatalysts with satisfactory current density at low overpotential. Pt-based nanomaterials, which are regarded as the best candidate catalysts for the HER, have been severely limited due to their natural scarcity and high-costs.7-11 Therefore, exploring high-efficiency and earth-abundant materials for the future of hydrogen economy and developing low-cost, robust and highly active HER

Hole-rich CoP nanosheets with an optimized dband center for enhancing pH-universal hydrogen evolution electrocatalysis[†]

Shuo Geng,‡^a Fenyang Tian,‡^a Menggang Li,^a Xin Guo,^a Yongsheng Yu, ^b*^a Weiwei Yang^{*a} and Yanglong Hou ^b*^b

Tailoring the d-band center is an effective method to promote the hydrogen evolution reaction (HER) activity of electrocatalysts. Herein, we demonstrate that the d-band center can be tuned through a hole-creating method to enhance pH-universal HER activity using CoP as a basic platform. The density functional theory (DFT) calculation reveals that the d-band center and the valence electron number of Co sites around the holes are upshifted, which boosts H adsorption. In addition, introducing holes into the nanosheets of CoP can optimize the ΔG_{H^*} of the Co atoms around the holes. Inspired by the DFT results, a soft template method was developed to synthesize hole-rich CoP nanosheets. With the advantages of hole-rich and unique nanosheet features, the hole-rich CoP nanosheets show low HER overpotentials with only 84 and 94 mV to achieve a current density of 10 mA cm⁻² in both acidic and alkaline media, better than that of the other dimensional counterparts. In addition, the hole-rich CoP nanosheets also show satisfactory stability after long-term HER tests. This strategy of regulating the d-band center is expected to be extended to other transition metal phosphide electrocatalysts for enhancing the HER performance.

electrocatalysts replacing Pt-based catalysts are significant and urgent.

In the last decade, transition metal phosphides attracted lot of attention and are regarded as potential alternatives to Ptbased HER catalysts, culminating in the advent of the striking nanostructural design of cobalt phosphide (CoP).12-14 Generally, the P atoms in CoP can draw electrons from the metal and then serve as proton acceptors and act as the active sites for H₂ generation.15,16 The hydrogen adsorption Gibbs free-energy $(\Delta G_{\mathrm{H}^*})$ of the Co sites in CoP is more positive than the Co sites of cobalt metal, which means that the Co-H bond is weakened and the H* is easily desorbed from Co sites.17 However, too positive ΔG_{H^*} makes the H adsorption difficult, which is detrimental to the HER. Therefore, further optimizing the ΔG_{H^*} of Co sites in CoP is required but still challenging. The regulation of electronic and geometric structures can be considered as the most efficient methods to optimize the ΔG_{H^*} , which is highly relevant to the variation of the d-band center. It is widely accepted that the downshift of the d-band center facilitates H desorption and upshift of the d-band center promotes H adsorption. A series of methods, such as cation and anion doping,18-23 heterostructure fabrication24,25 and strain engineering,26 have been designed to tune the d-band center of electrocatalysts. However, although a large number of studies have suggested that the construction of holey structures can enhance the electrochemical performance, the actual

^aMIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, Heilongjiang 150001, China. E-mail: ysyu@hit.edu.cn; yangww@hit.edu.cn

^bCollege of Engineering, Peking University, Beijing 100871, China. E-mail: hou@pku. edu.cn

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[‡] These authors contributed equally to this work.

relationship between holey structures and varied d-band center is often overlooked.

Herein, we used CoP as a model catalyst to successfully demonstrate that the creation of holes on the surface of CoP can optimize the d-band center which facilitates the HER activity according to the density functional theory (DFT) investigations. Furthermore, well-characterized hole-rich CoP nanosheets can be successfully synthesized and serve as highly active and stable HER electrocatalysts, which further confirms this basic concept. Finally, we also highlight the dominant role of the unique 2D nanosheet morphology in this enhanced catalytic system. Therefore, combining the hole-rich and nanosheet features, a high-performance HER electrocatalyst is achieved under alluniversal pH conditions.

