A Co-MOF-derived Co$_9$S$_8$@NS-C electrocatalyst for efficient hydrogen evolution reaction†

Yun-Wu Li, Qian Wu, Rui-Cong Ma, Xiao-Qi Sun, Dan-Dan Li, Hong-Mei Du, Hui-Yan Ma,* Da-Cheng Li, Su-Na Wang* and Jian-Min Dou

The exploitation of efficient hydrogen evolution reaction (HER) electrocatalysts has become increasingly urgent and imperative; however, it is also challenging for high-performance sustainable clean energy applications. Herein, novel Co$_9$S$_8$ nanoparticles embedded in a porous N,S-dual doped carbon composite (abbr. Co$_9$S$_8$@NS-C-900) were fabricated by the pyrolysis of a single crystal Co-MOF assisted with thiourea. Due to the synergistic benefit of combining Co$_9$S$_8$ nanoparticles with N,S-dual doped carbon, the composite showed efficient HER electrocatalytic activities and long-term durability in an alkaline solution. It shows a small overpotential of $\sim$86.4 mV at a current density of 10.0 mA cm$^{-2}$, a small Tafel slope of 81.1 mV dec$^{-1}$, and a large exchange current density ($J_0$) of 0.40 mA cm$^{-2}$, which are comparable to those of Pt/C. More importantly, due to the protection of Co$_9$S$_8$ nanoparticles by the N,S-dual doped carbon shell, the Co$_9$S$_8$@NS-C-900 catalyst displays excellent long-term durability. There is almost no decay in HER activities after 1000 potential cycles or it retains 99.5% of the initial current after 48 h.

1. Introduction

Due to the energy crisis and environmental problems, sustainable utilization of renewable energy has shown rapid development in the world. As high efficiency and clean energy, hydrogen energy is giving rise to a new dawn in the future energy systems and is well on the way.1,2 Thus, exploring numerous HER electrocatalysts to generate sufficient H$_2$ by water-splitting is an effective and efficient tactic.1,2 It is known that noble metal Pt is by far the most efficient and benchmark HER electrocatalyst; however, it suffers from resource exhaustion, which blocks its widespread applications.3–5 Therefore, various alternative noble-metal-free catalysts, such as transition metal derived nanomaterials (Mo, W, Co, Fe, and Ni),6–10 N, S, P heteroatom-doped carbon materials,11 and their composites,12 have been scrutinized due to their high HER electrocatalytic activities, other important energy storage and conversion features,13 and low cost. Of note, Co(II)-based species are a type of high-profile candidates whose enhanced electrocatalytic activities have recently been noticed.7,8,14,15 Among them, cobalt and sulfide-rich Co$_9$S$_8$ have been applied in both electrocatalytic ORR and various batteries but scarcely in HER due to its low conductance and easy aggregation.14–15 To improve these defects, encapsulating metal sulfides into N or S doped carbon materials to generate hybrids gave us a profound inspiration.11 The heteroatom-doped carbon materials not only offer improved electrical conductivity, long-term durability and high selectivity but also can be used as shells to protect metal sulfides from aggregation. More specifically, N,S-dual doped carbon materials themselves have been employed as attractive HER electrocatalysts.11 Therefore, combining Co$_9$S$_8$ nanoparticles and N,S-dual doped carbon to prepare new composite materials and further improve their HER electrocatalytic activities is indeed an appealing task.15

In recent years, metal–organic framework (MOF)-derived hybrids are demonstrated as promoting electrocatalysts for energy storage and conversion.16,17 By pyrolysis of MOF precursors, the advanced features of MOFs, such as heteroatom-doped carbon skeletons, active metal nodes, adjustable structure components, robust frameworks, and periodic porosities, can be endowed or transferred into the derived hybrids with advantages toward electrocatalysis.16,17 To promise highly active electrocatalysts, one can also encapsulate small organic molecules containing heteroatoms to introduce and increase multiple active sites. Herein, we incorporated a small thiourea molecule with both N and S into a crystalline Co-MOF (LCU-105)18 to manage multi-component composites for HER. The skeleton ligands of Co-MOF and thiourea offer N,S-dual doped carbon substrates, which can not only favor electrical conductivity and improve potential active sites but can also embed Co(II) species to increase stability. As a result, Co$_9$S$_8$...
nanoparticles wrapped in the N,S-dual doped carbon composite (abbreviated as Co9S8@NS-C-900) were fabricated. The Co9S8@NS-C-900 composite displays efficient HER electrocatalytic activities and long-term durability. It showed a small overpotential of ~86.4 mV at a 10.0 mA cm−2 current density, a small Tafel slope of 81.1 mV dec−1, and a large exchange current density (j0) of 0.40 mA cm−2, performance comparable to Pt/C.

2. Experimental section

2.1. Chemicals and material characterization

All chemicals were purchased commercially and used as received. The powder X-ray diffraction (PXRD) was obtained on a D/MAX-rA (Rigaku) diffractometer with Cu Kα radiation (λ = 1.542 Å) at a scan rate of 4° min−1. Raman spectrum was collected using Monovista CRS500. X-ray photoelectron spectra (XPS) were collected using ESCALAB Xi+. N2 adsorption experiments were performed on a Micrometrics ASAP 2020M instrument. FT-IR spectra were recorded on a NICOLET 6700F-IR spectrometer using the KBr disc method in the range of 400–4000 cm−1. Transmission electron microscopy (TEM) was performed on a JEM-2100 at 200 kV.

2.2. Syntheses and structure of the Co-MOF precursor

The pure single crystals of the Co-MOF (LCU-105) precursor were synthesized according to our recently reported reference and for the detailed synthesis process see ESI.† The pure phase was confirmed by single-crystal X-ray diffraction (Table S1, ESI†) and PXRD (Fig. S2, ESI†) measurements. The Co-MOF structure displays a three-dimensional (3D) microporous framework (see Scheme 1 and Fig. S1†), which can well enclose small organic molecules, such as thiourea, presenting it as an excellent candidate as a precursor to fabricate multi-component composites. The crystallographic data of Co-MOF are listed in Table S1 (ESI†). The synthesis details of Co9S8@NS-C composites can be found in Scheme 1 and are discussed below.

