This article can be cited before page numbers have been issued, to do this please use: Z. Ma, H. Yuan, J. Sun, J. Yang, B. Tang, X. Wang and J. Li, Mater. Adv., 2021, DOI: 10.1039/D0MA00825G.

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Versatile Construction of Hierarchical Porous Electrode and Its Application in Electrochemical Hydrogen Production: A mini review

Zizai Ma, Hefeng Yuan, Jiaqi Sun, Jie Yang, Bin Tang, Xiaoguang Wang* and Jinping Li*

Rational design of earth-abundant transition metal-based porous electrode is of great importance for developing next-generation electrocatalysts of water splitting. Solid-vapor treatment is a simple and versatile synthetic method to prepare transition metal compound related architectures. With this great synthetic methodology, transition metal-based hierarchical porous electrodes with well-controlled composition and geometrical configuration have been rationally fabricated. The reaction mechanism of solid-vapor methodology in preparing transition metal based hierarchical porous catalysts and recent advances for electrochemical water splitting are illustrated and discussed. The current challenges and future prospects are also provided to stimulate the development of promising transition metal-based hierarchical porous electrodes for commercial applications.

Introduction

Energy is an important material foundation for the development of human society. The large-scale exploitation and utilization of traditional fossil energy with limited reserves has brought severe environmental challenges, such as harmful pollution and greenhouse effect, which has seriously hindered the sustainable development of society. As a clean secondary energy source, hydrogen has been considered as an ideal energy carrier with high mass-energy ratio, and its combustion products are non-polluting. A variety of strategies have been adopted to produce hydrogen, among which electrochemical water splitting has been regarded as one of the most promising routes. The water splitting consists of two half reactions: hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), which requires highly active electrocatalysts to overcome sluggish reaction kinetics and improve the reaction rates at low overpotentials. Therefore, developing suitable catalysts are of great importance for efficient electrochemical water splitting. Precious metals and their oxides such as Pt, Pd, RuO₂, etc. have been proved as superior catalysts for water splitting. However, the scarcity and high price considerably limits their large-scale application. Fortunately, transition metals such as Ni, Co, Fe, Mo and their sulfides, phosphides, borides, selenides and tellurides have been proven as promising alternatives to replace precious metal catalysts, and these catalysts have been reported with outstanding HER or OER activities and excellent stabilities. Moreover, some of those show bifunctional properties, which greatly simplifies the design process of the catalysts and pushes its potential for practical application.

Within the various catalysts synthetic processes, solid-vapor methodology attracts widespread attention from researchers due to its versatility, accessibility and variety. Great progress has been made in transition metal-based hierarchical porous catalysts via this strategy. On one hand, standing on the view of nanostructure engineering, porous nanostructures with numerous dimensions have been successfully fabricated, such as nanoparticles, nanowires, nanosheets, nanopolyhedrons and so on. And these porous architectures provide large internal reactive surface areas, straightforward mass and electron transport through broad “highway” for electrochemical reactions. On the other hand, from the perspective of ingredients, transition metal-based sulfides, phosphides, borides, selenides, tellurides and other derivatives as “highway” for electrochemical reactions. The coupling of several metallic or nonmetallic elements provides a favorable approach for the development of efficient and practical catalysts.

In this review, we are trying to provide an understanding of recent advances in solid-vapor methodology as versatile strategy to construct catalysts for water splitting. We have summarized the fabrication process and mechanism, microstructure of transition metal-based hierarchical porous electrodes and their electrochemical applications. In each section, representative and well-recognized works will be discussed thoroughly, with focuses on characterization and catalytic mechanism proposals. Finally, the challenges and future opportunities in developing efficient catalysts for water splitting through solid-vapor methodology are stressed.
Preparation and reaction mechanism of transition metal-based hierarchical porous electrodes