Experimental section

Chemicals and materials

Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O), NaH₂PO₂, urea, and polyethylene oxide–polypropylene oxide–polyethylene oxide (P123) were obtained from Aladdin Company, China. Deionized water (18 M Ω cm⁻¹) was supplied by a Water Purifier Nanopure system. All the analytical reagents and grade chemicals were used as received without further purification.

Synthesis of hole-rich CoP nanosheets

Firstly, 2 mmol of $Co(NO_3)_2 \cdot 6H_2O$ and 10 mmol of urea were dissolved in 30 mL of deionized water under sonication, then 1 g of P123 was added into the above homogeneous solution and kept under sonication for 1 h. The as-obtained solution was added into a Teflon autoclave (45 mL) and reacted at 120 °C for 11 h. The as-obtained products were washed with deionized water several times and dried in a vacuum oven at 60 °C. Secondly, the above products were annealed at 350 °C for 2 h with a heating rate of 2 °C min⁻¹ in air to obtain Co₃O₄ samples. Thirdly, 20 mg of Co₃O₄ and 1 g of NaH₂PO₂ were placed at two separate positions in a ceramic boat, where NaH₂PO₂ was located at the upstream side of the tube furnace. Then the tube furnace was heated to 400 °C for 2 h with a heating rate of 2 °C min⁻¹ in an Ar/H₂ (95/5) atmosphere. Finally, hole-rich CoP nanosheets were obtained.

Synthesis of CoP nanoparticles

CoP nanoparticles were synthesized based on the previous literature.²⁷ Firstly, 0.8 g of Co(NO₃)₂·6H₂O and 0.2 g of sodium citrate were dissolved into 200 mL of deionized water. Then the mixture was stirred for 20 min to form a homogeneous solution. Next, 20 mL of NaOH solution (0.5 M) was added dropwise into the mixture. The generated precipitates were collected and washed with deionized water and then dried in a vacuum oven at 60 °C. Secondly, 20 mg of precursors and 1 g of NaH₂PO₂ were placed at two separate positions in a ceramic boat, where NaH₂PO₂ was placed at the upstream side of the tube furnace, and annealed at 400 °C for 2 h with a heating rate of 2 °C min⁻¹ in an Ar/H₂ (95/5) atmosphere.

Synthesis of CoP nanorods

CoP nanorods were synthesized by using the similar method to the hole-rich CoP nanosheets, except for the absence of P123.

Characterization

X-ray diffraction (XRD) was carried out on a Bruker AXS D8-Advanced diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å). Scanning electron microscopy (SEM) images were analyzed on a field emission scanning electron microscope (FESEM) from MERLIN Compact. Transmission electron microscopy (TEM) analyses were performed on a Philips CM 20 operating at 120 kV. High-resolution TEM (HRTEM) images and corresponding energy dispersive mapping were obtained on an FEI Tecnai Osiris with an accelerating voltage of 200 kV. Specific surface area was obtained on a 3H-2000PSI at liquid N₂ temperature. Xray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific) with Al Ka X-ray radiation as the X-ray source for excitation. The specific surface areas and pore diameter distributions of the catalysts were calculated using a Beishide 3H-2000PS1 Gas Sorption and Porosimetry system by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods.

Electrochemical measurements

All of the electrochemical measurements were performed in a three-electrode system on an electrochemical workstation (CHI660E, Chenhua, China). Graphite rod was used as the counter electrode and Ag/AgCl (saturated KCl-filled) was used as the reference electrode. A glassy carbon electrode with a diameter of 3 mm covered by a thin catalyst film or 20% commercial Pt/C electrocatalyst was used as the working electrode. Typically, 4 mg of catalyst and 10 µL of Nafion solution (5 wt%, DuPont) were dispersed in 1 mL of an ethanol/water mixed solution (volume ratio of 1/1) by sonicating for 1 h to form a homogeneous ink. Then 5 µL of the dispersion (containing 20 µg of catalysts) was pipetted onto a glassy carbon electrode (loading amount is 0.283 mg cm⁻²). HER tests were conducted in a N2-saturated 0.5 M H2SO4 and 1.0 M KOH. Linear sweep voltammetry was conducted between 0.0 and -0.8 V versus RHE with a scan rate of 5 mV s^{-1} . The Nyquist plots were measured with frequencies ranging from 100 kHz to 0.1 Hz at an overpotential of 150 mV. All of the final potentials have been calibrated with respect to a reversible hydrogen electrode (RHE) according to E (vs. RHE) = E (vs. Ag/AgCl) + 0.197 + 0.059pH. Cyclic voltammograms (CVs) of the as-prepared samples recorded in a non-faradaic region (0-0.1 V vs. RHE) at various scan rates (from 5 to 25 mV s⁻¹) in 0.5 M H₂SO₄ and in a non-faradaic region (0-0.1 V vs. RHE) at various scan rates (from 5 to 25 mV s^{-1}) in 1 M KOH were used to measure the electrochemical double layer capacitance (C_{dl}) . Stability tests were performed using a continuous CV technique in a potential scan range from 0.0 to -0.15 V (vs. RHE) at 100 mV s⁻¹ for multicycle operation (from 1000 cycles) and chronoamperometry technique (at a current density of 10 mA cm⁻²).