2.3. Fabrication of Co9S8@NS-C composites

The Co9S8@NS-C composites were synthesized using the above Co-MOF as a precursor via the pyrolysis route in Ar atmosphere, followed by the acid etching treatment (Scheme 1): (i) A mixture of crystalline Co-MOF and thiourea was carefully ground in an agate mortar to obtain the thiourea@Co-MOF precursor. (ii) The precursor was transferred to a tube furnace and carbonized under an Ar atmosphere at different temperatures (1000, 900 and 800 °C) for 3 h. The N,S-dual doped carbon composite wrapping both the CoO2 and Co9S8 nanoparticles was formed. (iii) The obtained three samples were thoroughly etched with 3 M HCl solutions 3 times to remove the residual CoO2 (Scheme 1), and then repeatedly rinsed in ultra-pure water and ethanol. After drying at 60 °C in a vacuum for 8 h, black catalyst powder was synthesized (Scheme 1). These samples are abbreviated as Co-MOF-1000, Co-MOF-900 and Co-MOF-800. The calcined Co-

RSC Advances

Paper

5948 | RSC Adv., 2021, 11, 5947–5957

© 2021 The Author(s). Published by the Royal Society of Chemistry
Co₉S₈@NS-C-900 composite was evaluated by N₂ adsorption studies (Fig. 2a). The N₂ adsorption capacity rises rapidly at the beginning, afterward it grows slowly to reach a maximum of 90.7 cm³ g⁻¹. The isotherm displays a clear reversible adsorption behaviour, which shows a typical type-I porous feature. The corresponding BET (Brunner–Emmet–Teller) was calculated as ca. 239 m² g⁻¹ using the above N₂ adsorption data. This high BET surface area supplies the exposure of additional active sites, which are beneficial for the HER activity. The diameters of pores are between 4.4 and 19 Å, and the pore maximum is at 7.9 Å, indicating the easy transportation of H₂ in the electrocatalytic process appropriately.

The chemical composition of the Co₉S₈@NS-C-900 composite was further checked via XPS (Fig. 2b–f). The survey spectrum displays that the composite consists of Co, S, N, C and O elements (Fig. 2b). The Co 2p high-resolution spectrum after fitting displays that it comprises four typical characteristic peaks (Fig. 2c): the peaks at 777.04 and 796.75 eV are assigned to Co³⁺; the peaks at 781.40 and 798.03 eV are ascribed to Co²⁺. However, the peaks at 785.94 eV and 802.97 are indexed to satellite peaks. The S 2p high-resolution spectrum is...
bonds, indicating the existence of Co$_9$S$_8$ and CoN peak at 1402 cm$^{-1}$.

The peak at 400.1 eV is indexed to the graphitic-N species. The peak located at 401.2 eV is regarded as the oxidized-N species. FT-IR was performed to identify the chemical bonds and further responsive to better HER performance and long-term durability.

3.2. Morphological analysis of the Co$_9$S$_8$@NS-C-900 composite

The morphology and microstructure of the Co$_9$S$_8$@NS-C-900 composite were evaluated using SEM and TEM, respectively. SEM imaging reveals that the Co$_9$S$_8$@NS-C-900 composite displays interconnected aggregates composed of nanoflakes, and their sizes were within about 10–40 μm (Fig. 3a–c). These carbon nanoflakes intertwine each other to generate porous aggregates, providing transport channels for HER. TEM images also indicate that the composite co-exists in two types of planes: one is the Co$_9$S$_8$ crystalline phase and the other is the N,S-dual doped carbon amorphous phase (Fig. 4c,d). From Fig. 4c and d, a characteristic lattice plane distance ca. 0.497 nm was observed, which can be ascribed to the (200) plane of the cubic Co$_9$S$_8$ phase. This analysis coincides with PXRD results. Moreover, from the

![Image](image-url)
HAADF (high-angle annular dark-field) image and EDS mappings displayed in Fig. 4e–i, it can be seen that Co, S, N and C elements are uniformly distributed in the N,S-dual-doped carbon nanoflakes. From both HAADF image and EDS mappings of Co and S elements (Fig. 4e–g), Co9S8 nanoparticles are also clearly visible by highlights. Based on SEM and TEM results, it can be concluded that Co9S8 nanoparticles are successfully embedded in N,S-dual-doped carbon nanoflakes.

