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An Efficient Ternary CoP_{2x}Se_{2(1-x)} Nanowire Array for overall Water Splitting

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Developing earth-abundant and efficient bifunctional electrocatalysts for realizing hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in alkaline condition is an intriguing challenge. Here, a ternary necklace-like CoP_{2x}Se_{2(1-x)} nanowire arrays are synthesized via simultaneously phosphorizing and selenizing Co(OH)\textsubscript{2} nanowires. Owing to the substitution of P atom in the ternary system, the optimal electronic structure of the CoP_{2x}Se_{2(1-x)} can be obtained and the stability can also be enhanced for hydrogen evolution. Thus, the ternary CoP_{2x}Se_{2(1-x)} NWs is highly active for electrochemical hydrogen evolution in both acidic and alkaline media, achieving a current density of 10 mA cm\textsuperscript{-2} at overpotentials of 70 mV and 98 mV, respectively. To realize the overall water splitting, we further illustrated the experiment by using the CoP_{2x}Se_{2(1-x)} NWs as cathode and Co(OH)\textsubscript{2} NWs as anode, which requires a cell voltage of 1.65 V to afford a water splitting current density of 10 mA cm\textsuperscript{-2} in strong alkaline media (1.0 M KOH).

Introduction

Compared with fossil fuels, hydrogen energy is one of the promising alternatives for renewable fuel due to its sustainable and environmentally friendly characteristics.\textsuperscript{1-7} Electrocatalytic water splitting is an efficient route to produce pure hydrogen and oxygen gas. Typically, it is composed of hydrogen evolution reaction (HER, 2H\textsuperscript{+} + 2e\textsuperscript{−} →H\textsubscript{2}) in cathode electrode and oxygen evolution reaction (OER, 2H\textsubscript{2}O → 4e\textsuperscript{−} + 4H\textsuperscript{+} + O\textsubscript{2}) in anode electrode.\textsuperscript{8-30} To date, Pt-based and Ir/Ru-based materials are regarded as the benchmarks for HER and OER, respectively. Unfortunately, their high cost hinders the practical application in large-scale. It is, thus, extremely urgent to develop inexpensive and earth-abundant alternative electrocatalysts. In the last few years, great efforts have been made in developing non-noble metal catalysts, including transition metal chalcogenides,\textsuperscript{11-19} phosphides,\textsuperscript{20-24} and carbides\textsuperscript{25, 26} for HER, as well as transition metal phosphate,\textsuperscript{27} oxides\textsuperscript{28, 31} and hydroxides\textsuperscript{32, 35} for OER. Notably, overall water splitting must be operated in the same electrolyte in the practical process.\textsuperscript{36} What’s more, water splitting conducted in alkaline solution has emerged as a much more effective method for commercial hydrogen production due to the scare electrocatalyst and much more energy-intensive of OER in acidic media.\textsuperscript{37, 38} Therefore, it’s attractive to develop novel non-noble bifunctional electrocatalysts with high activity and stability for overall water splitting in alkaline solution.

Nowadays, transition metal dichalcogenides (TMDs) such as NiSe\textsubscript{2},\textsuperscript{39} and CoSe\textsubscript{2},\textsuperscript{40, 41} and transition metal phosphides (TMPs) like CoP\textsubscript{2},\textsuperscript{42, 43} FeP,\textsuperscript{44} and NiP\textsubscript{2}\textsuperscript{45} have been extensively developed for HER with high performance and stability in both acidic and basic media due to their excellent catalytic performance and high stability. Unlike the binary materials, component controllably synthesized ternary materials, such as WSe\textsubscript{2-x}Se\textsubscript{x},\textsuperscript{46} MoS\textsubscript{2-x}S\textsubscript{x},\textsuperscript{47} CoPS\textsubscript{1-x},\textsuperscript{48, 49} and NiP\textsubscript{2-x}Se\textsubscript{x} and CoSe\textsubscript{2-x}Se\textsubscript{x}\textsuperscript{50} are found to require a much lower overpotentials. Encouraged by this and considering the fact that substitution of the P atom in CoSe\textsubscript{2} would tangibly modify the electronic structure of the resulting ternary material, we designed a rational synthesis of CoP_{2x}Se_{2(1-x)}. Benefitting from the advantage of the controllability of our method, the optimum P to Se ratio can improve the activity and stability via tailoring the electronic structure and allowing the exposure of more active sites. It is therefore reasonable to predict that CoP\textsubscript{2}Se_{2(1-x)} could be a promising candidate for HER.