DFT calculation

In this work, the DFT calculations were carried out by the planewave technique with exchange-correlation interactions modeled by the GGA-pw91 functional, as implemented in the Vienna Ab initio Simulation Package (VASP). According to our theoretical models, the diameter of the holes is 6.51 Å, which is much larger than the covalent radius of Co and P. In addition, the diameter of the holes is large enough to ignore the van der Waals forces between the walls of holes. Therefore, we can ensure that the gaps in the models used for DFT calculations are holes, rather than the defects. Considering the accuracy and cost of calculation, the model was built consisting of six layers of atoms and the supercell dimension is 10.14 Å \times 12.89 Å. Three layers of atoms on the surface are relaxed and the three layers of atoms on the bottom are fixed. All the calculations were performed using plane-wave cut off energy of 400 eV. For kspace sampling, the $3 \times 3 \times 1$ Monkhorst-Pack grid was used in the calculations. The convergence threshold of energy and forces were set to be 10^{-5} eV and 0.02 eV A⁻¹, respectively.

The hydrogen adsorption free energy ΔG_{H^*} was calculated as follows:

$$\Delta G_{\mathrm{H}^*} = \Delta E_{\mathrm{H}^*} + \Delta E_{\mathrm{ZPE}} - T\Delta S$$

where $\Delta E_{\text{H}*}$, ΔE_{ZPE} , *T* and ΔS represent the adsorption energy, zero-point energy, temperature and entropy change, respectively. $\Delta E_{\text{H}*}$ is calculated as follows:

$$\Delta E_{\mathrm{H}^*} = \Delta E_{\mathrm{sub}^+\mathrm{H}^*} - E_{\mathrm{sub}} - 1/2E_{\mathrm{H}^*}$$

Results and discussion

We first used CoP as a basic platform to examine how the holes affect ΔG_{H^*} , which tends to represent the general catalytic mechanism towards the HER, according to the DFT calculations. Generally speaking, an electrocatalyst with a value of



Fig. 1 DFT calculation for hole-rich CoP catalysts with enhanced HER activity. (a) The free energy diagram of Co and P atoms at the top sites of the CoP (011) surface with and without holes, respectively. (b) Partial density of states (PDOS) of CoP with and without holes, respectively. The electron density difference maps of CoP (c) with and (d) without holes. Yellow and cyan represent electronic accumulation and depletion, respectively.

 ΔG_{H^*} close to 0 is believed to be the best candidate for the HER. In our paper, the (011), (112), (211) and (301) planes were exposed in the hole-rich CoP nanosheets according to XRD patterns. As shown in Table S1,† the surface energy of different facets of CoP nanosheets follows the order of (011) < (211) <(112) < (301), so we chose the (011) facet as the simulation in this study. For this purpose, we created two models simulating the CoP with and without holes to depict the variation of ΔG_{H^*} (Fig. S1[†]). Fig. 1a shows the ΔG_{H^*} of Co and P atoms on the CoP (011) surface before and after the creation of holes. The ΔG_{H^*} of Co and P atoms at the top sites of the CoP (011) surface without holes are about 0.305 eV and 0.108 eV, respectively, which are consistent with the recently reported values.17 After introducing the holes into the CoP (011) surface, the ΔG_{H^*} of the Co and P at the top sites of hole edge decreased to 0.136 eV and 0.092 eV, respectively, indicating the optimized H adsorption/desorption behaviors for the hole-rich CoP surface during the HER process.

