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Ni_{1-x}Co_xO_y, Ni_{1-x}Co_xS_y and Ni_{1-x}Co_xP_y Catalysts Prepared from Ni_{1-x}Co_x-ZIF-67 for Hydrogen Production by Electrolysis in Alkaline Media

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Ni_{1-x}Co_xO_y, Ni_{1-x}Co_xS_y and Ni_{1-x}Co_xP_y catalysts prepared from Ni_{1-x}Co_x-ZIF-67 for hydrogen production by electrolysis in alkaline media

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Abstract: The uniform homeotypic bimetallic $\text{Ni}_{1-x}\text{Co}_x\text{O}_y$, $\text{Ni}_{1-x}\text{Co}_x\text{S}_y$ and $\text{Ni}_{1-x}\text{Co}_x\text{P}_y$ catalysts were synthesized from $\text{Ni}_{1-x}\text{Co}_x$ -ZIF-67 crystals (120-135 nm) reacting with oxygen, sublimed sulfur and sodium hypophosphite, respectively under control conditions. The catalysts were deposited on glassy carbon electrode (GCE), and their electro-catalytic activity for hydrogen production in alkaline media by electrolysis was investigated. The electrocatalytic activity of the catalysts towards hydrogen evolution reaction (HER) decreased in the following order $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y > \text{Ni}_{0.2}\text{Co}_{0.8}\text{O}_y > \text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_y > \text{Ni}_{0.1}\text{Co}_{0.9}$ -ZIF-67. The $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$ exhibited the highest electrocatalytic activity towards HER due to the high crystallinity, high specific surface area and the synergistic effect of nickel and cobalt that accelerate the electron transfer process.

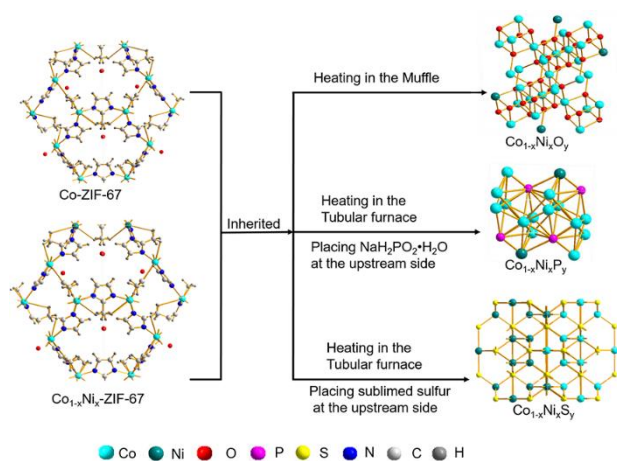
Introduction

Transition metals have been recently suggested as appropriate catalysts for hydrogen evolution reaction (HER)^[1]. The transition metal catalysts are used in alkaline media, and the alkaline water electrolysis is a competitively priced process in comparison to proton exchange membrane water electrolysis^[2]. Due to the low cost, environmental benign, and high theoretical catalytic activity, Co-based materials are particularly attractive among other transition metal-based electrocatalysts for water splitting^[3]. Multiple methods were used to prepare Co-based materials. For instance, Co_4N was synthesized by simple nitridation reaction and high temperature treatment with $\text{Co}(\text{OH})\text{F}$ nanowire arrays^[3c]. CoO nanorods (NRs) were fabricated by surface strain engineering^[4].

Metal-organic frameworks (MOFs) materials have been recently proven to be promising sacrificial template or self-template to produce electrocatalysts due to their sufficient exposed active sites, abundant organic ligands, and mesoporous structure^[5]. For example, Li et al.^[3a] synthesized Co_3O_4 nanocrystals embedded in N-doped mesoporous graphitic carbon layer/multiwalled carbon nanotube (MWCNT) hybrids by a facile carbonization and subsequent oxidation of MWCNT-based MOFs, which led to high electrochemical performance. In 2017, Cao et al.^[3d] reported the preparation of hollow CoS_2 tubular arrays by a sulfidation under thermal treatment of wire-like MOFs nanoarrays for water splitting. The

self-agglomeration of Co-MOFs materials usually led to a high overpotential and decreased reaction rate.

In order to improve the efficiency and avoid self-agglomeration of Co-based materials, it is important to understand the structure-activity relationship between their electrocatalytic activities and the dispersion and valence state of the Co-based materials^[6]. Different Co-based materials including sulfides, oxides, phosphides^[7], etc. show diverse electrocatalytic activity for HER^{[8] [9]}. In addition, reducing the size of particles of Co-based materials, especially going to ultra-small nanoclusters or even single atoms^[10], is considered as an effective way to improve their catalytic performance. Furthermore, the introduction of a second metal component in the Co-based materials improved the resistance to corrosion in the alkaline media, and prevented the Co nanoparticles from agglomeration^[11]. Several investigations have focused on MOF-derived bimetallic or multi-metallic derivatives, leading to advanced electrocatalytic performance compared with single Co-based materials^[12]. For examples, He and co-workers fabricated carbon containing Ni-Co mixed metal phosphide nanoboxes (NiCoP/C) by ZIF-67^[12a]. Liang and et al. reported the Ni₂P-CoP bimetallic phosphides derived from the NiCo-MOFs, which showed efficient performance for both HER and the oxygen evolution reaction (OER)^[12c]. Mostly Co-MOFs under thermal decomposition conditions in the presence of a second metal were applied to fabricate new multi-metallic materials^[13]. Firstly, the Co-MOFs was prepared, then the second metal (Ni) under acidic etching or thermal decomposition was introduced resulting in mesoporous structures collapse with self-agglomerated metals. The preparation of nanosized homogenous bimetallic MOFs derivatives for HER is still a challenge^[12c].



Scheme 1. Schematic diagram representing the preparation of $\text{Ni}_{1-x}\text{Co}_x\text{-ZIFs-67}$, $\text{Ni}_{1-x}\text{Co}_x\text{O}_y$, $\text{Ni}_{1-x}\text{Co}_x\text{S}_y$ and $\text{Ni}_{1-x}\text{Co}_x\text{P}_y$ from $\text{Ni}_{1-x}\text{Co}_x\text{-ZIFs-67}$

This article reports the preparation of homeotypic bimetallic catalysts ($\text{Ni}_{1-x}\text{Co}_x\text{O}_y$, $\text{Ni}_{1-x}\text{Co}_x\text{S}_y$ and $\text{Ni}_{1-x}\text{Co}_x\text{P}_y$) using nanosized bimetallic precursor $\text{Ni}_{1-x}\text{Co}_x\text{-ZIF-67}$ (Scheme 1). The uniform bimetallic $\text{Ni}_{1-x}\text{Co}_x\text{-ZIF-67}$ crystals (120-135 nm) were prepared from Co-ZIF-67 at low temperature (0°C) (see Experimental Section). Hence the $\text{Ni}_{1-x}\text{Co}_x\text{-ZIF-67}$ were allowed to convert into $\text{Ni}_{1-x}\text{Co}_x\text{O}_y$, $\text{Ni}_{1-x}\text{Co}_x\text{S}_y$ and $\text{Ni}_{1-x}\text{Co}_x\text{P}_y$ materials by temperature-programmed reactions with oxygen, sublimed sulfur and sodium hypophosphite, respectively. Then, the homeotypic bi-metallic materials were deposited on glassy carbon electrode (GCE) and applied in alkaline ($\text{pH}=14$) electrolysis for hydrogen production. The effect of the state of Ni and Co species on the electrocatalytic performance of the catalysts for hydrogen evolution in alkaline media was studied in detail.