Herein, we successfully synthesize the ternary necklace-like CoP_{2x}Se_{2(1-x)} nanowire arrays, which provide much more electrochemical active area, on carbon fiber via phosphorization and selenization reaction. Being an electrocatalyst for HER in acidic media, the CoP_{2}Se_{2(1-x)} electrode achieves current density of 10 mA cm\textsuperscript{-2} at overpotential of 70 mV in acid solution and shows high stability. Significantly, the CoP_{2}Se_{2(1-x)} electrode also exhibits excellent electrocatalytic activity and durability in alkaline...
condition. It needs only 98 mV to reach current density of 10 mA cm$^{-2}$ which is very close to the HER performance in acidic solution. Furthermore, to realize a practical utilization, we designed overall water splitting setup in such a way that the CoP$_2$S$_{2x}$NWs and Co(OH)$_2$ NWs served as cathode and anode, respectively. Accordingly, this configuration requires a cell voltage of 1.65 V to reach a current density of 10 mA cm$^{-2}$, suggestive of its promising feature for practical realization of water splitting.

Experimental section

Synthesis of Co(OH)$_2$ NWs

The Co(OH)$_2$ nanowires on a CF was synthesized by a method that we have reported in our previous work. First, the CFs were ultrasonically washed by acetone, ethanol and ultrapure water in sequence, and then dried at 60 °C. Subsequently, 1.90 g CoCl$_2$·6H$_2$O, 2.424 g CO(NH$_2$)$_2$ were dissolved in 40 mL ethanol for 10 min. To form a seed layer on CFs, the soaked CFs were calcined at 450 °C for 4 h under an argon flow. Then, 1.90 g CoCl$_2$·6H$_2$O and 2.424 g CO(NH$_2$)$_2$ were dissolved in 40 mL ultrapure water. After transferring the solution into a 50 mL Teflon-lined stainless steel autoclave, one piece of the seeded CFs was immersed in the solution. The autoclave was then heated in an electrical oven at 90 °C for 4 h under an argon flow. After cooling down to room temperature, the obtained Co(OH)$_2$ NWs washed with water and ethanol. Eventually, the Co(OH)$_2$ NWs dried at 60 °C for further use.

Synthesis of CoP$_2$S$_{2(1-x)}$ NWs

A horizontal quartz tube furnace is utilized to convert the Co(OH)$_2$ NWs into CoP$_2$S$_{2(1-x)}$ NWs. The Co(OH)$_2$ NWs on CF was placed at the downstream side of the furnace and a mixture of phosphorus and selenium powder was placed at the upstream side of the furnace. At the beginning, the tube furnace was flushed under a 100 sccm Ar flow for three times to create an oxygen-free environment. The reaction temperature maintained for 60 min to fully convert the Co(OH)$_2$ NWs into CoP$_2$S$_{2(1-x)}$ NWs, followed by natural cooling down. During the synthesis process, the flow of Ar is kept at a rate of 100 sccm.

Characterizations

The morphologies of Co(OH)$_2$ NWs and CoP$_2$S$_{2(1-x)}$ NWs were characterized by Hitach S-4800 scanning electron microscopy (SEM) under 20 kV and TecnaiF20 transmission electron microscopy (TEM) at 200 kV. STEM-EDX elemental mapping was characterized by TecnaiF20 and the energy dispersive X-ray spectroscopy (EDX) was performed on Hitach S-4800. X-ray diffraction (XRD) patterns (Philips X’Pert Pro Super) were obtained using Cu Ka radiation ($\lambda$ = 1.5418 Å) and X-ray photoelectron spectroscopy (XPS) was tested on ESCALAB250Xi. The pH of the electrolyte was performed by the METTLER TOLEDO pH meter (FE20).