3.3. HER electrocatalytic activity of the Co9S8@NS-C-900 composite

As the porous feature of the Co9S8@NS-C-900 composite is suitable for electrolyte transportation, HER electrocatalytic activities of the as-prepared sample were tested in the KOH (1 M) solution. HER polarization curves of various catalysts (including benchmark 20% Pt/C, Co-MOF-1000, Co-MOF-900 and Co-MOF-800) were obtained from LSV (5 mV s⁻¹). From
Fig. 5a, it can be seen that Co₉S₈@NS-C-900 shows the smallest onset potential ($E_{\text{onset}}$) of ca. −4.8 mV at 1 mA cm⁻² current density, smaller than that of Co-MOF-1000 ($E_{\text{onset}} = −54$ mV) and Co-MOF-800 ($E_{\text{onset}} = −108$ mV), and close to Pt/C ($E_{\text{onset}} = 0$ mV). To deliver a 10.0 mA cm⁻² current density, the operating overpotential of Co₉S₈@NS-C-900 is −86.4 mV. This is lower than that for Co-MOF-1000 (−176 mV), Co-MOF-800 (−292 mV), several reported noble-metal-free HER catalysts, and also close to most Pt/C catalysts (−41.6 mV). To evaluate the HER kinetics of these catalysts for comparing with the benchmark Pt/C, Tafel slopes were extracted from the LSV curves. From Fig. 5b, it can be seen that the Tafel slopes obey the following sequence: Pt/C (44.8 mV dec⁻¹) < Co₉S₈@NS-C-900 (81.1 mV dec⁻¹) < Co-MOF-1000 (116.3 mV dec⁻¹) < Co-MOF-800 (182.2 mV dec⁻¹), which is consistent with the results from Fig. 5a. The Co₉S₈@NS-C-900 composite has the smallest Tafel slope among the three Co-MOF-derived catalysts and is close to that of Pt/C, showing efficient HER kinetics. The Tafel value of Co₉S₈@NS-C-900 also confirms that the HER mechanism abides by a Volmer−Heyrovský pathway, which means that the HER rate-determining progress depends on H₂ desorption by Hads reacting with H₂O. The HER inherent activities of these catalysts were evaluated by the exchange current densities ($J_0$) extracted from the Tafel slopes by applying the extrapolation method. The $J_0$ value of 0.40 mA cm⁻² for Co₉S₈@NS-C-900 outperforms the values of 0.30 mA cm⁻² for Co-MOF-1000, and 0.26 mA cm⁻² for Co-MOF-800, and only a little lower than that of Pt/C with the value of 0.54 mA cm⁻², but the value is higher than that for most of the reported noble-metal-free HER catalysts. Therefore, the Co₉S₈@NS-C-900 catalyst has a small overpotential, a small Tafel slope and a large $J_0$ value, which was integrated to evaluate its efficient electrocatalytic activity towards HER. The comparison of the HER activity for some cobalt-based materials reported in literature is listed in Table S2 (ESI†). From the table, the HER catalytic performance of Co₉S₈@NS-C-900 is better than that of most of similar Co₉S₈, and its composite catalysts under alkaline conditions. It can also match most of the other cobalt-based HER catalysts, but is lower than that for some high-performance materials.

Long-term durability is a key factor to evaluate the catalyst performance. Therefore, the cyclability of the Co₉S₈@NS-C-900 catalyst was tested. In Fig. 5c, the Co₉S₈@NS-C-900 catalyst displays excellent cycling stability, and there is almost no loss in the HER activity after 1000 potential cycles. Furthermore, the long-term durability of the Co₉S₈@NS-C-900 catalyst was also evaluated by chronocamperometric measurements. As displayed in the $i$–$t$ (current−time) plot (Fig. 5c, inset), the Co₉S₈@NS-C-900 catalyst retains 99.5% of the initial current after 48 h, also indicating that it exhibits excellent cycling stability in the KOH solution. Furthermore, the EIS of three Co-MOF-derived
catalysts and Pt/C were also tested to estimate their catalytic kinetics. From Fig. 5d, Nyquist curves are presented for these electrocatalysts. We know that Nyquist radius could respond to $R_{ct}$ (charge transfer resistance) and can effectively estimate the electrocatalytic activities. From Fig. 5d, 20% Pt/C has the smallest radius among all catalysts, which is consistent with its best electrocatalytic activity as a commonly accepted benchmark of HER. In three Co-MOF-derived catalysts, the Co$_9$S$_8$@NS-C-900 catalyst has the smallest radius than that of others and a little larger than that of Pt/C, which displayed slightly worse HER performance than Pt/C and the best HER electrocatalytic performance among three Co-MOF-derived species. The simulated equivalent circuit (Fig. 5d inset) was also built by fitting the ESI data, and it is composed of three resistances: the solution resistance ($R_s$), hydrogen adsorption resistance ($R_{ad}$), and $R_{ct}$. Due to the same equipment and outer solutions, $R_s$ and $R_{ad}$ are supposed to be quite similar. $R_{ct}$ of Co-MOF-1000, Co-MOF-900, and Co-MOF-800 are 361.2, 145.8 and 663.2 Ω, respectively. The smallest $R_{ct}$ of the Co-MOF-900 electrode among them suggests its fastest reaction kinetics during the HER process. All told, the Co$_9$S$_8$@NS-C-900 composite is an efficient HER catalyst possessing excellent cycling stabilities and superior electrocatalytic activities.

4. Conclusion

In conclusion, a porous Co$_9$S$_8$@NS-C-900 composite was fabricated by the pyrolysis of crystalline Co-MOF involving thiourea. The N,S-dual-doped carbon shell can protect Co$_9$S$_8$ nanoparticles from corrosion and aggregation by encapsulating them, and further prompt the stability and conductivity of the whole electrocatalyst. Therefore, benefiting from the synergistic interaction of Co$_9$S$_8$ nanoparticles and N,S-dual-doped carbon substrate, the Co$_9$S$_8$@NS-C-900 composite exhibits efficient electrocatalytic activities and long-term durability towards HER in alkaline electrolytes. In particular, the electrocatalyst requires a small overpotential of −86.4 mV at a 10.0 mA cm$^{-2}$ current density, a small Tafel slope of 81.1 mV dec$^{-1}$, and a large exchange current density ($j_0$) of 0.40 mA cm$^{-2}$, representing a promising noble-free-metal electrocatalyst that approaches the performance of the state-of-the-art Pt/C electrocatalyst.

Author contributions

Yun-Wu Li: conceptualization, investigation, funding acquisition, writing—original draft. Qian Wu: data curation, project administration. Rui-Cong Ma: project administration, validation. Xiao-Qi Sun: investigation, data curation. Dan-Dan Li: formal analysis, resources. Hong-Mei Du: methodology, writing—review & editing. Hui-Yan Ma: supervision, conceptualization, visualization, writing—review & editing. Da-Cheng Li: writing—review & editing. Su-Na Wang: supervision, validation, funding acquisition, writing—review & editing. Jian-Min Dou: conceptualization, writing—review & editing. All the authors gave their final approval for publication.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21771095, 21571092 and 21601079), the Natural Science Foundation of Shandong Province (ZR2017JL013), and the Youth Innovation Team of Shandong Colleges and Universities (2019JC027).