Solid-vapor treatment (Fig. 1) has been widely used to produce several transition metal-based catalysts, including transition metal sulfides, phosphides, borides, selenides, tellurides and other derivatives. Generally, it is conducted by high temperature reactions under protective gas flow by putting non-metallic source on the upstream while the metal precursors on the downstream in the furnace tube. In the process, the powder on upstream converts to vapor-phase at high temperature and reacts with the precursor material as the gas flow passes to the downstream. Typically, non-metallic sources mainly include the simplest raw materials such as red phosphorus, sodium hypophosphite, sulfur powder, boron powder, selenium powder, tellurium powder, etc. While the transition metal precursor is usually a transition metal foam/metal foil, or metal oxide/hydroxide supported on substrates such as carbon cloth and carbon paper. In terms of element composition, the essence of the solid-vapor method is that the gas phase (Se, P, S, Te et al. gas or related elemental compounds) reacts with the precursor (metal simple substance, alloy or compound) at high temperature to generate ionic compounds. The anion and cation of the final product depend on the solid precursor (determining the cation) and gas phase (determining the anion), respectively. According to the principle of crystal growth kinetics, nanocrystalline grains will grow along the shape direction with the lowest energy, that is, the preferred orientation. Thus, some of the formed structures are nanowires, while some are nanosheets or other topography by the solid-vapor method. Meanwhile, the growth environment also plays a key role in the formation of different nanostructures. The reaction temperature, pressure, time, concentration etc. are all influence factors. In other words, the different topography structure depends not only on growth kinetics, but also on thermodynamics.

This method realizes the extensive growth of transition metal-based porous nanostructures with large scale and high quality on different substrates for hydrogen or oxygen evolution. Firstly, the preparation of the catalyst and the electrode are integrated, which shortens the fabrication process and reduces the cost. Moreover, binder agents are no more required because of the superior interfaces between nanocatalysts and substrates, thus reducing the contact resistance and facilitating charge transportation. What’s more, the component of products could be easily regulated to improve the physical and chemical properties by tailoring the ratio of precursors and fabrication parameters. With these benefits, many projects have been proposed to enhance the catalytic activity of transition metal-based catalysts for water splitting via solid-vapor routes.

Nanostructures of transition metal-based hierarchical porous electrodes via solid-vapor treatment

Nanostructure is one of the key factors in improving the efficiency of electrodes for water splitting. Specifically, nanostructures of various dimensions and morphologies have been explored by solid-vapor treatment, in this section, we will summarize recent advances in nanostructure engineering of transition metals-based through this strategy.

Nanoparticles

Sung and co-workers reported a simple and effective approach to prepare high-performance iron phosphide (FeP) nanoparticle electrocatalysts (Fig. 2). In the preparation, polydopamine-coated iron oxide nanoparticles are thermally treated with a phosphorus source. Through a single-step heating procedure, carbonization of dopamine coating and phosphidation of iron oxide nanoparticles take place simultaneously, producing carbon-shell-coated FeP nanoparticles. And different nanoparticles size can be prepared by tuning the heat treatment procedures. Furthermore, they demonstrated that carbon-shell-protected FeP nanoparticles have both high catalytic activity and long-term durability for HER.

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Fig. 1 A schematic of the fabrication processes of transition metal-based hierarchical porous electrodes via solid-vapor method.

Fig. 2 (a) Schematic representation of carbon-shell-coated FeP NP preparation. (b−e) TEM images of as-synthesized iron oxide NPs (b), carbon-shell-coated FeP NPs (c,d), and FeP NPs prepared without carbon shell (e).

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Solid-vapor treatment is a simple and versatile synthetic method for synthesizing catalysts materials, which not only obtain corresponding product from one kind of non-metal source and transition metal source, but also combine several metal source precursors and non-metal sources to prepare hybrids or compounds. For example, Yu et al. proposed small FePSe₃ nanoparticles anchored on N-doped carbon framework (FePSe₃/NC)
synthesized by high-temperature carbonization, followed by simultaneous phosphorization and selenization process. The resulting highly open carbon framework contributed to large surface area to host FePSe$_3$ nanoparticles. The small nanoparticles with metallic nature and high electrical conductivity can expose more accessible edge sites, producing a moderate hydrogen adsorption Gibbs free energy. As a result, the as-synthesized FePSe$_3$/NC exhibited remarkable HER catalytic activity in a wide pH range, belonging to the advanced non-noble-metal electrocatalyst. An FeP/Ni$_2$P hybrid nanoparticles catalyst$^{50}$ supported on 3D Ni foam was prepared by twice phosphidation of bimetallic precursor, which exhibits both extremely high OER and HER activities in the same alkaline electrolyte. This work proves once again the flexibility and universality of the solid-vapor methodology.