Results and Discussion

Characterization of $\text{Ni}_x\text{Co}_{1-x}\text{-ZIF-67}$, $\text{Ni}_x\text{Co}_{1-x}\text{O}_y$, $\text{Ni}_x\text{Co}_{1-x}\text{P}_y$, and $\text{Ni}_x\text{Co}_{1-x}\text{S}_y$ catalysts

The crystal structure of Co-ZIF-67 and $\text{Ni}_{0.1}\text{Co}_{0.9}\text{-ZIF-67}$ was characterized by XRD. The XRD diffraction pattern of $\text{Ni}_{0.1}\text{Co}_{0.9}\text{-ZIF-67}$ is similar to the mono-metallic Co-ZIF-67 sample (Fig. 1a). Cobalt and nickel with consecutive atomic numbers easily formed homeotypic crystals. As shown in Fig.

S1a, the XRD patterns of samples $\text{Ni}_x\text{Co}_{1-x}\text{-ZIF-67}$ with different Ni/Co ratios contain broad peaks, but their positions are identical with the simulated pattern of Co-ZIF-67^[14]. No impurity was found in samples $\text{Ni}_x\text{Co}_{1-x}\text{-ZIF-67}$, implying that Ni^{2+} ions are effectively incorporated into the Co-ZIF-67^[15]. The intensity of the peaks for $\text{Ni}_x\text{Co}_{1-x}\text{-ZIF-67}$ (Fig.S1a) decreased with an increase of nickel content, which is related to the changes of charge distribution and electrostatic fields as a result of the existence of both nickel and cobalt within the framework^[16]. While the XRD patterns of samples Co_3O_4 and $\text{Ni}_{0.2}\text{Co}_{0.8}\text{O}_y$ (Fig. 1b) contain peaks at 31.3° and 36.8° 2Theta corresponding to (100) and (101) planes of Co_3O_4 ^[17], and a peak at 43.0° corresponding to (200) plane of NiO ^[11c, 18]. This result indicates that the $\text{Ni}_x\text{Co}_{1-x}\text{-ZIF-67}$ is fully transformed to $\text{Ni}_{0.2}\text{Co}_{0.8}\text{O}_y$. The XRD patterns of samples CoP and $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$ are shown in Fig. 1c. The Bragg peaks at 31.6 , 36.6 , 46.3 and 48.7° 2Theta correspond to the (011), (111), (112) and (211) planes of CoP^[3b, 12a, 12c], and the peak at 41.0° 2Theta corresponds to (321) plane of Ni_3P ^[12b, 19], which confirm the transformation from $\text{Ni}_x\text{Co}_{1-x}\text{-ZIF-67}$ to CoP and $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$. The nanosized bimetallic atomic arrangement in the $\text{Ni}_x\text{Co}_{1-x}\text{-ZIF-67}$ is demonstrated as well (Fig. S1c). The XRD patterns of Co_9S_8 and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_y$ samples are depicted in Fig. 1d. The peaks at 15.3 , 29.8 , 31.2 and 47.5° 2Theta correspond to (111), (311), (222) and (511) planes of Co_9S_8 ^[20], and the peak at 44.4° is related to the (102) plane of NiS ^[11a], indicating the formation of Co_9S_8 and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_y$.

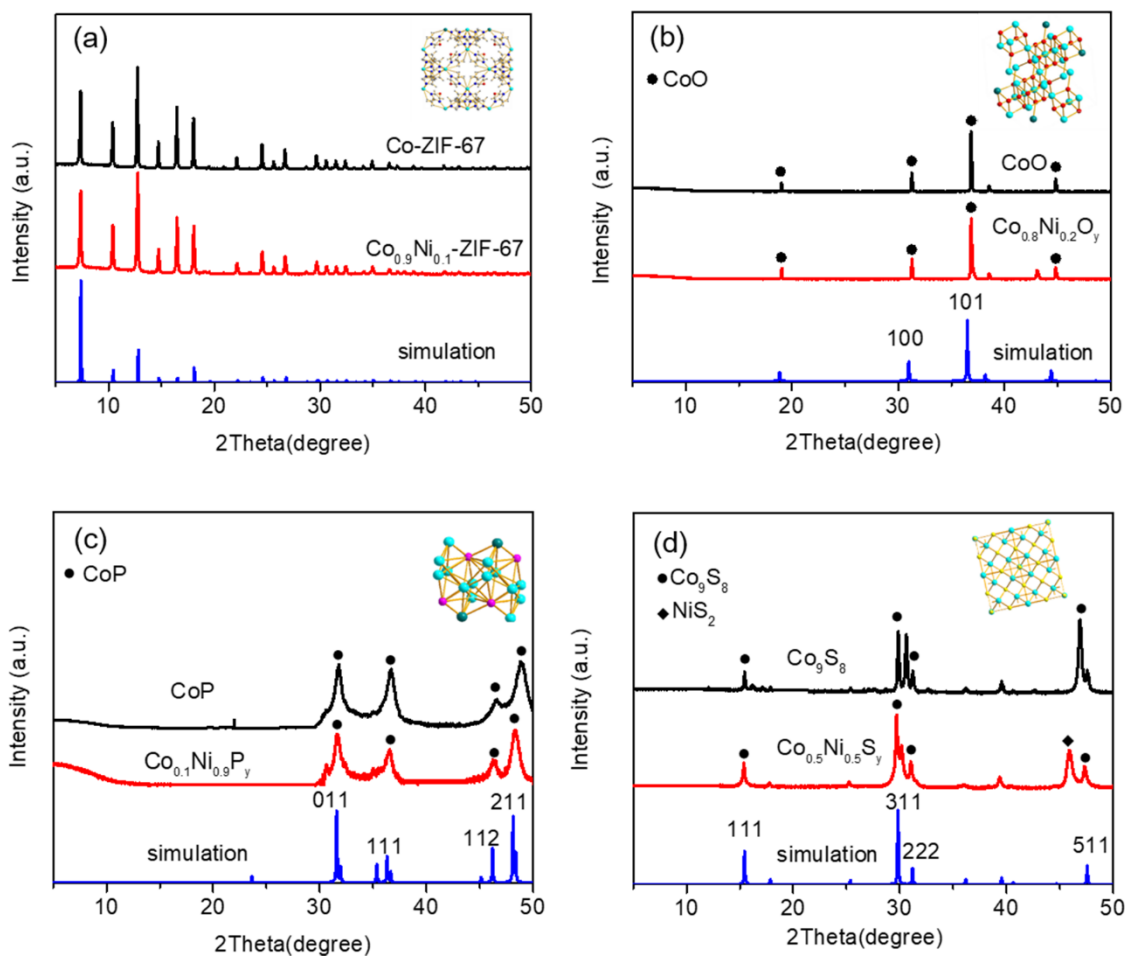


Figure 1. XRD patterns of Co-ZIF-67 and $\text{Ni}_{0.1}\text{Co}_{0.9}\text{-ZIF-67}$ (a), Co_3O_4 and $\text{Ni}_{0.2}\text{Co}_{0.8}\text{O}_y$ (b), CoP and $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$ (c) and Co_9S_8 and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_y$ (d).