References

1 (a) Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov and T. F. Jaramillo, Combining theory and experiment in electrocatalysis: Insights into materials design, Science, 2017, 355, eaad4998; (b) Y. Zheng, Y. Jiao, A. Vasileff and S. Z. Qiao, The Hydrogen Evolution Reaction in Alkaline Solution: From Theory, Single Crystal Models, to Practical Electrocatalysts, Angew. Chem., Int. Ed., 2018, 57, 7568–7579; (c) W. J. Jiang, T. Tang, Y. Zhang and J. S. Hu, Synergistic Modulation of Non-Precious-Metal Electrocatalysts for Advanced Water Splitting, Acc. Chem. Res., 2020, 53, 1111–1123; (d) C. L. Hu, L. Zhang and J. L. Gong, Recent progress made in the mechanism comprehension and design of electrocatalysts for alkaline water splitting, Energy Environ. Sci., 2019, 12, 2620–2645; (e) C. Wei, R. R. Rao, J. Y. Peng, B. T. Huang, I. E. L. Stephens, M. Risch, Z. C. J. Xu and S. H. Yang, Recommended Practices and Benchmark Activity for Hydrogen and Oxygen Electrocatalysis in Water Splitting and Fuel Cells, Adv. Mater., 2019, 31, 1806296; (f) J. Zhang, Q. Y. Zhang and X. L. Feng, Support and Interface Effects in Water-Splitting Electrocatalysts, Adv. Mater., 2019, 31, 1808167.

2 (a) J. Zhu, L. S. Hu, P. X. Zhao, L. Y. Suk Lee and K. Y. Wong, Recent Advances in Electrocatalytic Hydrogen Evolution Using Nanoparticles, Chem. Rev., 2020, 120, 851–918; (b) C. G. Morales-Guio, L. A. Stern and X. L. Hu, Nanostructured hydrotreating catalysts for electrochemical hydrogen evolution, Chem. Soc. Rev., 2014, 43, 6555–6569; (c) J. A. Trindell, Z. Y. Duan, G. Henkelman and R. M. Crooks, Well-Defined Nanoparticle Electrocatalysts for the Refinement of Theory, Chem. Rev., 2020, 120, 814–850; (d) Y. T. Yang, H. Xie, M. J. Chen, A. D’Alola, J. Choc, G. Wu and Q. Li, Precious metal-free approach to hydrogen electrocatalysis for energy conversion: From mechanism understanding to catalyst design, Nano Energy, 2017, 42, 69–89; (e) X. C. Du, J. W. Huang, J. J. Zhang, Y. C. Yan, C. Y. Wu, Y. Hu, C. Y. Yan, T. Y. Lei, W. Chen, C. Fan and J. Xiong, Modulating Electronic Structures of Inorganic Nanomaterials for Efficient Electrocatalytic Water Splitting, Angew. Chem., Int. Ed., 2019, 58, 4484–4502; (f) B. Ginovska-Pangovska, A. Dutta, M. L. Reback, J. C. Linehan and
W. J. Shaw, Beyond the active site: the impact of the outer production sphere on electrocatalysts for hydrogen oxidation, Acc. Chem. Res., 2014, 47, 2621-2630.

3 (a) Z. X. Fan and H. Zhang, Template Synthesis of Noble Metal Nanocrystals with Unusual Crystal Structures and Their Catalytic Applications, Acc. Chem. Res., 2016, 49, 2841–2850; (b) L. Zhang, K. Doyle-Davis and X. L. Sun, Pt-Based Electro catalysts with High Atom Utilization Efficiency: From Nanostructures to Single Atoms, Energy Environ. Sci., 2019, 12, 492–517; (c) Y. J. Li, Y. J. Sun, Y. N. Qin, W. Y. Zhang, L. Wang, M. C. Luo, H. Yang and S. J. Guo, Recent Advances on Water Splitting Electrocatalysis Mediated by Noble-Metal-Based Nanostructured Materials, Adv. Energy Mater., 2020, 10, 1903120; (d) Y. X. Du, H. T. Sheng, D. Astruc and M. Z. Zhu, Atomically Precise Noble Metal Nanoclusters as Efficient Catalysts: A Bridge between Structure and Properties, Chem. Rev., 2020, 120, 526–622.

4 (a) J. Kim, H. Kim, W. J. Lee, B. Ruqia, H. Baik, H. S. Oh, S. M. Paek, H. K. Lim, C. H. Choi and S. I. Choi, Theoretical and Experimental Understanding of Hydrogen Evolution Reaction Kinetics in Alkaline Electrolytes with Pt-Based Core-Shell Nanocrystals, J. Am. Chem. Soc., 2019, 141, 18256–18263; (b) Q. Yang, G. W. Li, K. Manna, F. R. Fan, C. Felser and Y. Sun, Topological Engineering of Pt-Group-Metal-Based Chiral Crystals toward High-Efficiency Hydrogen Evolution Catalysts, Adv. Mater., 2020, 32, 1908518; (c) J. Park, S. Lee, H. E. Kim, A. Cho, S. Kim, Y. Ye, J. W. Han, H. Lee, J. H. Jang and J. Lee, Investigation of the Support Effect in Atomically Dispersed Pt on WO3-x for Utilization of Pt in the Hydrogen Evolution Reaction, Angew. Chem., Int. Ed., 2019, 58, 16038–16042; (d) A. Alinezhad, L. Gloag, T. M. Benedetti, S. Cheong, R. F. Webster, M. Roelsgaard, B. B. Iversen, W. Schuhmann, J. J. Gooding and R. D. Tilley, Direct Growth of Highly Strained Pt Islands on Branched Ni Nanoparticles for Improved Hydrogen Evolution Reaction Activity, J. Am. Chem. Soc., 2019, 141, 16202–16207; (e) J. P. Ji, Y. P. Zhang, L. B. Tang, C. Y. Liu, X. H. Gao, M. H. Sun, J. H. Zheng, M. Ling, C. D. Liang and Z. Lin, Platinum single-atom and cluster anchored on functionalized MWCNTs with ultrahigh mass efficiency for electrocatalytic hydrogen evolution, Nano Energy, 2019, 63, 103849.