Electrochemical measurements

The test for hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) were performed in a typical three-electrode configuration at an electrochemical station (CHI 660D). The HER measurements were conducted in 0.5 M H$_2$SO$_4$ (pH=0.69) and 1M KOH solution (pH=13.71). When 0.5 M H$_2$SO$_4$ solution was used as electrolyte in the three-electrode system, the CF covered with CoP$_2$S$_{2(1-x)}$ NWs used as the working electrode (WE) and a platinum wire and a saturated calomel electrode (SCE) served as the counter electrode (CE) and reference electrode (RE), respectively. In acidic media, the equation E (RHE) = E (SCE) + 0.242 + 0.059 pH is considered. Linear sweep voltammetry (LSV) measurements were measured at a scan rate of 5 mV s$^{-1}$ from +0.1 to -0.4V vs. reversible hydrogen electrode (RHE). To estimate the double-layer capacitance, cyclic voltammetry (CV) experiments were performed from 0 to +0.1 V vs. RHE with various scan rates (20-200 mV/s). We used a mercuric oxide electrode (MOE) as WE when HER measurements were tested in 1 M KOH solution. In alkaline media, the equation E (RHE) = E (MOE) + 0.098 + 0.059 pH is considered. LSV measurements were tested from +0.1 to -0.4V vs. RHE at a scan rate of 2 mVs$^{-1}$. CV experiments were performed from +0.05 to +0.15 V vs. RHE with different values of scan rates (20-200 mV/s) to assess the double-layer capacitance. The OER measurements were measured in 1 M KOH using the CF covered with CoP$_2$S$_{2(1-x)}$ NWs as the WE, a platinum wire as the CE and a MOE as the RE. LSV was conducted from 1.0 to 1.8 V vs. RHE at a scan rate of 2 mV s$^{-1}$. The overall water splitting was evaluated in 1 M KOH using a two-electrode configuration. The CoP$_2$S$_{2(1-x)}$ NWs on CF served as the cathode for HER, and Co(OH)$_2$ on CF used as anode for OER. The polarization curve was performed at scan rate of 2 mV s$^{-1}$. All the potentials were calibrated to a RHE and all polarization curves were corrected for iR losses.