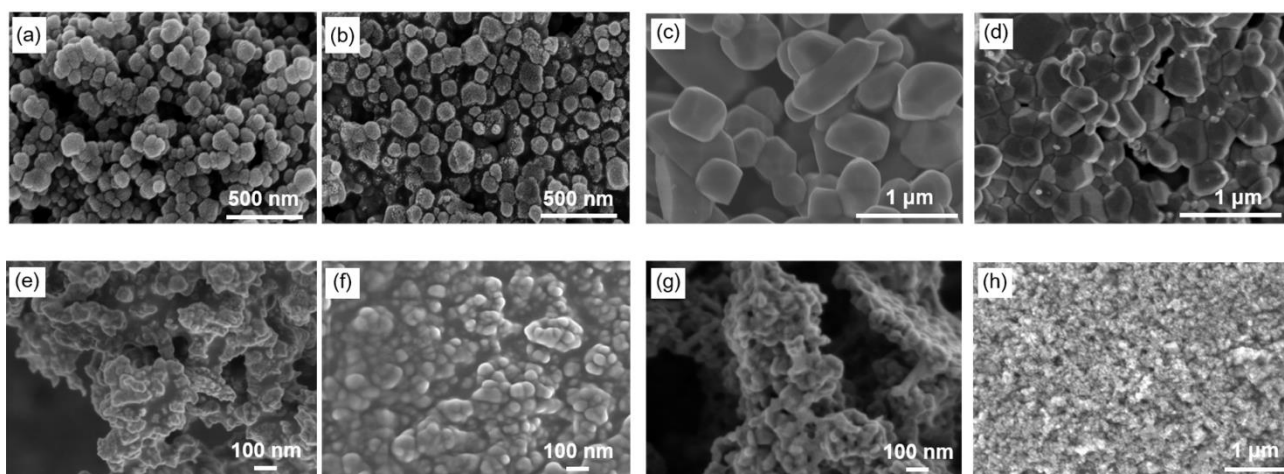


Figure 2. SEM images of Co-ZIF-67 (a), $\text{Ni}_{0.1}\text{Co}_{0.9}\text{-ZIF-67}$ (b), Co_3O_4 (c), $\text{Ni}_{0.2}\text{Co}_{0.8}\text{O}_y$ (d), CoP (e), $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$ (f), Co_9S_8 (g) and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_y$ (h)

The SEM images for all samples (Co-ZIF-67 and Ni_{0.1}Co_{0.9}-ZIF-6, Co₃O₄ and Ni_{0.2}Co_{0.8}O_y, CoP, Ni_{0.1}Co_{0.9}P_y, Co₉S₈ and Ni_{0.5}Co_{0.5}S_y) are presented in Fig. 2. The Co-ZIF-67 crystals (Fig. 2a) have a diameter of 86 nm and nearly spheroidal shape. As shown in Fig. 2b, the Ni_{0.1}Co_{0.9}-ZIF-67 crystals have similar morphology and a size of 135 nm. After oxidation, the derived Co₃O₄ crystals (Fig. 2c) have dodecahedral shape with an average size of 300 nm, while the Ni_{0.2}Co_{0.8}O_y crystals have an average size of 206 nm (Fig. 2d). The crystal size of the samples increases about twice after oxidation of the Ni_xCo_{1-x}-ZIF-67, indicating that two or three Ni_xCo_{1-x}-ZIF-67 nanoparticles coalesce into one Ni_xCo_{1-x}O_y particle. In the case of phosphides, the derived CoP showed an average size of 34 nm (Fig. 2e), and the Ni_{0.1}Co_{0.9}P_y crystals have an average size of 23 nm (Fig. 2f), which are smaller than the Ni_xCo_{1-x}-ZIF-67. The derived Co₉S₈ crystals have an average size of 15 nm (Fig. 2g), while the Ni_{0.5}Co_{0.5}S_y has a size of 12 nm (Fig. 2h), which are considerably smaller than the Ni_xCo_{1-x}-ZIF-67 crystals. The energy dispersive X-ray (EDS) elemental mapping and the elements proportion presented in Fig. S3 also confirm the uniform distribution of all elements in the Co-ZIF-67 (a) (Co, C, N, O), Ni_{0.1}Co_{0.9}-ZIF-67 (b) (Co, Ni), Co₃O₄ (c) (Co, O), Ni_{0.2}Co_{0.8}O_y (d) (Ni, Co, O), CoP (e) (Co, P), Ni_{0.1}Co_{0.9}P_y (f) (Ni, Co, P), Co₉S₈ (g) (Co, S) and Ni_{0.5}Co_{0.5}S_y (h) (Ni, Co, S). Additionally, the chemical composition of the materials was characterized by ICP-AES (Table S1). The content of metals (Co & Ni) in the oxide, sulfide and phosphide is much higher than in the Co-ZIF-67 and Ni_{0.1}Co_{0.9}-ZIF-67 samples, indicating that most of the C, N and H elements were pyrolyzed after the high-temperature treatment and the target products were prepared successfully. The transmission electron microscopy (TEM) images for all samples (Co-ZIF-67 and Ni_{0.1}Co_{0.9}-ZIF-6, Co₃O₄ and Ni_{0.2}Co_{0.8}O_y, CoP, Ni_{0.1}Co_{0.9}P_y, Co₉S₈ and Ni_{0.5}Co_{0.5}S_y) are shown in Fig. S2. The TEM results are consistent with SEM. The Ni_{0.1}Co_{0.9}-ZIF sample contains the same Co lattice with a Co-ZIF-67(111) interlayer spacing of 0.20 nm (Fig. 2a,b). The lattice fringes of Co₃O₄ and Ni_{0.2}Co_{0.8}O_y display interplanar spacings of 0.24 nm, which match well with the (311) planes of the Co₃O₄ (Fig. 3c,d). TEM images reveal that the Ni_{0.1}Co_{0.9}P_y retained small size with rough surface (Fig. S2 e,f). Moreover, the resolved interplanar distances of 0.09 and 0.12 nm from the HRTEM image can be ascribed to the (211) and (111) planes of CoP, respectively (Fig. S2 e,f insert image). Ni_{0.1}Co_{0.9}P_y and Ni_{0.5}Co_{0.5}S_y crystals with the

similar sizes are revealed by both TEM and SEM. The carbon cladding outside the metal particles (Fig. S2g), the carbon layer of the entire nanoparticle are evenly formed and thinner (Fig. S2h); the carbon-coated metal particles can be clearly seen. The interplanar distances of 0.14 and 0.15 nm resolved from the HRTEM image are ascribed to the (311) and (222) planes of Co_9S_8 , respectively (Fig. S2 g,h insert image).