5 (a) D. Zhao, K. Sun, W. C. Cheong, L. R. Zheng, C. Zhang, S. J. Liu, X. Cao, K. L. Wu, Y. Pan, Z. W. Zhuang, B. T. Hu, D. S. Wang, Q. Peng, C. Chen and Y. D. Li, Synergistically Interactive Pyridinic–N–MoP Sites: Identified Active Centers for Enhanced Hydrogen Evolution in Alkaline Solution, Angew. Chem., Int. Ed., 2020, 59, 8982–8990; (b) C. Huang, X. W. Miao, C. R. Pi, B. Gao, X. M. Zhang, P. Qin, K. F. Huo, X. Peng and P. K. Chu, MoO3/C/VC heterojunction embedded in graphitic carbon network: An advanced electrocatalyst for hydrogen evolution, Nano Energy, 2019, 60, 520–526; (c) F. Li, G. F. Han, H. J. Noh, Y. L. Lu, J. Xu, Y. F. Bu, Z. P. Fu and J. B. Baek, Construction of Porous Mo3P/Mo Nanobelts as Catalysts for Efficient Water Splitting, Angew. Chem., Int. Ed., 2018, 57, 14139–14143; (d) Z. X. Sun, M. F. Yang, Y. W. Wang and Y. H. Hu, Novel Binder-Free Three-Dimensional MoS2-Based Electrode for Efficient and Stable Electrocatalytic Hydrogen Evolution, ACS Appl. Energy Mater., 2019, 2, 1102–1110; (e) J. S. Li, Y. Wang, C. H. Liu, S. L. Li, Y. G. Wang, L. Z. Dong, Z. H. Dai, Y. F. Li and Y. Q. Lan, Coupled molybdenum carbide and reduced graphene oxide electrocatalysts for efficient hydrogen evolution, Nat. Commun., 2016, 7, 11204; (f) D. Z. Wang, D. Z. Zhang, C. Y. Tang, P. Zhou, Z. Z. Wu and B. Z. Fang, Hydrogen evolution catalyzed by cobalt-promoted molybdenum phosphide nanoparticles, Catal. Sci. Technol., 2016, 6, 1952–1956; (g) Z. Z. Wu, C. Y. Tang, P. Zhou, Z. H. Liu, Y. S. Xu, D. Z. Wang and B. Z. Fang, Enhanced hydrogen evolution catalysis from osmotically swollen ammoniated MoS2, J. Mater. Chem. A, 2015, 3, 13050–13056.

6 (a) M. A. Lukowski, A. S. Daniel, C. R. English, F. Meng, A. Forticaux, R. J. Hamers and S. Jin, Highly active hydrogen evolution catalysis from metallic WS2 nanosheets, Energy Environ. Sci., 2014, 7, 2608–2613; (b) L. Cheng, W. J. Huang, Q. F. Gong, C. H. Liu, Z. Liu, Y. G. Li and H. J. Dai, Ultrathin WS2 Nanoflakes as a High-Performance Electro catalyst for the Hydrogen Evolution Reaction, Angew. Chem., Int. Ed., 2014, 53, 7860–7863; (c) H. J. Yan, C. G. Tian, L. Wang, A. P. Wu, M. C. Meng, L. Zhao and H. G. Fu, Phosphorus-Modified Tungsten Nitride/Reduced Graphene Oxide as a High-Performance, Non-Noble-Metal Electro catalyst for the Hydrogen Evolution Reaction, Angew. Chem., Int. Ed., 2015, 54, 6325–6329; (d) Y. Y. Ma, Z. L. Lang, L. K. Yan, Y. H. Wang, H. Q. Tan, K. Feng, Y. J. Xia, J. Zhong, Y. Liu, Z. H. Kang and Y. G. Li, High efficient hydrogen evolution triggered by a multi-interfacial Ni/WC hybrid electro catalyst, Energy Environ. Sci., 2018, 11, 2114–2123; (e) Z. G. Chen, W. B. Gong, S. Cong, Z. Wang, G. Song, T. Pan, X. Q. Tang, J. Chen, W. B. Lu and Z. G. Zhao, Eutectoid-structured WC/W6C heterostructures: A new platform for long-term alkaline hydrogen evolution reaction at low overpotentials, Nano Energy, 2020, 68, 104335.

7 (a) S. Anantharaj and V. Aravindan, Developments and Perspectives in 3d Transition-Metal-Based Electro catalysts for Neutral and Near-Neutral Water Electrolysis, Adv. Energy Mater., 2019, 9, 1902666; (b) V. S. Thoi, Y. J. Sun, J. R. Long and C. J. Chang, Complexes of earth-abundant metals for catalytic electrochemical hydrogen generation under aqueous conditions, Chem. Soc. Rev., 2013, 42, 2388–2400; (c) Y. M. Shi and B. Zhang, Recent advances in transition metal phosphide nanomaterials: synthesis and applications in hydrogen evolution reaction, Chem. Soc. Rev., 2016, 45, 1529–1541; (d) Y. N. Guo, T. Park, J. W. Yi, J. Henzie, J. Kim, Z. L. Wang, B. Jiang, Y. Bando, Y. Sugahara, J. Tang and Y. Yamauchi, Nanoarchitectonics for Transition-Metal-Sulfide-Based Electro catalysts for Water Splitting, Adv. Mater., 2019, 31, 1807134; (e) J. H. Wang, W. Cui, Q. Liu, Z. C. Xing, A. M. Asiri and
X. P. Sun, Recent Progress in Cobalt-Based Heterogeneous Catalysts for Electrochemical Water Splitting, *Adv. Mater.*, 2016, **28**, 215–230.