**Nanowires**

Nanowire structure is another popular and attractive morphology for designing high-efficient electrocatalysts. Sun’s group have reported a series of phosphides nanowire catalysts by solid-vapor treatment, such as FeP,$^{51}$ CoP,$^{52}$ Al-doped CoP,$^{53}$ Cu$_3$P,$^{54}$ etc. Li et al. decorated CoP hybrid nanowires with PANI nanodots, which would favor proton accept ability and accelerated electron transfer for HER.$^{55}$

Additionally, as shown in Fig. 3, N doped 3D dandelion-flower-like CoS$_2$ nanowires with many branched needles on Ni foam (N-CoS$_2$/NF) was developed by using NH$_4$HCO$_3$ and sulfur powder as N and S source, respectively.$^{56}$ TEM image showed porous structures in the...
nanowire arrays. Numerous lattice defects (labeled by circle) suggested more active sites, which was conducive to the enhanced electrocatalytic activity. Co, S and N element were distributed homogeneously on the nanorods, indicating the successful N doping. Owing to that more electrons around Co atoms will transfer to N atoms than to S atoms, the positive charged Co-top sites and Co-bridge sites were beneficial for the H$_2$O adsorption and H* adsorption, respectively. So, the resulting N-CoS$_2$/NF acting as both anode and cathode exhibited an outstanding electrocatalytic performance for overall water splitting in alkaline media.

Kuang et al. fabricated a bimetallic sulfides hybrid nanowire (NiS$_2$/MoS$_2$ HNW), which showed an efficient HER activity over a wide pH range.57 After S vapor deposition, NiS$_2$/MoS$_2$ HNW had a rougher surface, composed of highly dispersed 2D MoS$_2$ nanoflakes and nanosized NiS$_2$ particles in this case, creating a hierarchical and porous structure. The special roughly and porous 1D nanowires endowed fast electron/mass transfer from the interior and surface of the catalyst. The Ni site served as an excellent OH adsorption center and the Mo site possessed superior adsorption capability to H*, lowering the energy barrier and accelerate the sluggish HER kinetics.

Our group also developed Al-doped CoS$_2$ nanowire catalysts by solid-vapor treatment.58 Specifically, the rigid Al-Co (Al$_2$Co$_3$) intermetallic nanoporous framework was obtained via selective etching $\alpha$-Al phase through dealloying of Al$_{66}$Co$_{34}$ (at. %) plate. After suffering a facile solid-vapor sulfurization toward the dealloying-derived Al-Co intermetallic sample, a self-supported Al-doped CoS$_2$ electrode (Al-CoS$_2$) was constructed (Fig. 4). Such hierarchical topography comprising both continuous 3D micron-level ligament-channel network and high-density hair-like nanowires on ligament surface, not only can provide more active sites for the adsorption of intermediate H* but also is good for releasing the detached bubbles during HER process, thus effectively reducing the overpotential so as to enhance the HER performance.

Nanosheets

Sheet-like structures are the most common morphology which have been extensively studied by many researchers. 2D lateral structure with coupled heterogeneous components along intraplane direction rather than vertical direction, enables to expose abundant active interface completely on catalyst surface and increase the contact with the electrolyte. Owing to its good structural stability, large exposed surface area and high mass loading of active species, excellent HER or OER performance can be realized by tuning microstructure size and composition.59,61 For instance, 2D Fe-containing cobalt phosphide/cobalt oxide (Fe-CoP/CoO) lateral heterostructure was synthesized via a selective low-temperature phosphorization process.62 The as-prepared Fe-CoP/CoO configured with logical component design and in-plane component tunability exhibits strong interfacial coupling effect between cobalt phosphide (CoP) and cobalt oxide (CoO). Beneficial from the promising direct and full contact with the electrolyte, the Fe-CoP/CoO shows superior electrocatalytic OER performance. Wang et al. reported Ni$_2$P$_2$-Ni$_2$P (Fig. 5),63-65 Ni-Fe$_2$P$_2$ nanosheet arrays on Ni foam or carbon fiber paper by a convenient one-step phosphorization treatment. 3D microporous skeleton covered with high-density upright nanosheets, which not only maximizes the number of exposed active sites, but also facilitates the diffusion of electrolyte and the release of generated gas bubbles.