Based on the variation of the ΔG_{H^*} between the CoP with and without holes, the effect of holes on P atoms was tinier than that of Co atoms. Therefore, we used the density of electronic states (DOS) and Bader analysis to analyze the electronic structure of the Co atoms, and they reveal the enhanced mechanism of electrocatalytic activities. The DOS value of hole-rich CoP at the Fermi level is higher than that without holes (Fig. 1b), which suggests that hole-rich CoP can provide more electrons during the catalytic process. Furthermore, the d-band centers of Co atoms on surfaces with and without holes are found to be -1.23and -1.48 eV, respectively. The coordination number of atoms around the hole is low, and the surface of the hole undergoes relaxation, so the d-band electron interaction of Co atoms around the hole is weak, leading to the upward shift of the dband center.28 The upward shift of the d-band center indicates the enhanced interaction between H and Co atoms, which is conducive to the optimization of ΔG_{H^*} of the catalyst surface. The charge density difference and Bader charge of CoP with and without holes are further compared to understand the effect of holes on the valence electron migration. As shown in Fig. 1c and d, the valence electron number of Co atoms at the hole edge is 8.847, which is higher than that at the same position of CoP without holes (8.828). P atoms of CoP can take away the outer electrons of Co atoms, and the P atoms that coordinated with Co atoms around the holes are relatively few, thus the charge density of Co atoms at the edge of the holes is much higher. The increase of the charge density of Co atoms is beneficial to enhancing the hydrogen adsorption ability, thus the ΔG_{H^*} of the surface of CoP can be further optimized to enhance the HER activity. Therefore, it is anticipated that a hole-rich CoP catalyst will generate an unexpected HER activity.

Encouraged by the above-mentioned theoretical analysis, we attempted to synthesize hole-rich CoP catalysts to meet the practical value of the variation of ΔG_{H^*} . Annealing metal-containing precursors in air to release CO₂ or H₂O is considered as one of the simplest and high-efficiency methods to fabricate holes on a material surface.²⁹ Therefore, we attempted to synthesize hole-rich CoP nanosheets *via* a three-step method, which consists in a hydrothermal method with the soft template P123, calcinations of precursors in an air atmosphere and the



Fig. 2 Synthesis and structural characterization of hole-rich CoP nanosheets. (a) The synthesis schematics of hole-rich CoP nanosheets. (b) SEM image and (c) TEM image of hole-rich CoP nanosheets. (d) XRD patterns of hole-rich Co_3O_4 and CoP nanosheets. (e) HRTEM image of hole-rich CoP nanosheets. The high resolution XPS spectra of (f) Co 2p and (g) P 2p in CoP nanoparticles and hole-rich CoP nanosheets.

final phosphation process (Fig. 2a). The final products exhibit a nanosheet-stacked morphology with a rough surface, confirmed by the SEM image (Fig. 2b). We further obtained the time-lapse SEM images of hydrothermal intermediates at different reaction stages to confirm the evolution process of the unique 2D structure, and we find that the nanosheets are derived from the self-assembly of nanorods (Fig. S2[†]). The Cocontaining precursors are composed of Co(OH)2, Co(NH3)5(- $NO_2)(NO_3)_2$ and $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$ (Fig. S3[†]). After annealing under atmospheric conditions, the smooth nanosheets are transformed into hole-rich Co3O4 nanosheets (Fig. S4[†]). The anisotropic growth of nanosheets can be attributed to the presence of P123 because only a nanorod array is formed in the absence of P123 (Fig. S4[†]). On further phosphation in the presence of NaH₂PO₂, TEM image reveals that the hole-rich morphology can be well preserved (Fig. 2c), which is line with the SEM results. Note that a large amount of homogeneous holes can be observed on the surface of the nanosheets.