8 (a) Y. R. Zheng, P. Wu, M. R. Gao, X. L. Zhang, F. Y. Gao, H. X. Ju, R. Wu, Q. Gao, R. You, W. X. Huang, S. J. Liu, S. W. Hu, J. F. Zhu, Z. Y. Li and S. H. Yu, Doping induced structural phase transition in cobalt diselenide enables enhanced hydrogen evolution catalysis, *Nat. Commun.*, 2018, **9**, 2533; (b) X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmekova and T. Asefa, Cobalt-Embedded Nitrogen-Rich Carbon Nanotubes Efficiently Catalyze Hydrogen Evolution Reaction at All pH Values, *Angew. Chem., Int. Ed.*, 2014, **53**, 4372–4376; (c) J. X. Feng, S. Y. Tong, Y. X. Tong and G. R. Li, Pt-like Hydrogen Evolution Electrocatalysis on PANI/CoP Hybrid Nanowires by Weakening the Shackles of Hydrogen Ions on the Surfaces of Catalysts, *J. Am. Chem. Soc.*, 2018, **140**, 5118–5126; (d) C. Tang, R. Zhang, W. B. Lu, L. B. He, X. E. Jiang, A. M. Asiri and X. P. Sun, Fe-Doped CoP Nanoarray: A Monolithic Multifunctional Catalyst for Highly Efficient Hydrogen Generation, *Adv. Mater.*, 2017, **29**, 1602441; (e) T. Liu, P. Li, N. Yao, G. Z. Cheng, S. L. Chen, W. Luo and Y. D. Yin, CoP-Doped MOF-Based Electrocatalysts for pH-Universal Hydrogen Evolution Reaction, *Angew. Chem., Int. Ed.*, 2018, **59**, 4679–4684.

9 (a) K. Srinivas, Y. J. Lu, Y. F. Chen, W. L. Zhang and D. X. Yang, FeNi2FeO4 Heterogeneous Nanoparticles Anchored on 2D MOF Nanosheets/1D CNT Matrix as Highly Efficient Bifunctional Electrocatalysts for Water Splitting, *ACS Sustainable Chem. Eng.*, 2020, **8**, 3820–3831; (b) D. Y. Chung, S. W. Jun, G. Yoon, H. Kim, J. M. Yoo, K. S. Lee, T. Kim, H. Shin, A. K. Sinha, S. G. Kwon, K. Kang, T. Hyeon and Y. E. Sung, Large-Scale Synthesis of Carbon-Shell-Coated FeP Nanoparticles for Robust Hydrogen Evolution Reaction Electrocatalyst, *J. Am. Chem. Soc.*, 2017, **139**, 6669–6674; (c) X. H. Fan, F. T. Kong, A. G. Kong, A. L. Chen, Z. Q. Zhou and Y. K. Shan, Covalent Porphyrin Framework-Derived Fe9P6FeN-Coupled Nanoparticles Embedded in N-Doped Carbons as Efficient Trifunctional Electrocatalysts, *ACS Appl. Mater. Interfaces*, 2017, **9**, 32840–32856; (d) J. Jin, J. Yin, H. B. Liu, M. Lu, J. Y. Li, M. Tian and P. X. Xi, Transition Metal (Fe, Co and Ni)-Carbide-Nitride (M-C-N) Nanocatalysts: Structure and Electrocatalytic Applications, *ChemCatChem*, 2019, **11**, 2780–2792; (e) Y. R. Zheng, P. Wu, G. X. Li, H. Liu, L. L. Zeng, L. L. Zhao, J. Jia, M. Y. Zhang, W. J. Zhou, H. Liu and Y. Y. Hu, Electrochemical Flocculation Integrated Hydrogen Evolution Reaction of Fe@N-Doped Carbon Nanotubes on Iron Foam for Ultralow Voltage Electrolysis in Neutral Media, *Adv. Sci.*, 2019, **6**, 1901458.

10 (a) R. Subbaraman, D. Tripkovic, D. Strmenic, K. C. Chang, M. Uchimura, A. P. Paulikas, V. Stamenkovic and N. M. Markovic, Enhancing Hydrogen Evolution Activity in Water Splitting by Tailoring Li2Ni(OH)2Pt Interfaces, *Science*, 2011, **334**, 1256–1260; (b) D. D. Zhang, J. Y. Shi, Y. Qi, X. M. Wang, H. Wang, M. R. Li, S. Z. Liu and C. Li, Quasi-Amorphous Metallic Nickel Nanopowder as an Efficient and Durable Electrocatalyst for Alkaline Hydrogen Evolution, *Adv. Sci.*, 2018, **5**, 1801216; (c) C. J. Lei, Y. Wang, Y. Hou, P. Liu, J. Yang, T. Zhang, X. D. Zhuang, M. W. Chen, B. Yang, L. C. Lei, C. Yuan, M. Qiu and X. L. Feng, Efficient Alkaline Hydrogen Evolution on Atomically Dispersed Ni–N, Species Anchored Porous Carbon with Embedded Ni Nanoparticles by Accelerating Water Dissociation Kinetics, *Energy Environ. Sci.*, 2019, **12**, 149–156; (d) Z. Fang, L. Peng, Y. Qian, X. Zhang, Y. Xie, J. J. Cha and G. Yu, Dual Tuning of Ni-Co-A (A = P, Se, O) Nanosheets by Anion Substitution and Holey Engineering for Efficient Hydrogen Evolution, *J. Am. Chem. Soc.*, 2018, **140**, 5241–5247; (e) Y. B. Li, X. Tan, S. Chen, X. Bo, H. J. Ren, S. C. Smith and C. Zhao, Processable Surface Modification of Nickel-Heteroatom (N, S) Bridge Sites for Promoted Alkaline Hydrogen Evolution, *Angew. Chem., Int. Ed.*, 2019, **58**, 461–466.