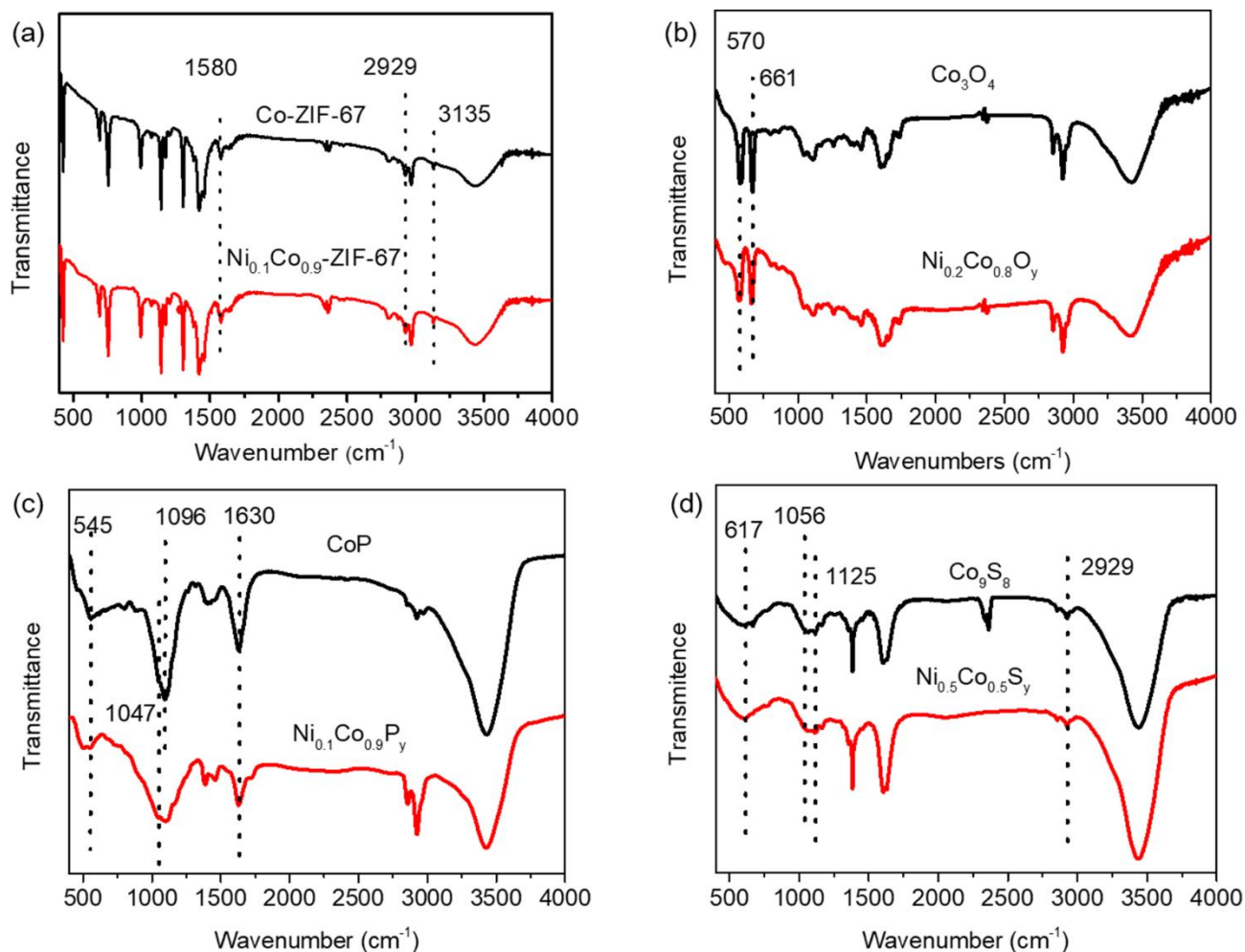


Figure 3. FT-IR spectra of Co-ZIF-67 and $\text{Ni}_{0.1}\text{Co}_{0.9}$ -ZIF-67 (a), Co_3O_4 and $\text{Ni}_{0.2}\text{Co}_{0.8}\text{O}_y$ (b), CoP and $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$ (c), Co_9S_8 and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_y$ (d)

The N_2 adsorption-desorption study was applied to reveal the porous nature of the samples (Figure S4). The specific surface area of samples Co-ZIF-67 and $\text{Ni}_{0.1}\text{Co}_{0.9}$ -ZIF-67 is $1402.4 \text{ m}^2\text{g}^{-1}$ and $1242.8 \text{ m}^2\text{g}^{-1}$, respectively. The isotherm of Co-ZIF-67 and $\text{Ni}_{0.1}\text{Co}_{0.9}$ -ZIF-67 are identified as type I, which is characteristic of microporous materials. The corresponding Density Functional Theory (DFT) results and

pore size distribution curve further indicates that Co-ZIF-67 contains the micropores. The BET specific surface area for sample Co_3O_4 , is $2.2 \text{ m}^2\text{g}^{-1}$, while for $\text{Ni}_{0.2}\text{Co}_{0.8}\text{O}_y$ is $3.2 \text{ m}^2\text{g}^{-1}$. The isotherms of CoP and $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$ are identified as type IV characteristic of mesoporous materials. CoP had a BET surface area of $19.4 \text{ m}^2\text{g}^{-1}$, while for $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$ is $12.3 \text{ m}^2\text{g}^{-1}$ (Fig. S5 a, b). The specific surface area of Co_9S_8 is $105.1 \text{ m}^2\text{g}^{-1}$ and for $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_y$ is $107.5 \text{ m}^2\text{g}^{-1}$ (Figure S5 c, d and Table S2.) The above results suggest that for the oxide and sulfide, the bimetallic catalysts with larger specific surface area would provide abundant catalytic active sites and facilitates the transport of electron and active species during the catalysis process. While only the phosphide are characteristic of mesoporous materials, we assume that the mesoporous structure is beneficial for charge and mass transport for electrocatalysis.

The FT-IR spectra of Co-ZIF-67 and $\text{Ni}_{0.1}\text{Co}_{0.9}$ -ZIF-67 are shown in Fig. 3a. The IR bands are primarily attributed to the ligand 2-Methylimidazole (2-MIM). The peaks in the range of $600\text{-}1500 \text{ cm}^{-1}$ correspond to the stretching and bending modes of the imidazole rings, whereas the band at 1580 cm^{-1} is attributed to the C-N stretching mode of 2-MIM. Additionally, the bands at 2929 and 3135 cm^{-1} correspond to the C-H stretching mode of the aromatic ring and the aliphatic chain of the 2-MIM, respectively^[21]. This result reveals that the bi-metallic $\text{Ni}_{0.1}\text{Co}_{0.9}$ -ZIF-67 crystals have been successfully prepared.