The XRD pattern of the as-obtained nanosheets shows several obvious diffraction peaks located at 31.6°, 46.3°, 48.2° and 56.9°, corresponding to the (011), (112), (211) and (301) planes of CoP (JCPDS 29-0497, Fig. 2d), respectively. Two kinds of obvious lattice fringes measured at 0.19 and 0.28 nm can be observed in the HRTEM image (Fig. 2e) of CoP nanosheets, corresponding to the (211) and (011) planes of the CoP phase, respectively, which are matched well with the result of the XRD pattern. In addition, we can also find a clear amorphous phase on the edges of the nanosheets, which is marked with a red dotted line. SAED pattern further reveals high crystallinity and the presence of (011), (112) and (211) planes of CoP phases. The specific surface area of the hole-rich CoP nanosheets was calculated to be 68.3 m² g⁻¹ from the N₂ adsorption/desorption isotherms, which is bigger than that of CoP nanoparticles (20.4 $m^2 g^{-1}$) and CoP nanorods (53.4 $m^2 g^{-1}$), and the BJH pore size

distribution curve further demonstrates the hole-rich structure of CoP nanosheets (Fig. S5†). In addition, there are no vacancies in hole-rich CoP nanosheets (Fig. S6a†).

To probe the surface chemical compositions and valence states in CoP, we further conducted high-resolution XPS tests. The elements Co, P, C and O can be all observed in the survey spectrum, further implying the formation of CoP phases (Fig. S6b[†]). The O and C signals originate from the absorbed O species in air and binding energy calibration, respectively. As shown in the high-resolution XPS spectra of Co 2p (Fig. 2f), one peak at 779.1 eV can be assigned to Co $2p_{3/2}$ of Co⁰, and another two peaks at 781.7 and 798.3 eV can be assigned to Co $2p_{3/2}$ and Co $2p_{1/2}$, respectively, which are attributed to the oxidized Co species (Co^{2+/3+}). The remaining two peaks deconvoluted at 784.1 and 803.2 eV are the satellite peaks of Co $2p_{3/2}$ and Co $2p_{1/2}$ 2, respectively. In addition, the high-resolution XPS spectra of P 2p core levels can also be deconvoluted into three peaks which are located at 129.2 eV for P $2p_{3/2}$, 130.1 eV for P $2p_{1/2}$ and 134 eV for oxidized P species caused by the surface oxidation process due to exposure in air (Fig. 2g). Moreover, the binding energy of $Co^0 2p_{3/2}$ (779.1 eV) is higher than that of metallic Co (777.9 eV) and that of P $2p_{3/2}$ (129.2 eV) is lower than that of elemental P (130.2 eV).30 The positive shift of Co 2p and negative shift of P 2p suggest a strong charge transfer from Co to P and the formation of CoP.31 We here chose the as-synthesized CoP nanoparticles as the basic platform for the control samples with non-hole features to visualize the change of XPS binding energy. The binding energy of Co 2p in hole-rich CoP nanosheets shows a positive shift compared with that of CoP nanoparticles, while that of P 2p shows a negative shift (Fig. 2e and g) indicating that the electrons are transferred from P to Co. This implies that the electron in CoP is richer around Co after introducing holes than that without holes, corresponding to the results of DFT calculation.

To highlight the strength of the unique nanosheet structures, we also synthesized CoP 1D nanorods and 0D nanoparticles based on the modified methods from CoP nanosheets (Fig. S7 and S8[†]). Then, we compared the electrocatalytic HER activity of three CoP catalysts with commercial 20% Pt/C by using a three electrode system by recording polarization curves in N2-saturated 0.5 M H2SO4. As shown in Fig. 3a, the CoP nanosheets show the highest HER activity among the three CoPbased catalysts. For example, to achieve a current density of 10 mA cm⁻², the CoP nanosheets only require an overpotential of 84 mV versus RHE in 0.5 M H₂SO₄, which is much lower than those of CoP nanoparticles (434 mV) and CoP nanorods (188 mV), as well as most reported Co-based phosphide catalysts under similar conditions (Table S2[†]). In addition, a comparison of the overpotential at a current density of 10 mA cm⁻² (η_{10}) of different catalysts is shown in Fig. 3b. Generally, the Tafel slope is used to depict the reaction kinetics and the rate-determining steps of the catalysts in the HER process, and a smaller Tafel slope of the catalysts means faster HER kinetics.12 Therefore, the HER kinetics of the CoP electrocatalysts were studied based on Tafel slopes obtained from the corresponding HER polarization curves (Fig. 3c). The Tafel slope of the CoP nanosheets was derived to be 61 mV dec $^{-1}$, much smaller than that of the