11 (a) R. Paul, L. Zhu, H. Chen, J. Qu and L. M. Dai, Recent Advances in Carbon-Based Metal-Free Electrocatalysts, *Adv. Mater.*, 2019, **31**, 1806403; (b) B. R. Sathe, X. X. Zhou and T. Asefa, Metal-free B-doped graphene with efficient electrocatalytic activity for hydrogen evolution reaction, *Catal. Sci. Technol.*, 2014, **4**, 2023–2030; (c) K. G. Qu, Y. Zheng, X. X. Zhang, K. Davey, S. Dai and S. Z. Qiao, Promotion of Electrocatalytic Hydrogen Evolution Reaction on Nitrogen-Doped Carbon Nanosheets with Secondary Heteroatoms, *ACS Nano*, 2017, **11**, 7293–7300; (d) L. Z. Zhang, Y. Jia, X. C. Yan and X. D. Yao, Activity Origins in Nanocarbons for the Electrocatalytic Hydrogen Evolution Reaction, *Small*, 2018, **14**, 1800235; (e) F. Xiao, Z. M. Chen, H. Wu, Y. Wang, E. P. Cao, X. D. Lu, Y. Q. Wu and Y. Z. Ren, Phytic Acid-Guided Ultra-Thin N,P Co-Doped Carbon Coated Carbon Nanotubes for Efficient All-pH Universal Hydrogen Evolution, *Nanoscale*, 2019, **11**, 23027–23034.

12 (a) H. L. Fei, J. C. Dong, D. L. Chen, T. D. Hu, X. D. Duan, I. Shakir, Y. Huang and X. F. Duan, Single atom electrocatalysts supported on graphene or graphene-like carbons, *Chem. Soc. Rev.*, 2019, **48**, 5207–5241; (b) Z. S. Shi, W. Q. Yang, Y. T. Gu, T. Liao and Z. Q. Sun, Metal-Nitrogen-Doped Carbon Materials as Highly Efficient Catalysts: Progress and Rational Design, *Adv. Sci.*, 2020, **7**, 2001069; (c) X. J. Zhu, J. L. Dai, L. G. Li, D. K. Zhao, Z. X. Wu, Z. H. Tang, L. J. Ma and S. W. Chen, Hierarchical carbon microflowers supported defect-rich Co3S4 nanoparticles: An efficient electrocatalyst for water splitting, *Carbon*, 2020, **160**, 133–144; (d) X. P. Gao, Y. A. Zhou, S. Q. Liu, Z. W. Cheng, Y. J. Tan and Z. M. Shen, Single Cobalt Atom Anchored on N-Doped Graphyne for Boosting the Overall Water Splitting, *Appl. Surf. Sci.*, 2020, **502**, 144155; (e) S. V. Mohite, R. M. Xing, B. Y. Li, S. S. Latthe, Y. Zhao, X. Y. Li, L. Q. Mao and S. H. Liu, Spatial Compartmentalization of Cobalt Phosphide in P-Doped Dual Carbon Shells for Efficient Alkaline Overall Water Splitting, *Inorg. Chem.*, 2020, **59**, 1996–2004; (f) S. Yu, S. L. Song, R. Li and B. Z. Fang, The lightest solid meets the lightest gas: an overview of carbon
aerogels and their composites for hydrogen related applications, *Nanoscale*, 2020, 12, 19536–19556.

13 (a) G. F. Liao, Y. Gong, L. Zhang, H. Y. Gao, G. J. Yang and B. Z. Fang, Semiconductor polymeric graphitic carbon nitride photocatalysts: the “holy grail” for the photocatalytic hydrogen evolution reaction under visible light, *Energy Environ. Sci.*, 2019, 12, 2080–2147; (b) G. F. Liao, J. S. Fang, Q. Li, S. H. Li, Z. S. Xu and B. Z. Fang, Ag-Based nanocomposites: synthesis and applications in catalysis, *Nanoscale*, 2019, 11, 7062–7096; (c) G. Q. Suo, J. Q. Zhang, D. Li, Q. Y. Yu, W. A. Wang, M. He, L. Feng, X. J. Hou, Y. L. Yang, X. H. Ye and L. Zhang, N-doped carbon/ultrathin 2D metallic cobalt selenide core/sheath flexible framework bridged by chemical bonds for high-performance potassium storage, *Chem. Eng. J.*, 2020, 388, 124396; (d) D. Li, J. Q. Zhang, S. M. Ahmed, G. Q. Suo, W. A. Wang, L. Feng, X. J. Hou, Y. L. Yang, X. H. Ye and L. Zhang, Amorphous carbon coated SnO2 nano-seeds on hard carbon hollow spheres to boost potassium storage with high surface capacitive contributions, *J. Colloid Interface Sci.*, 2020, 574, 174–181; (e) G. Q. Suo, J. Q. Zhang, D. Li, Q. Y. Yu, M. He, L. Feng, X. J. Hou, Y. L. Yang, X. H. Ye, L. Zhang and W. A. Wang, *J. Colloid Interface Sci.*, 2020, 566, 427–433; (f) J. F. Wang, H. X. Liu, Q. Wang, J. H. Huo, W. Y. Ge, X. B. Duan and S. Q. Guo, *Appl. Surf. Sci.*, 2021, 540, 148351.