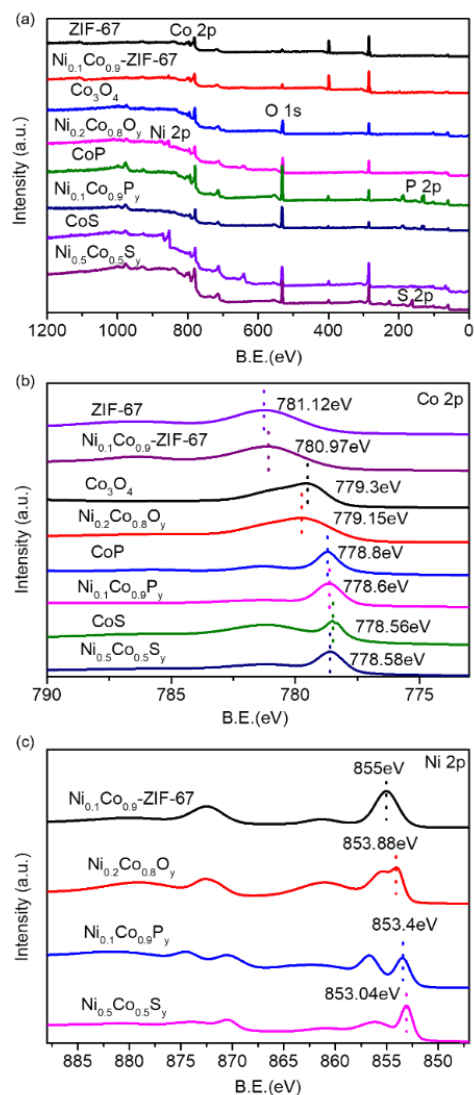


Figure 4. XPS spectra of Co-ZIF-67, Ni_{0.1}Co_{0.9}-ZIF-67, Co₃O₄, Ni_{0.2}Co_{0.8}O_y, CoP, Ni_{0.1}Co_{0.9}P_y, Co₉S₈ and Ni_{0.5}Co_{0.5}S_y catalysts in the range 100-1200 eV (a), 775-790 eV Co 2p (b), and 850-890 eV Ni 2p(c)

While several peaks in the range of 600~1500 cm⁻¹ are not present in the spectra of Co₃O₄ and Ni_{0.2}Co_{0.8}O_y, and the stretching mode of C–N bonding and the aliphatic chain of the 2-MIM at 1580 cm⁻¹ and 3135 cm⁻¹, respectively become obscured (Fig. 4b). The C-H stretching mode of the aromatic ring at 2929 cm⁻¹ is present. The peaks at 661 cm⁻¹ and 570 cm⁻¹ corresponding to the Co-O vibration [22] confirm that the ZIF-67 structure collapsed and Co is oxidized into Co₃O₄.

The FT-IR analysis verifies the presence of P-O bands in the spectra of CoP and Ni_{0.1}Co_{0.9}P_y as

shown in Figure 3c. Several bands in the region of 1150 - 1000 cm^{-1} are assigned to the P-O vibrations of the PO_4 group [23]. While the signals associated with the C-N stretching and the aliphatic chain of 2-MIM (1580 cm^{-1} and 3135 cm^{-1}) are present in the spectra of Co_9S_8 and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_y$ (Fig. 3d) indicating that ZIF-67 structure almost collapsed after sulfuration. The new band at 617 cm^{-1} belongs to the Co-S bending vibration of the Co_9S_8 [20b]. The peak at 1125 cm^{-1} is assigned to the S-O bending vibration [24], indicating that Co is sulfured into Co_9S_8 . The IR study confirmed that $\text{Ni}_x\text{Co}_{1-x}\text{O}_y$, $\text{Ni}_x\text{Co}_{1-x}\text{P}_y$ and $\text{Ni}_x\text{Co}_{1-x}\text{S}_y$ catalysts have been successfully synthesized.

The XPS spectra of all catalysts are shown in Fig. 4. The standard binding energy of the main peak of cobalt species (Co 2p_{3/2}) at 777.9 eV is present in all as-synthesized catalysts. While the Co 2p_{3/2} core level region contains a main peak at 780.97 eV ($\text{Ni}_{0.1}\text{Co}_{0.9}$ -ZIF-67), 779.15eV ($\text{Ni}_{0.2}\text{Co}_{0.8}\text{O}_y$), 778.6 eV ($\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$) and 778.56eV ($\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_y$), indicating the differences of the energy shift in the Co 2p spectra (Fig. 4b). The as-prepared materials show higher binding energy in the Ni 2p_{3/2} region compared with nickel species (852.3 eV), for instance, 855 eV for $\text{Ni}_{0.1}\text{Co}_{0.9}$ -ZIF-67, 853.88eV for $\text{Ni}_{0.2}\text{Co}_{0.8}\text{O}_y$, 853.4eV for $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$ and 853eV for $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_y$ (Fig. 4c).

The XPS spectra of $\text{Ni}_x\text{Co}_{1-x}\text{O}_y$, $\text{Ni}_x\text{Co}_{1-x}\text{P}_y$, and $\text{Ni}_x\text{Co}_{1-x}\text{S}_y$ catalysts are shown in the SI (Figs. S5-S7). The $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$ (Fig. S6), shows low binding energy (Co 2p_{1/2} and Ni 2p_{1/2}) compared to metallic Ni, Co, and P. The binding energies of Ni 2p and Co 2p exhibit positive shifts while P 2p is negatively shifted which is mainly due to the partial electron transfer from Ni and Co to P.

The positive metallic (Ni and Co) and negative P centers can play a role of hydride-acceptor and proton-acceptor sites, respectively, during the electrocatalytic process [19, 25]. Therefore, the positively charged Co and Ni and the negatively charged O, P and S centers could act as hydride-acceptor and proton-acceptor, respectively. The acceptor could promote the formation of cobalt hydride, which could facilitate the following H_2 evolution by electrochemical desorption [3b, 9a, 19, 25b, 26].