Fig. 3 The electrocatalytic HER performance of different CoP electrocatalysts and commercial Pt/C in 0.5 M H_2SO_4 . (a) HER polarization curves with a scan rate of 5 mV s⁻¹, (b) the comparison of overpotentials at a current density 10 mA cm⁻², (c) the corresponding Tafel plots, (d) the capacitive currents at 0.25 V *versus* RHE as a function of scan rate, (e) electrochemical impedance spectra (the inset is the enlarged high frequency region and the electrical equivalent circuit), and (f) the polarization curves of hole-rich CoP nanosheets before and after 1000 CV scans (the inset is the time-dependent current density curve).

other CoP catalysts with different dimensions, indicating that the HER process of hole-rich CoP nanosheets follows the Volmer–Heyrovsky mechanism. The exchange current densities (j_0) of these samples were calculated by employing the extrapolation method to the Tafel plots (Fig. S9†). The hole-rich CoP nanosheets could afford a much higher j_0 of 0.421 mA cm⁻² than CoP nanoparticles (0.081 mA cm⁻²) and CoP nanorods (0.312 mA cm⁻²).

The enhanced HER electrocatalytic activity of CoP nanosheets can be explained by double-layer capacitance which is linearly proportional to the actual electrochemically active surface areas (ECSAs). From the CVs of the CoP nanosheets, nanoparticles and nanorods with various scan rates (Fig. S10ac[†]) in 0.5 M H₂SO₄, the capacitances were calculated to be 1.32, 0.23 and 0.35 mF cm⁻², respectively, indicating that the CoP nanosheets possess the highest ECSA and best exposure of the active sites among these catalysts (Fig. 3d). The large C_{dl} of CoP nanosheets demonstrates that the hole-rich nanosheets can create more electroactive sites, thus improving the HER performance. To further visualize the enhanced HER activity of CoP nanosheets, we also normalize the current density using the ECSAs (Fig. S11[†]). The normalized polarization curves reveal that CoP nanosheets show lower onset potential than the other counterparts.

Electrochemical impedance spectroscopy (EIS) measurements were conducted in the frequency range from 10 kHz to 0.1 kHz to understand the HER kinetics happening at the interface of the electrode and electrolyte. As shown in Fig. 3e, the charge transfer resistance of hole-rich CoP nanosheets (31 Ω) is much lower than that of CoP nanoparticles (1765 Ω) and CoP nanorods (116 Ω) under acidic conditions, indicating a rapid electronic transport and low mass transport resistance in terms of HER kinetics. The rapid interfacial charge transfer can be ascribed to the enhanced conductivity²⁴ and interfacial contact of hole-rich nanosheets with the electrolyte. The stability of hole-rich CoP nanosheets was further tested by longterm CV scanning and chronoamperometric tests. Fig. 3f shows that the polarization curve of hole-rich CoP nanosheets after 1000 CV cycles still overlaps with the initial polarization curve, implying the long-term stability of the CoP nanosheet catalysts. In addition, the current densities show little degradation in the chronoamperometric test, indicating that the catalytic activity of the hole-rich CoP nanosheets remains unchanged at least for 20 h (the inset of Fig. 3f). The morphology and composition of the hole-rich CoP nanosheets after durability tests can still be well maintained, further revealing the stability of CoP nanosheets (Fig. S12 and S13†).

We can attribute the superior electrocatalytic HER performance of the hole-rich CoP nanosheets to the optimized d-band center caused by the creation of holes, as well as the increase of electroactive sites due to the unique nanosheet structure. First of all, the charge transfer from Co to P in CoP catalysts gives rise to more positive ΔG_{H^*} of the Co sites compared with that of Co metal, thus weakening the H* adsorption ability, generating the intrinsic HER activity of CoP.32-35 In addition, the construction of holes on the surface of CoP nanosheets tunes the d-band center, which is further conducive to the optimization of ΔG_{H^*} of the Co and P sites around the holes to enhance the HER activity. Furthermore, the unique hole-rich 2D nanosheet morphology can facilitate the electrolyte infiltration and gas venting through the inside of the CoP, shorten the electron transfer distance, and provide more accessibility to the CoP surface, inducing the generation of more electroactive sites.³⁶⁻⁴² Finally, the existence of surface amorphous phases also provides additional exposed atoms and active sites for enhanced HER activity.43-46