Results and discussion

Fig. 1. TEM image (a), HRTEM image (b), STEM image and EDX elemental mapping(c) of a CoP$_2$S$_{2(1-x)}$ NW. (d) EDX spectra of CoP$_{0.4}$S$_{0.6}$, CoP$_{0.6}$S$_{0.4}$, CoP$_{0.7}$S$_{0.3}$ and CoP$_{1.4}$Se$_{0.6}$. (e) XRD patterns of bare CF, CoSe$_2$ NWs and CoP$_2$S$_{2(1-x)}$ NWs. (f) The orthorhombic macarite-type structure (left) and cubic pyrite-type.
The ternary CoP$_2$Se$_{2(1−x)}$ NWs were prepared through selenizing and phosphorizing Co(OH)$_2$ NWs, simultaneously. (see the Experimental Section).\textsuperscript{51, 52} In general, we first grew Co(OH)$_2$ NWs (Fig. S1a-b), which is utilized as the precursor for achieving CoP$_2$Se$_{2(1−x)}$ NWs (Fig. S2a and b), on carbon fiber (CF) through hydrothermal method. Scanning electron microscopy (SEM) and transmission electron microscope (TEM) were used to observe the morphologies of Co(OH)$_2$ NWs (Fig. S1a-b) and CoP$_2$Se$_{2(1−x)}$ NWs. Low magnification TEM (Fig. 1a) reveals that the diameter of the CoP$_2$Se$_{2(1−x)}$ NW is around 200 nm with the length of several micrometers. Different with the smooth surface of Co(OH)$_2$ NWs (Fig. S1b), the resulting CoP$_2$Se$_{2(1−x)}$ NWs have a rough surface (Fig. 1a) with the necklace-like morphology. Moreover, the high-resolution TEM (HRTEM) image in Fig. 1b demonstrates the lattice fringes with the interplanar spacing of 0.244 nm, which belongs to the (0002) planes of the space group $P6_3/mmc$ of hexagonal CoP\textsubscript{3}.\textsuperscript{53} Furthermore, the composition of the CoP$_2$Se$_{2(1−x)}$ NW can be controlled uniformly in the CoP$_2$Se$_{2(1−x)}$ NW. Therefore, the corresponding energy-dispersive X-ray (EDX) element al mapping fringes with the interplanar spacing of 0.244 nm, which belongs to the (0002) planes of the space group $P6_3/mmc$ of hexagonal CoP\textsubscript{3}.\textsuperscript{53} One of the regions has two peaks with one located at binding energy of 129.60 eV and the other at 130.1 eV (P 2p\textsubscript{1/2} and P 2p\textsubscript{3/2}), which corresponds to phosphorus anions. The second region is centred at 133.6 and 135.5 eV (unresolved doublet) and these two peaks can be assigned to the phosphate-like P. This is agree with the reported results.\textsuperscript{49} Meanwhile, the quantitative analysis also shows that the ratio of P and Se is near to 2 : 1 and this result is consistent with the EDX data.
binary CoSe₂ NWs (7.48 mF cm⁻²), indicating the increased electrochemically active surface area of ternary CoP₁.₃₇Se₀.₆₃ NWs. The morphology of CoSe₂ NWs and ternary CoP₁.₃₇Se₀.₆₃ NWs are similar, thus the increase in Cdl can be associated to the proliferation of active sites on the CoP₁.₃₇Se₀.₆₃ NWs, which is consistent with some reported results. Moreover, the stability of CoP₁.₃₇Se₀.₆₃ NWs was investigated with chronoamperometric measurement. Fig. 3d shows that the decrease of catalytic current density is negligible for up to 12 h of electrolysis, indicating the good stability of the CoP₁.₃₇Se₀.₆₃ NWs for HER in acid solution. The SEM image and XRD pattern (Fig. S6a and Fig. 57) of the CoP₁.₃₇Se₀.₆₃ NWs after the stability measurement also verify the robustness of CoP₁.₃₇Se₀.₆₃ NWs.

Fig. 3. Polarization curves of CoP₁.₃₇Se₀.₆₃ NWs, bare CF and Pt foil for HER in 0.5 M H₂SO₄ (a) and 1 M KOH (e). Comparison of the overpotentials of the different CoP₁.₃₇Se₀.₆₃ NWs and Pt foil at the current density of 10 mA cm⁻² for HER in 0.5 M H₂SO₄ (b) and 1 M KOH (f). The corresponding Tafel plots of CoP₁.₃₇Se₀.₆₃ NWs and Pt foil in 0.5 M H₂SO₄ (c) and 1 M KOH (g). Chronoamperometric curve of CoP₁.₃₇Se₀.₆₃ NWs at a constant potential in 0.5 M H₂SO₄ (d) and 1 M KOH (h).