Electrocatalytic performance of $\text{Ni}_x\text{Co}_{1-x}$ -ZIF-67, $\text{Ni}_x\text{Co}_{1-x}\text{O}_y$, $\text{Ni}_x\text{Co}_{1-x}\text{P}_y$, and $\text{Ni}_x\text{Co}_{1-x}\text{S}_y$ for hydrogen evolution reaction (HER)

The electrocatalytic property of the nickel-cobalt based catalysts towards HER is evaluated. Fig. S5 shows LSV curves in alkaline media ($\text{pH} = 14 \pm 0.5$) for $\text{Ni}_x\text{Co}_{1-x}\text{-ZIF}$ (a), $\text{Ni}_x\text{Co}_{1-x}\text{O}_y$ (b), $\text{Ni}_x\text{Co}_{1-x}\text{P}_y$ (c), $\text{Ni}_x\text{Co}_{1-x}\text{S}_y$ (d) at a scan rate of 10 mV s^{-1} , respectively. It was found that at a current density of 10 mA cm^{-2} , the catalysis showed overpotential in the following order, phosphide < oxide < sulfide < ZIF-67 in both mono-metallic and bi-metallic derivatives with specific metal ratio: $\text{CoP} < \text{Co}_3\text{O}_4 < \text{Co}_9\text{S}_8 < \text{ZIF-67}$ and $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y < \text{Ni}_{0.2}\text{Co}_{0.8}\text{O}_y < \text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_y < \text{Ni}_{0.1}\text{Co}_{0.9}\text{-ZIF-67}$. The comparison of alkaline HER activities of as-prepared catalysts with the same ratio in the precursor are listed in the supporting information (Table S3). Obviously, the phosphide with the metal ratio $\text{Co: Ni} = 10:0, 9:1, \text{ and } 7:3$ showed the lowest overpotential at current density of 10 mA cm^{-2} , while the others (samples $\text{Ni}_{0.2}\text{Co}_{0.8}\text{O}_y$, $\text{Ni}_{0.4}\text{Co}_{0.6}\text{O}_y$ and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_y$) show the lowest overpotential. The phosphide performed superior in the high Co: Ni ratio, while the oxide and sulfide showed good performance in the middle ratio, indicating the optimum synergistic effect of Ni and Co in samples $\text{Ni}_x\text{Co}_{1-x}\text{O}_y$, $\text{Ni}_x\text{Co}_{1-x}\text{P}_y$ and $\text{Ni}_x\text{Co}_{1-x}\text{S}_y$. The LSV, Tafel plot and Electrochemical Impedance Spectroscopy (EIS) results are shown in the Figure. 5. The Fig. 5a shows linear sweep voltammetry (LSV) curves for $\text{Ni}_{0.1}\text{Co}_{0.9}\text{-ZIF-67}$, $\text{Ni}_{0.2}\text{Co}_{0.8}\text{O}_y$, $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_y$, and $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$ catalysts in alkaline media ($\text{pH} = 14 \pm 0.5$) in comparison with bare glassy carbon electrode (GCE) and commercial Pt/C catalyst. The $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$ is the most active for alkaline HER with a low overpotential of 160 mV to deliver 10 mA cm^{-2} . As shown in Table S4, (supporting information), compared with other as-prepared catalysts and previously reported Co -based catalysts, clearly the $\text{Ni}_x\text{Co}_{1-x}\text{P}_y$ catalysts have relatively lower overpotentials at the current densities of both 10 and 20 mA cm^{-2} . Moreover, the $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$ has the lowest Tafel slope of 100 mV dec^{-1} , being smaller than that of $\text{Ni}_{0.1}\text{Co}_{0.9}\text{-ZIF-67}$ ($109.11 \text{ mV dec}^{-1}$), $\text{Ni}_{0.2}\text{Co}_{0.8}\text{O}_y$ ($129.28 \text{ mV dec}^{-1}$) and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_y$ ($279.43 \text{ mV dec}^{-1}$) catalysts (Fig. 5b). To evaluate the catalytic activities, the electrochemical impedance spectroscopy analysis for $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$ catalyst under the same operating conditions was conducted. For $\text{Ni}_{0.1}\text{Co}_{0.9}\text{-ZIF-67}$, $\text{Ni}_{0.2}\text{Co}_{0.8}\text{O}_y$, $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_y$, and $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$ catalysts, low charge transfer resistances of $24.8, 21.0, 49.8, \text{ and } 10.2 \text{ } \Omega$, respectively are measured (Fig. 5c). In the equivalent circuit, R_s is related to the electrical transport property of a catalyst. The charge transfer resistance (R_{ct}) is associated with the

catalytic kinetics at the catalyst/electrolyte interface, small R_{ct} values contribute to faster charge transfer. The sharply decreased diameter of $Ni_{0.1}Co_{0.9}P_y$ in the Nyquist plots of Fig. 5c suggests a much faster electron-transfer kinetics. The $Ni_{0.5}Co_{0.5}S_y$ showed the largest R_{ct} which demonstrates the lowest electron-transfer kinetics.

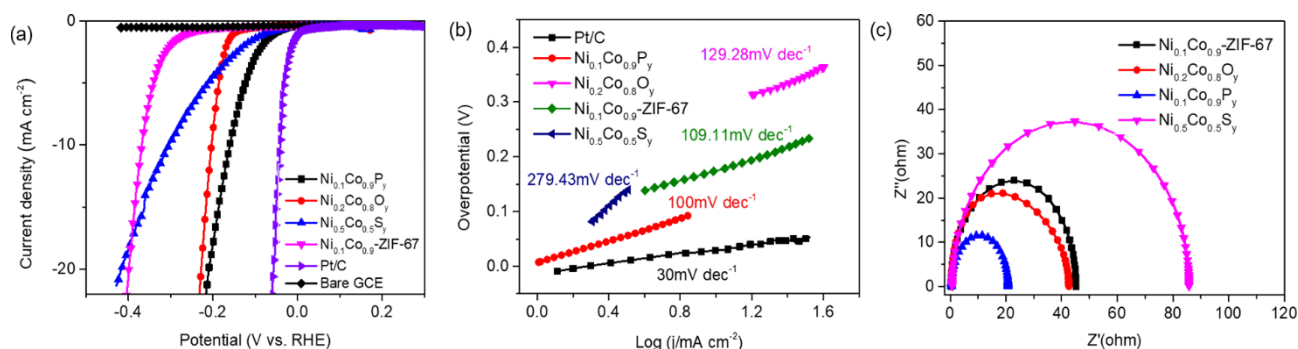


Figure 5. Polarization curves of $Ni_{0.1}Co_{0.9}$ -ZIF-67, $Ni_{0.1}Co_{0.9}P_y$, $Ni_{0.2}Co_{0.8}O_y$, $Ni_{0.5}Co_{0.5}S_y$, commercial Pt/C catalyst and bare GCE measured in alkaline media (pH = 14 ± 0.5 , 1 M KOH) (a), Tafel plots (b) and Electrochemical Impedance Spectroscopy (EIS) Nyquist plots (c)