The unique hole-rich nanosheets can also endow CoP with enhanced electrocatalytic HER activity in an alkaline environment. As shown in Fig. 4a, the CoP nanosheets still show higher HER activity compared to CoP nanoparticles and CoP nanorods, and most reported Co-based phosphide catalysts under similar conditions (Table S2†). In addition, the obvious comparison of



Fig. 4 The electrocatalytic HER performance of different CoP electrocatalysts and commercial Pt/C in 1.0 M KOH. (a) HER polarization curves with a scan rate of 5 mV s⁻¹, (b) the comparison of overpotential at a current density of 10 mA cm⁻², (c) the corresponding Tafel plots, (d) the capacitive currents at 0.25 V *versus* RHE as a function of scan rate, (e) electrochemical impedance spectra (the inset is the enlarged high frequency region and the electrical equivalent circuit), and (f) the polarization curves of hole-rich CoP nanosheets before and after 1000 CV scans (the inset is the time-dependent current density curve).

 η_{10} of the different catalysts is depicted by a histogram (Fig. 4b). The Tafel slope of the CoP nanosheets is 67 mV dec⁻¹ (Fig. 4c), which is smaller than the other dimensional CoP catalysts, indicating fast HER kinetics of CoP nanosheets. From the CVs of the CoP nanosheets, nanoparticles and nanorods with various scan rates (Fig. S14a-c⁺) in 1.0 M KOH, the capacitances of the different catalysts are calculated to be 4.22, 1.2 and 1.63 mF cm $^{-2}$, respectively, indicating that the CoP nanosheets have the highest ECSAs and best exposure of the active sites among these catalysts in 1.0 M KOH (Fig. 4d). Furthermore, the charge transfer resistance of CoP nanosheets (28 Ω) is much lower than that of CoP nanoparticles (570 Ω) and CoP nanorods (112 Ω) in alkaline solution, indicating a rapid electronic transport and low mass transport resistance towards HER kinetics (Fig. 4e). The stability of the CoP nanosheets is further tested by conducting long-term CV scanning cycles and chronoamperometric tests. Fig. 4f shows that the polarization curve of CoP nanosheets after 1000 CV cycles still overlaps with the initial polarization curve, and the current densities show little degradation in the chronoamperometric test, indicating that the catalytic activity of hole-rich CoP nanosheets can be maintained for at least for 20 h. The morphology and composition of hole-rich CoP nanosheets after durability tests are nearly unchanged, further indicating the excellent stability of CoP nanosheets (Fig. S12 and S13[†]).

Conclusions

In summary, we successfully demonstrated a novel strategy wherein the construction of holes on the surface of electrocatalysts can tailor the d-band center of electrocatalysts, further facilitating the HER activity. As a typical model system, holerich CoP nanosheets are synthesized and exhibit excellent allpH HER performance. DFT calculation firstly reveals that the introduction of holes can upshift the d-band center of CoP, which strengthens the H adsorption, beneficial to the enhanced HER activity. Under acidic conditions, the optimized hole-rich CoP nanosheets show a low overpotential of 84 mV versus RHE and a low Tafel slope of 61 mV dec⁻¹, as well as superior long-term stability. Similar results can also be confirmed in the alkaline environment. We explained that the excellent HER performance originates from the optimized d-band center induced by the presence of holes and the increase of electroactive sites caused by the unique 2D nanosheet structure. Such a d-band center tuning strategy via creation of holes directs us to design more transition metal compound-based hole-rich nanostructures for the future high-performance electrocatalytic HER, as well as other electrocatalytic reactions related to the d-band center.

Author contributions

W. W. Y., Y. S. Y. and Y. L. H. conceived the project. S. G. designed and conducted the experiment. F. Y. T. conducted the DFT calculation. M. G. L. and X. G. revised data plots. W. W. Y., Y. S. Y. and Y. L. H. revised the paper. All authors reviewed and

edited the paper. S. G. and F. Y. T. contributed equally to this work.

Conflicts of interest

There are no conflicts to declare.

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