Similarly, many heterogeneous electrocatalysts are designed by strong coupled compounds. 3D hierarchical architecture of NiP$_2$-Ni$_2$S$_2$/NF displayed extremely high catalytic activity and outstanding stability toward both HER and OER. This was attributed to the strong coupling interactions between NiP$_2$ and Ni$_2$S$_2$ effectively regulating the electronic structure and decreasing the energy barrier.16 2D nanoheterojunctions between homologous CoP/NiCoP nanosheets on N-doped carbon (NC) matrix was prepared via successive carbonization and phosphorization. Owing to the large surface area of Co$_2$N$_x$ nanosheets, well-dispersed active nanoheterojunctions CoP/NC could be exposed for increasing contact area with electrolytes and accelerating rapid interfacial charge transfer. The resulting CoP/NC hybrid exhibited remarkable HER activities and excellent long-term stability over a wide pH range.57 Mixed-transition-metal (MTM)-based electrocatalysts generally possess desirable electrical conductivity and synergistic electronic modulation of multi-metal atoms. Anion regulated Ni-Co-based electrocatalysts (Ni–Co–A, A = P, Se, O) had the structural characteristic of holey nanosheet. It was discovered that P substitution could tune the electron configuration and lower the H* adsorption energy on the active sites greatly of Ni–Co–P holey nanostructures. Therefore, NCP catalyst had ultralow overpotential of 58 mV at 10 mA cm$^{-2}$.64 Similarly, Co, Fe co-doping in NiSe$_2$ can contribute to a strong electronic interaction between the cations and significant lattice distortion, which could increase the number of active sites. Using a vapor selenization technique, the as-prepared Fe$_{0.05}$Co$_{0.13}$-NiSe$_2$ nanosheet array was composed of densely packed nanoparticles (Fig. 6). The local wavy lattice structure was caused by the incorporation of Co and Fe into NiSe$_2$ lattice optimizing adsorption energy of reaction intermediates. Furthermore, this holey structure was advantageous for the penetration of electrolyte, electron transfer and gas bubble release.69 For Co-MOF precursor reacting with Na$_2$WO$_4$ solution and then suffering from sulfurization, the as-prepared W$_{0.5}$Co$_{0.5}$ heterostructure can provide good electrical conductivity, sufficient active sites, and modulated coordination and electronic properties, possessing outstanding HER activity at all pH values.70

Nanopolygons

Fig. 5 (a) Low- and (b,c) high-magnification SEM images of Ni$_2$P$_2$-Ni$_2$P-NS array cathode. (d) EDX spectrum.61 Reproduced with permission from ref. 63. Copyright 2015, Wiley-VCH.
Nanoframes are generally prepared by template growth, framework etching, and chemical vapor deposition. Lian et al.\textsuperscript{71} adopted bimetallic MOF-Co-Fe Prussian Blue Analogues (Co–Fe PBAs) as the structural template, followed by etching with urea and phosphorizing with sodium hypophosphite, and fabricate nanoframes of Co-Fe phosphides for use as the bifunctional electrocatalyst for overall water splitting (Fig. 7). The outstanding performance is attributed to the enhanced electrochemically active surface area, and the promoted mass diffusion and charge transportation.
hollow structural framework and surface morphology are important prerequisites for achieving a large surface area with numerous active sites and better reaction kinetics and stability. M-doped CoP (M=Ni, Mn, Fe) hollow polyhedron frames (HPFs) were synthesized by a self-templating transformation strategy on ZIF-67 template and subsequent oxidation and phosphidation.\(^72\) Like wisely, tetrahedral nanocage-like NiS\(_2\)/NiSe\(_2\) heterostructure was formed during the simultaneous sulfuration/selenylation process via using Ni-based acetate hydroxide precursor. The porous nanopolygon morphology can expose more accessible active sites and providing convenient charge/ionic diffusion pathway. The NiS\(_2\)/NiSe\(_2\) heterostructure could effectively regulate the interfacial electronic structure for modulating the adsorption behavior of oxygen-containing intermediates in the OER process.\(^73\) Similarly, Liu et al. developed regular hollow polyhedral cobalt phosphate (CoP hollow polyhedron) electrocatalysts for HER and OER templated by Co-centered MOFs through simple oxidation and phosphorization calcinations.\(^74\) You et al. prepared Co-P/NC catalysts by direct carbonization of Co-based zeolitic imidazolate framework (ZIF-67) followed by phosphidation. Benefiting from the large specific surface area, controllable pore texture, and high nitrogen content of ZIF (a subclass of metal–organic frameworks), the optimal Co-P/NC showed high specific surface area of 183 m\(^2\) g\(^{-1}\) and large mesopores, and exhibited remarkable catalytic performance for both HER and OER.\(^75\) He et al. reported a Fe-doped cobalt telluride nanoparticle encapsulated in nitrogen-doped carbon nanotube frameworks (Fe-Co\(_{1.11}\)Te\(_{2}\)@NCNTF) by tellurization of Fe-etched ZIF-67 under a mixed H\(_2\)/Ar atmosphere.\(^76\)