The following trend for the catalysts at the same current density of 10 or 20 $mA\ cm^{-2}$ is observed: $Ni_{0.1}Co_{0.9}P_y > Ni_{0.2}Co_{0.8}O_y > Ni_{0.5}Co_{0.5}S_y > Ni_{0.1}Co_{0.9}$ -ZIF-67. To evaluate the stability of the catalysts, long-term electrolysis in 1.0 M KOH is carried out. The four catalysts show almost the same LSV curve with negligible cathode current drop after 2000 cycles, which confirms their high stability for alkaline HER (Fig. S9). To get further insight into the structure-activity correlation between HER performance and different catalysts, a series of DFT calculations were performed (SI). For an ideal electrocatalyst, a moderate H adsorption free energy is close to zero ($\Delta G_{H^*} \approx 0$), which is in favor of the adsorption and desorption steps, thus facilitating the proton-electron-transfer process. Therefore, proton adsorption free energy was adopted to correlate the HER performance. The results are illustrated in Fig.6 and the optimized adsorption structures are presented in Fig. S11. We firstly compared the H adsorption free energy of Co_9S_8 , Co_3O_4 and CoP (Fig. 6a), and the H adsorption free energy of Co_9S_8 (1.01 eV), Co_3O_4 (-0.74 eV) and CoP (0.09 eV) are similar with the experimental results. Due to the lowest H adsorption free energy, the CoP shows excellent HER performance. We further built the Ni doped CoP model to

simulate the $\text{Ni}_{1-x}\text{Co}_x\text{P}_y$ (Fig. 6b), of which the ΔGH^* are: $\text{Co}_{0.7}\text{Ni}_{0.1}\text{P}$ (0.08197 eV), $\text{Co}_{0.6}\text{Ni}_{0.2}\text{P}$ (0.09327 eV), and $\text{Co}_{0.5}\text{Ni}_{0.3}\text{P}$ (0.116582 eV). As the Ni decreases, the $\text{Ni}_{1-x}\text{Co}_x\text{P}_y$ showed lower ΔGH^* in the order $\text{Co}_{0.5}\text{Ni}_{0.3}\text{P} > \text{Co}_{0.6}\text{Ni}_{0.2}\text{P} > \text{Co}_{0.7}\text{Ni}_{0.1}\text{P}$, which is in accordance with the experimental result demonstrating that the phosphide performance is superior in the sample with high Co: Ni ratio. In conclusion, the CoP shows superior HER performance in contrast to the Co_9S_8 and Co_3O_4 . The $\text{Co}_{0.7}\text{Ni}_{0.1}\text{P}$ shows the highest electrochemical performances according to the DFT calculations, while sample $\text{Co}_{0.9}\text{Ni}_{0.1}\text{P}_y$ with best HER performance was obtained experimentally.

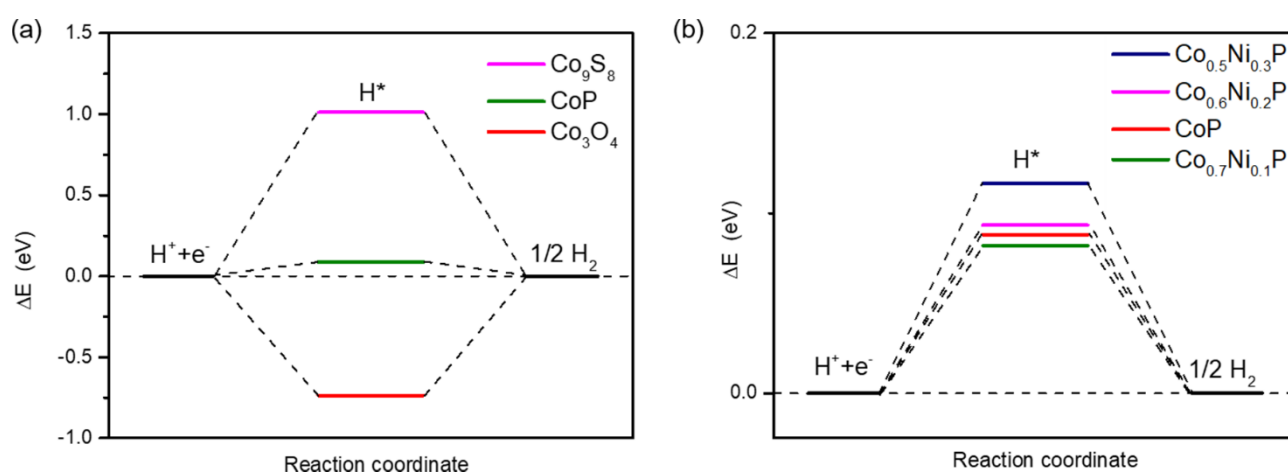


Figure 6. Calculated free energy diagram of the HER on the Co_3O_4 (110), Co_9S_8 (111), CoP (101) (a), and $\text{Co}_{0.5}\text{Ni}_{0.3}\text{P}$, $\text{Co}_{0.6}\text{Ni}_{0.2}\text{P}$, CoP , $\text{Co}_{0.7}\text{Ni}_{0.1}\text{P}$ (b)

The electrochemical activity of the catalysts for HER are comparable and slightly improved than those reported in the open literature so far [11a, 18, 27]. The HER activity of $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$ in comparison with the materials already published are summarized in Table S4. The phosphides have high affinities for H_2 and they could be suitable for HER electrocatalysis. The best performance of the $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$ catalyst is attributed to the following reasons: (i) the nanosized bimetallic structure provide abundant active sites for the electrochemical reaction, (ii) Ni and Co atoms are atomically arranged in the $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}_y$, (iii) the electron transfer from Ni and Co to P improve the electron-donating ability of the catalyst, leading to the high HER activity, (iv) DFT results further indicate that the synergistic effect between Co and Ni with metal ratio of 9:1 in phosphide can increase the binding strength of H, thus improving the electrocatalytic

performance. Overall, the Ni_{0.1}Co_{0.9}P_y has been considered as a highly efficient and stable electrocatalyst for HER.

Conclusions

In summary, nanosized homeotypic bimetallic Ni_{1-x}Co_xO_y, Ni_{1-x}Co_xS_y and Ni_{1-x}Co_xP_y catalysts were prepared from Ni_{1-x}Co_x-ZIF-67 by temperature-programmed reactions with oxygen, sublimed sulfur and sodium hypophosphite, respectively. Compared to the monometallic Co-based materials, the homologous bimetallic Ni_{1-x}Co_x-ZIF-67, Ni_{1-x}Co_xO_y, Ni_{1-x}Co_xS_y and Ni_{1-x}Co_xP_y catalysts exhibit better electrocatalytic activity for hydrogen production in alkaline water electrolysis.

The high HER activity of the Ni_{0.1}Co_{0.9}P_y modified electrode is related to the appropriate nickel-cobalt metal ratio, high crystallinity, and nickel-cobalt synergistic accelerating electron transfer from Ni and Co to P. This correlation between the composition and properties of nickel-cobalt nanoparticles and their electrocatalytic performance for hydrogen evolution in alkaline media are the base for further design of better transition metals catalyst toward the HER.

Experimental Section

Chemical and reagents

Cobalt acetate (Co(CH₃CO₂)₂•4H₂O), nickel acetate (Ni(CH₃CO₂)₂•4H₂O), 2-methylimidazole (C₄H₆N₂), triethylamine ((C₂H₅)₃N), potassium hydroxide (KOH, pellets), thiourea (CH₄N₂S), nafion (5 wt%), ethanol (C₂H₆O) were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents and solvents were used as received without further treatment.