We further evaluated the HER activity of CoP₁.₃₇Se₀.₆₃ NWs in strong basic media (1 M KOH) wherein a mercuric oxide electrode (MOE) served as reference electrode. Fig. 3e exhibits the HER activity of CoP₁.₃₇Se₀.₆₃ NWs with the overpotential of 98 mV at 10 mA cm⁻² in alkaline condition is very similar to that of Pt foil (82 mV at 10 mA cm⁻²). The HER performance of the CoP₁.₃₇Se₀.₆₃ NWs is also better than some reported binary Co-based materials. In comparison with CoSe₂ (Fig. S3), CoP₀.₆₄Se₁.₅₅, CoP₀.₆₃Se₁₀.₄₃ and CoP₁.₃₇Se₀.₆₃ (Fig. S4c), CoP₁.₃₇Se₀.₆₃ NWs exhibits the best HER activity in alkaline solution. As shown in Fig. 3f, the overpotential required to achieve a current density of 10 mA cm⁻² for CoP₁.₃₇Se₀.₆₃ NWs is much lower than CoSe₂ (362 mV), CoP₀.₆₄Se₁.₅₅ (253 mV), CoP₀.₆₃Se₁₀.₄₃ (154 mV) and CoP₁.₃₇Se₀.₆₃ (120 mV), indicating that the CoP₁.₃₇Se₀.₆₃ NWs is the optimal one for HER in alkaline media. The comparison of the corresponding Tafel slopes of various atomic ratios of P to Se in CoP₁.₃₇Se₀.₆₃ further suggests that the CoP₁.₃₇Se₀.₆₃ NWs shows the optimal performance for HER in basic solution. The cyclic voltammogram (CV) curves of CoP₁.₃₇Se₀.₆₃ NWs, CoSe₂ NWs between 0.05 and 0.15 V vs. RHE with different values of scan rates (10 mV s⁻¹ to 1000 mV s⁻¹) in alkaline condition (Fig. S5d–e) were conducted. According to Fig. S4f, the Cdl of CoP₁.₃₇Se₀.₆₃ NWs and CoSe₂ NWs are 20.2 mF cm⁻² and 5.7 mF cm⁻², respectively. This result shows a consistent trend with the one in acidic media. The CoP₁.₃₇Se₀.₆₃ NWs also exhibits excellent stability in alkaline solution (Fig. 3f). After 12 h of electrolysis, there is only a minor deterioration of catalytic current density. The SEM image and XRD pattern of CoP₁.₃₇Se₀.₆₃ NWs after HER test show that our electrodes are stable in strong alkaline solution. In general, the excellent HER performance and good stability of CoP₁.₃₇Se₀.₆₃ NWs make it an ideal HER catalyst in both acidic and alkaline solutions.
verifying a favorable OER kinetics for Co(OH)\textsubscript{2} NWs. Fig. 4c shows a multi-step chronopotentiometric curve for Co(OH)\textsubscript{2} NWs in 1.0 M KOH. The current is increased from 50 to 450 mA cm\textsuperscript{-2} and remains stable for the rest 500 s and the other steps also show similar results, indicating the excellent mass transportation and mechanical robustness of the Co(OH)\textsubscript{2} NWs. The time-dependent current density curve (Fig. 4d) was also studied to probe the long-term stability of Co(OH)\textsubscript{2} NWs. According to Fig. 4d, there is no obvious current density change for up to 12 hours OER test, implying the excellent stability of Co(OH)\textsubscript{2} NWs for OER in strong alkaline solution.

In summary, ternary CoP\textsubscript{1.37}Se\textsubscript{0.63} NW arrays on carbon fiber was successfully fabricated via simultaneous phosphorization and selenization of Co(OH)\textsubscript{2} NWs. The CoP\textsubscript{1.37}Se\textsubscript{0.63} NWs can be directly used as an excellent and durable electrode for HER under both acidic and alkaline conditions. After optimizing the composition, CoP\textsubscript{1.37}Se\textsubscript{0.63} NWs can afford a current density of 10 mA cm\textsuperscript{-2} for HER at 70 mV and 98 mV in acidic and alkaline media, respectively. Furthermore, the Co(OH)\textsubscript{2} NWs also shows marked high and stable catalytic activity toward OER in alkaline solution and requires only 290 mV to reach a current density of 10 mA cm\textsuperscript{-2}. The overall electrochemical water splitting in a strong alkaline solution (1.0 M KOH) is further conducted with CoP\textsubscript{1.37}Se\textsubscript{0.63} NWs as cathode and Co(OH)\textsubscript{2} NWs as anode. This setup requires a voltage of 1.65 V to generate 10 mA cm\textsuperscript{-2} water-splitting current density. Our work offers an earth-abundant, binding-free material and efficient catalysts for practical overall water splitting in alkaline media.

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Table of contents:

Varying compositions of ternary CoP$_{2x}$Se$_{(2(1-x))}$ nanowires (NW) are synthesized via hydrothermal method followed by CVD method. Among them, CoP$_{1.37}$Se$_{0.63}$ NW needs overpotentials of only 70 mV and 98mV to achieve a current density of 10 mA/cm$^2$ in acidic and alkaline solution, respectively. This evidences the fact that this ternary material shows high catalytic activity in both acidic and alkaline condition.