In general, a proper template is needed to realize porous nanopolymorphs morphology. Metal–organic frameworks (MOFs) are often utilized as sacrificial templates to synthesis porous and electroactive materials.\(^77\),\(^78\) Combined with the solid-vapor method, various nanopolygon catalysts can be rationally designed for different applications.\(^79\),\(^80\)

## Electrochemical applications

### Hydrogen evolution reaction

Hydrogen as a clean and renewable energy has long been expected to replace finite fossil fuels for future energy infrastructure. Electrocatalytic water splitting is an important technology for producing hydrogen in high purity and large quantities.\(^81\),\(^82\) Up till now, Pt-based precious metals are still the state-of-the-art catalysts for hydrogen evolution. However, the high cost and limited reserve of Pt-based electrocatalysts require seeking for highly efficient non-noble metal catalysts. Therefore, it is important to explore highly active and stable nonprecious-metal catalysts to resolve the problems of leaching or corrosion in strong acidic or alkaline electrolyte.

Many efforts have been made to design a hybrid catalyst with different components to effectively facilitate different parts of the multistep HER process, which should consist of water dissociation promoter for accelerating the sluggish water adsorption and dissociation dynamics.\(^83\) The CoS|Ni|P catalyst was prepared by the following steps: electrodeposition, sulfurization, soak in Ni-ink and phosphorization.\(^84\) As shown in Fig. 8, the as-obtained CoS|Ni|P was composed of densely packed nickel phosphate nanoparticles (NiP\(_2\)/NiP\(_4\)) and cobalt phosphosulfide/phosphate (CoPS/CoP\(_3\)) nanosheets. CoS|Ni|P displayed outstanding electrochemical activity delivering a geometric current density of 10 mA cm\(^{-2}\) at 41 mV, comparable to that of Pt wire (31 mV) and outperforming many reported transition-metal phosphides, selenides, and sulfides. And there was no obvious decline for the cathodic current density of the polarization curve after 5000 CV cycles, showing its good durability. The unique hybrid structure with increased surface

**Fig. 8** Typical SEM images of (a) CoS\(_2\), (b) CoS|P, and (c) CoS|Ni|P at different magnifications. (d) The polarization curves of Ni foam, CoS\(_2\), CoS|P, CoS|Ni|P, and Pt wire electrodes. (e) Cycling stability of CoS|Ni|P before and after 5000 cycles.\(^84\) Reproduced with permission from ref. 84. Copyright 2019, Wiley-VCH.
area, together with the high porosity, good electrical contact between the catalyst and conductive support, fast charge transfer between the electrolyte and catalyst surface, are the reasons for the fast reaction kinetics for the HER process. Besides, CoP/NiP2/CoP39 CoP/CoP2,45 NiS2/MoS2,57 CoSe2@MoS2,86 Ni-MoSe2@CoSe2,87 et al. have also been approved to be efficient electrocatalysts for the HER.