Preparation of Co-ZIF-67: Co-ZIF-67 nanocrystals were synthesized following the procedure described by Wang et.al. ^[14a] with slight modification. In a typical synthesis, solution A was prepared by cobalt acetate (0.4152 g, 0.00167 mol) dissolved in 15 ml distilled water. Solution B was prepared by

dissolving 2-methylimidazole (1.3686 g, 0.0167 mol) and TEA (1.6868 g, 0.167 mol) in 15 ml distilled water. Both solutions were stirred with 800 r/min for 30 min. Then the two solutions were mixed in ice-water bath for 10 min. Purple crystals were collected by centrifugation and washed several times with distilled water and dried at 60 °C oven for 12 h. The obtained samples were denoted as Co-ZIF-67.

Preparation of $\text{Ni}_x\text{Co}_{1-x}$ -ZIF-67: the cobalt acetate in the synthesis precursor was replaced with a mixture of cobalt acetate and nickel acetate, the Co/Ni molar ratios were adjusted from 9:1 to 1:1. The preparation of the $\text{Ni}_x\text{Co}_{1-x}$ -ZIF-67 was performed in ice-water bath for 10 min. The washing and drying procedure were same as before. The obtained samples were denoted as $\text{Ni}_x\text{Co}_{1-x}$ -ZIF-67.

Synthesis of mono- and bi- metallic $\text{Ni}_x\text{Co}_{1-x}\text{O}_y$, $\text{Ni}_x\text{Co}_{1-x}\text{S}_y$, $\text{Ni}_x\text{Co}_{1-x}\text{P}_y$ catalysts

Preparation of $\text{Ni}_x\text{Co}_{1-x}\text{O}_y$: the $\text{Ni}_x\text{Co}_{1-x}$ -ZIF-67 samples were put into a muffle furnace and annealed at 800 °C for 4 h under air (ramping of 2 °C min⁻¹). The final black powder was collected at room temperature (the samples are denoted as $\text{Ni}_x\text{Co}_{1-x}\text{O}_y$).

Preparation of $\text{Ni}_x\text{Co}_{1-x}\text{S}_y$ [20a, 20b]: $\text{Ni}_x\text{Co}_{1-x}$ -ZIF-67 (0.2g) and sublimed sulfur (0.1g) were placed at two separate positions in a porcelain boat; the sublimed sulfur was placed at the upstream side of the furnace. The obtained samples were denoted as $\text{Ni}_x\text{Co}_{1-x}\text{S}_y$.

Preparation of $\text{Ni}_x\text{Co}_{1-x}\text{P}_y$ [12c, 26, 28]: $\text{Ni}_x\text{Co}_{1-x}$ -ZIF-67 (0.2g) and $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$ (1g) were placed at two separate positions in a porcelain boat; $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$ was placed at the upstream side of the furnace. The molar ratio of Co/P was 1:20. The obtained samples were denoted as $\text{Ni}_x\text{Co}_{1-x}\text{P}_y$.

Characterization

The structure of the samples was characterized by X-ray powder diffraction (Siemens D5005 diffractometer) with Cu K α radiation ($\lambda=1.5418$ Å) in Bragg-Brentano ($\theta\sim 2\theta$) configuration. The structure and morphology of the as-prepared samples were characterized by a field emission scanning electron microscope (JEOL JSM-7900F). Transmission electron microscopy (TEM) images were

obtained using a JEM 2100 transmission electron microscope operating at 200 kV. The distribution of the elements of the samples was measured by EDS-SEM using JEOL-7900F SEM and Oxford Instruments X-MaxN Energy-Dispersive Spectroscopy. The hydrogen and nitrogen adsorption-desorption experiments were performed at 77K using Quantachrome autosorb iQ3 gas sorption analyzer. The external surface area was determined by the Brunauer-Emmett-Teller Method (BET). The infrared (IR) spectra of samples were collected by NEXUS FT-IR using the KBr technique. Chemical composition of the as-synthesized samples were characterized by X-ray photoelectron spectroscopy with PH 5000 Versaprobe system using monochromatic Al K α radiation ($h\nu=1486.6$ eV). Inductively Coupled Plasma (ICP) was performed by Agilent ICPOES 720.

Electrochemical Measurements

All electrochemical measurements were carried out in nitrogen-purged 1 M KOH solution (pH=14 \pm 0.5) at room temperature on a CHI660E electrochemical workstation using a standard three-electrode system: a saturated calomel electrode (SCE) used as a reference electrode, a carbon rod used as a counter electrode, and a glassy carbon electrode (GCE, 0.1256 cm², geometric area) used as a working electrode. The working electrode was prepared as follows. Typically, the catalytic powder (3.6 mg) and activated carbon (0.09 mg) are added into a mixture of 1 mL ethanol and 80 μ L Nafion (5 wt%) and sonicated for 40 min to obtain a homogeneous mixture further called ink. Then (10 μ L) of the catalyst ink was deposited onto the GCE surface (loading 0.358 mg cm⁻²).

The polarization curves were obtained by linear voltammetry sweeping (LSV) from 0.27 V to -0.53 V (vs RHE) with a scan rate of 10 mV s⁻¹ in 1 M KOH. Alternating current (AC) impedance measurements were carried out at -0.3 and - 0.41 V from 100 kHz to 0.1 Hz. The stability of the catalysts was characterized under continuous cyclic voltammetry (CV) measurements from -0.05 to 0.2 V (vs RHE) at a sweep rate of 50 mV s⁻¹. During the experiments, a flow of nitrogen was maintained over the electrolyte

to eliminate dissolved oxygen. All results were calibrated with respect to the reversible hydrogen electrode (RHE) by $E(\text{RHE}) = E(\text{V vs SCE}) + 0.245 \text{ V} + 0.059 \text{ pH}$ [14a].

Theoretical calculations were performed using Vienna ab initio simulation packages (VASP) based on density functional theory (DFT). [29] The core and valence electrons were described by the projector augmented wave (PAW) pseudopotentials. The generalized gradient approximation (GGA) in the scheme of proposed by Perdew, Burke, and Ernzerhof (PBE) was adopted to express the exchange correlation interactions with a cut off energy of 400 eV. [30] A 12 Å vacuum region was used to simulate the adsorption and all the top two layers of atoms in the structure are allowed to relax. The convergence of energy and forces were set to 1×10^{-5} eV and 0.03 eV, respectively. The free energy of hydrogen adsorption (ΔG_{H^*}) can be calculated as follows:

$$\Delta G(\text{H}^*) = \Delta E + 0.24 \text{ eV}$$

And ΔE is the adsorption energy, with defined as follows:

$$\Delta E = E(\text{substrate} + \text{adsorbate}) - E_{\text{substrate}} - E_{\text{adsorbate}}$$

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Keywords: ZIF-67 • Ni-Co-doping • organized bimetallic atomic arrangement • Hydrogen evolution reaction

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