Alternatively, heteroatom doping is another general pathway to improve the electrocatalytic activity by regulating the crystal structures, and modulating the electronic structures. And the influence of alien-metal dopants via solid-vapor treatment on the regulation of the electronic structure of electrocatalysts has been extensively investigated. Liao et al. have developed selenium-doped MoS2 (Se-MoS2) particles uniformly distributed on 3D interwoven cobalt diselenide (CoSe2) nanowire arrays acting as conductive scaffolds.85 The synthesis has undergone two selenization processes, the first is to prepare CoSe2, and the second step is to dope Se into MoS2. As a result, the heterogeneous Se-MoS2/CoSe2 exhibits an outstanding catalytic HER performance with extremely low overpotentials of 30 and 93 mV at 10 and 100 mA cm\(^{-2}\) in base, respectively (Fig. 9). Moreover, this hybrid catalyst shows exceptional catalytic performance with very low overpotentials of 84 and 95 mV at 10 mA cm\(^{-2}\) in acidic and neutral electrolytes, respectively, implying robust pH universality of this hybrid catalyst. Due to the metallic nature of Se, the substitution of S by Se not only improves the electrical conductivity of 2H-MoS2, but also increases edge site density in Se-MoS2 particles relative to MoS2 particles, because the Gibbs free energy for hydrogen adsorption on both Se-edge and Mo-edge of MoSe2 is lower than that of active Mo-edge in MoS2. The rough and curved structures were very beneficial for inducing exposing edge sites of layered transition metal chalcogenides.

In addition to the common Fe, Co, Ni, Mo-based transition metal catalysts, Ta, Nb, V-based catalysts can also be synthesized by the solid-vapor method.88 Recently, vertically oriented 1T-TaS2 nanosheets on nanoporous gold substrates is reported via a facile solid-vapor route. It was employed to synthesize TaS2 directly on the nanoporous gold substrate with sulfur and tantalum pentachloride as precursors. After 5 min growth, large-area uniform, vertical nanosheets were observed on the NPG substrate by scanning electron microscopy (SEM) characterizations (Fig. 10). By virtue of the abundant edge sites and excellent electrical transport property, such vertical 2H-TaS2 is employed as high efficiency electrocatalysts in the hydrogen evolution reaction, featured with rather low Tafel slopes 50 mV dec\(^{-1}\) and an overpotential (at 10 mA cm\(^{-2}\)) of 113 mV. H-TaS2 flakes hybridized with TaSe2 flakes was synthesized...
by Najafi et al. As heterogeneous stacking of Se- and S-based group 5-TMDs can enhance the HER activity of S-based parts.58 The H-TaS₂ flakes hybridized with the H-TaSe₂ flakes promoted an electron transfer from H-TaSe₂ flakes to H-TaS₂ flakes, effectively decreasing the ΔG° of the H-TaS₂ basal planes toward the ideal 0 eV. The H-TaS₂/H-TaSe₂ heterogeneous catalyst outperforms their single counterparts in 0.5 M H₂SO₄ and 1 M KOH, showing an overpotential at the cathodic current density of 10 mA cm⁻² of 120 and 230 mV respectively.

**Fig. 10** (a,b) SEM images of 1T-TaS₂ with different thicknesses and domain sizes (T = 30 nm/1 min and T = 30 nm/5 min, respectively). (c) Polarization curves of 2H-TaS₂ on Au foils, 1T-TaS₂ on Au foils, and commercial Pt, respectively. (d) Corresponding Tafel plots of the different samples in panel (c).58 Reproduced with permission from ref. 89. Copyright 2018, Wiley-VCH.

**Fig. 11** (a) Polarization curves of CoNi foam, CoNiB-700, NiB-700, and RuO₂ toward the OER. (b) Bar graph of the overpotentials at 10 mAc⁻² of CoNi foam, CoNiB-600-1000, NiB-700, and RuO₂. (c) Tafel slopes. (d) Comparison of the overpotentials and Tafel slopes of CoNiB-700 with other transition metal borides in 1.0 M KOH at 10 mA cm⁻².92 Reproduced with permission from ref. 92. Copyright 2019, Royal Society of Chemistry.

“C, requiring 262 mV at 10 mA cm⁻² (Fig. 11a-c).92 Similarly, FeNi foam surface formed loosely porous structure composed of numerous nanoparticles, requiring 272 mV at 10 mA cm⁻².93 These nanostructures of transition metal borides exhibited the coupling of crystalline and amorphous structure, conducive to expose more active. Also, benefiting from bimetallic component, electronic structure can be effectively regulated to reduce adsorption energies.

**Fig. 12** (a) Structure of CoS₈. The CoS₈ coordination octahedral (blue) and CoS₈ coordination tetrahedral (green) are shown. b) The calculated density of states (DOS) of CoS₈ and P-CoS₈ and the black dotted line marks the increased DOS at Fermi level after P doping. The Bader charge change on c) tetra-coordinated and d) hexa-coordinated Co atoms caused by P incorporation, Δp is the Bader charge change and positive values mean the increment of the outmost electrons as compared to pristine CoS₈.98 Reproduced with permission from ref. 98. Copyright 2019, Wiley-VCH.
Transition metal phosphides, sulfides, selenides, tellurides etc. also had been widely investigated as electrocatalysts for oxygen evolution via solid-vapor treatment, and rational design of catalysts is also an important concern.\textsuperscript{94-96} Hollow and conductive Fe–Co–P alloys as excellent OER electrocatalysts were developed by carbonization and phosphidation of Fe–Co metal–organic complex (MOC).\textsuperscript{97} The structure of Fe–Co MOC were highly uniform nanospheres. The formation of these nanospheres was associated with the Ostwald ripening process. Based on XANES and EXAFS results, high-valent state FeOOH was generated on the surface as the major oxidized species, while most Co component retained its low-valent nature during the OER process. The electrochemically induced high valent Fe can stabilize the low valent Co, enabling the both enhancement of OER activity and stability. The multifunctional alloy OER catalyst had an overpotential as low as 252 mV with delivering 10 mA cm\textsuperscript{-2}. Similarly, Qiu et al.\textsuperscript{98} firstly performed density functional theory (DFT) calculations to investigate the effect of P doping on the electronic structure of Co\textsubscript{9}S\textsubscript{8} (Fig. 12). Upon the incorporation of phosphorus into lattice sulfur atoms in Co\textsubscript{9}S\textsubscript{8}, the calculated density of states (DOS) of P-Co\textsubscript{9}S\textsubscript{8} exhibit an obvious increased electron density at the Fermi level, indicating that P atoms play a vital role in improving electrical conductivity of Co\textsubscript{9}S\textsubscript{8}. Then they constructed the P doped Co\textsubscript{9}S\textsubscript{8} nanocages as water oxidation catalysts via hard templates and phosphorization annealing strategy. The P-Co\textsubscript{9}S\textsubscript{8} nanocages allow highly efficient oxygen evolution catalysis, achieving a low overpotential of 280 mV at 10 mA cm\textsuperscript{-2} and long catalytic durability. A 3D bimetallic telluride (CoNiTe\textsubscript{2}/NF) composed of carnation-like structure is synthesized by hydrothermal and calcination method.\textsuperscript{99} Benefiting by the incorporation of the bimetallic telluride and the 3D structure, it shows significant OER activity, which needs overpotentials of $\eta_{100}$=181 mV, $\eta_{500}$=230 mV and $\eta_{1000}$=270 mV. Furthermore, it also exhibits good stability after holding the current density at 100, 500 and 1000 mA cm\textsuperscript{-2} for 24 h, respectively.

Overall water splitting

To date, numerous potential earth-abundant material candidates have been designed for HER and OER. Unfortunately, HER and OER electrocatalytic candidates generally perform well in different media. The incompatible integration of HER and OER electrocatalysts in the same electrolyte often results in inferior performance of overall water electrolysis. To date, overall acidic water splitting suffers from use of scarce and expensive acid-insoluble OER electrocatalysts with passable activity. Overall alkaline water splitting as a promising candidate for commercialization toward mass hydrogen production bears the low activity of HER electrocatalysts under strong alkaline conditions.\textsuperscript{100-102} As such, it is attractive to fabricate a bifunctional catalyst that simultaneously exhibits high activity for both HER and OER at pH 0-14, in order to improve overall water-splitting efficiency, simplify the system, and speed up the commercialization of water splitting.\textsuperscript{103} Recently, the controllable integration of HER and OER...
catalysts into one nanocomposite with the expected synergetic electrocatalysis for both HER and OER has recently become one of the hottest research topics in the field.\cite{104, 105} Among these, solid-vapor methodology is an effective strategy to develop self-supported porous electrodes.\cite{106, 107} For instance, Zhao et al.\cite{108} report a controllable synthesis strategy for nickel–cobalt bimetal phosphide nanotubes as efficient electrocatalysts for overall water splitting via low-temperature phosphorization from a bimetallic metal-organic framework precursor. By optimizing the molar ratio of Co/Ni atoms in MOF-74, a series of CoNiP catalysts were synthesized.\cite{109, 110} Benefiting from the unique advantage of MOF-74, which can coordinate with different metal centers without affecting the underlying framework structure, the obtained CoNiP nanotubes possess similar morphology to their MOF precursor and exhibit perfect dispersal of the active sites. The electrolyzer with CoNiP nanotubes as both the cathode and anode catalysts in alkaline solutions achieved a current density of 10 mA cm\textsuperscript{-2} at a voltage of 1.59 V, which is even better than the integrated Pt/C and RuO\textsubscript{2} counterparts. The high performance may be attributed to the large active surface area and the porosity of CoNiP nanotubes, the high conductivity of carbon, and the synergistic effect of NiCoP and CoP encapsulated within the nanotube morphology. Wang et al. synthesized a electrocatalyst of cobalt telluride nanoparticles encapsulated in nitrogen-doped carbon nanotube frameworks (CoTe\textsubscript{2}@-NCNTFs) by a straightforward telluride process under a hydrogen atmosphere using ZIF-67 as the template for overall water splitting. And the CoTe\textsubscript{2}@-NCNTF couple electrolyzer could obtain a current density of 10 mA cm\textsuperscript{-2} at a potential of 1.6 V vs. the RHE.\cite{111}

The performance of efficient electrocatalysts largely depends on their geometric morphology, active defects, and electronic regulation.\cite{112, 113} For example, a novel kind of N-NiMoO\textsubscript{2}/NiS\textsubscript{2} nanowires/nanosheets has been successfully fabricated with controllable nitridation to activate Ni sites and subsequent vulcanization to induce abundant epitaxial heterogeneous interfaces.\cite{114} From differential charge density of N-NiMoO\textsubscript{2}/NiS\textsubscript{2} heterojunction, electrons transferred from N-NiMoO\textsubscript{2} to NiS\textsubscript{2}, which can stabilize the H adatom and thus benefit the HER performance (Fig. 13). In contrast, the resulting decreased valence state of Ni in N-NiMoO\textsubscript{2} would be more efficient for the OER. The bifunctional N-NiMoO\textsubscript{2}/NiS\textsubscript{2} electrodes delivered a current density of 10 mA cm\textsuperscript{-2} at the cell voltage of 1.6 V, 3.39 times higher than that of the Pt–Ir system (2.95 mA cm\textsuperscript{-2}), and maintained 10 h long-term stability at 10 mA cm\textsuperscript{-2}.

Conclusion and perspective

In summary, advances in electrochemical catalysts fabricated by solid-vapor methodology have been evaluated and summarized. It was found that solid-vapor treatment demonstrates versatile applications in hierarchical nanostructure engineering and exhibits great potential in electrodes development. Firstly, the procedure and mechanism of the fabrication process has been investigated. Specifically, we summarized various morphologies developed for the efficient catalysts with respect to a large surface area and porous structure, including nanoparticles, nanowires, nanorods, nanosheets etc. Subsequently, an overview of the application of the as-prepared electrodes mainly focused on electrochemical water splitting (HER, OER and overall water splitting).

Despite great efforts invested in transition metal-based hierarchical porous catalysts for water splitting, there are still a number of aspects in this field that need to be improved. 1) Although the solid-vapor methods could synthesize numerous materials with different components and structures, there is still little known about the nature of the intermediates and impurities during the synthetic procedure. Thus, how to select the reaction raw materials and precursors to induce the configuration of high-quality catalysts with understanding at the molecular/atomic level and controllable large-scale engineering optimization for commercial applications is yet an unresolved challenge. 2) Most of the multi-compositional catalysts reported in the literatures only attribute the performance improvement to the synergistic effects between the different components without authentic understanding, which greatly restricts the optimization and integration of heterogeneous catalysts. Utilization of in situ characterization techniques, such as in-situ TEM, XAS, FTIR, can offer indeed valuable evidence for unveiling the intermolecular interaction even within time-resolution and spatial resolution measurement. 3) With the development of synthetic strategies and in-depth understandings of the relation among the structure, catalytic performance and mechanism, the cultivation of novel catalysts with facile configuration, low cost and excellent catalytic properties are in great demand.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by National Natural Science Foundation of China (21878201), Natural Science Foundation of Shanxi Province (201801D121059), The 7th Youth Talent Support Program of Shanxi Province, Program for the Outstanding Innovative Teams of Higher Learning Institutions of Shanxi “OIT”.

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