14 (a) X. M. Guo, W. Zhang, D. Zhang, S. L. Qian, X. Z. Tong, D. C. Zhou, J. H. Zhang and A. H. Yuan, CoS8/C@C submicron-spheres derived from bacteria for electrocatalytic oxygen reduction reaction, *ChemElectroChem*, 2019, 6, 4571–4575; (b) X. F. Liu, C. C. Hao, L. H. He, C. Yang, Y. B. Chen, C. B. Jiang and R. H. Yu, Yolk-shell structured Co-C/VOID/CoS8 composites with tunable cavity for ultrabroad band and efficient low-frequency microwave absorption, *Nano Res.*, 2018, 11, 4169–4182; (c) P. Y. Zeng, J. W. Li, M. Ye, K. F. Zhuo and Z. Fang, In Situ Formation of CoS8@N-C Hollow Nanoparticles by Pyrolysis and Sulphurization of ZIF-67 for High-Performance Lithium-Ion Batteries, *Chem.–Eur. J.*, 2017, 23, 9517–9524; (d) Y. Y. Zhao, Q. Fu, D. S. Wang, Q. Pang, Y. Gao, A. Missiul, R. Nemausat, A. Sarapulova, H. Ehrenberg, Y. J. Wei and G. Chen, Co9S8@carbon yolk-shell nanocages as a high performance direct conversion anode material for sodium ion batteries, *Energy Storage Materials*, 2019, 18, 51–58; (e) H. X. Zhong, K. Li, Q. Zhang, J. Wang, F. L. Meng, Z. J. Wu, J. M. Yan and X. B. Zhang, In situ anchoring of CoS8 nanoparticles on N and S co-doped porous carbon tube as bifunctional oxygen electrocatalysts, *NGP Asia Mater.*, 2016, 8, e308.

15 (a) J. Du, R. Wang, Y. R. Lv, Y. L. Wei and S. Q. Zang, One-step MOF-derived Co/CoS8 nanoparticles embedded in nitrogen, sulfur and oxygen ternary-doped porous carbon: an efficient electrocatalyst for overall water splitting, *Chem. Commun.*, 2019, 55, 3203–3206; (b) N. Huang, S. F. Yan, M. Y. Zhang, Y. Y. Ding, L. Yang, P. P. Sun and X. H. Sun, A MoS2-CoS8 NC heterostructure as an efficient bifunctional electrocatalyst towards hydrogen and oxygen evolution reaction, *Electrochim. Acta*, 2019, 327, 134942; (c) H. Yu, X. Y. Sun, D. H. Tang, Y. Huang, W. T. Zhang, S. J. Miao, Z. A. Qiao, J. J. Wang and Z. Zhao, Molten salt strategy to synthesize alkali metal doped CoS8 nanoparticles embedded, N co-doped mesoporous carbon as hydrogen evolution electrocatalyst, *Int. J. Hydrogen Energy*, 2020, 45, 6006–6014; (d) L. G. Wang, X. X. Duan, X. J. Liu, J. Gu, R. Si, Y. Qiu, Y. M. Qiu, D. E. Shi, F. H. Chen, X. M. Sun, J. H. Lin and J. L. Sun, Atomically Dispersed Mo Supported on Metallic CoS8 Nanoflakes as an Advanced Noble-Metal-Free Bifunctional Water Splitting Catalyst Working in Universal pH Conditions, *Adv. Energy Mater.*, 2019, 9, 1903137; (e) J. G. Yan, L. G. Chen and X. Liang, CoS8 Nanowires@NiCo LDH Nanosheets Arrays on Nickel Foams towards Efficient Overall Water Splitting, *Sci. Bull.*, 2019, 64, 158–165.

16 (a) B. J. Zhu, R. Q. Zhou and Q. Xu, Metal–Organic Framework Based Catalysts for Hydrogen Evolution, *Adv. Energy Mater.*, 2018, 8, 1801193; (b) P. Q. Liao, J. Q. Shen and J. P. Zhang, Metal–organic frameworks for electrocatalysis, *Coord. Chem. Rev.*, 2018, 373, 22–48; (c) L. J. Kong, M. Zhong, W. Shuang, Y. H. Xu and X. H. Bu, Electrochemically active sites inside crystalline porous materials for energy storage and conversion, *Chem. Soc. Rev.*, 2020, 49, 2378–2407; (d) X. D. Wen and J. Q. Guan, Recent progress on MOF-derived electrocatalysts for hydrogen evolution reaction, *Applied Materials Today*, 2019, 16, 146–168; (e) H. Kobayashi, Y. Mitsuka and H. Kitagawa, Metal Nanoparticles Covered with a Metal–Organic Framework: From One-Pot Synthetic Methods to Synergistic Energy Storage and Conversion Functions, *Inorg. Chem.*, 2016, 55, 7301–7310; (f) D. Liu, X. M. Zhang, Y. J. Wang, S. Y. Song, L. F. Cui, H. B. Fan, X. C. Qiao and B. Z. Fang, A new perspective of lanthanide metal–organic frameworks: tailoring Dy-BTC nanospheres for rechargeable Li–O2 batteries, *Nanoscale*, 2020, 12, 9524–9532; (g) Y. W. Li, W. J. Zhang, J. Li, H. Y. Ma, H. M. Du, D. C. Li, S. N. Wang, J. S. Zhao, J. M. Dou and L. Q. Xu, Fe-MOF-Derived Efficient ORR/OER Bifunctional Electrocatalyst for Rechargeable Zinc–Air Batteries, *ACS Appl. Mater. Interfaces*, 2020, 12, 44710–44719.

17 (a) L. T. Yan, L. Cao, P. C. Dai, X. Gu, D. D. Liu, J. L. Li, Y. Wang and X. B. Zhao, Metal–Organic Frameworks Derived Nanotube of Nickel–Cobalt Bimetal Phosphides as Highly Efficient Electrocatalysts for Overall Water Splitting, *Adv. Funct. Mater.*, 2017, 27, 1703455; (b) C. R. Grice, W. W. Meng, L. Guan, F. H. Xu, Y. Yu, C. L. Wang, D. W. Zhao and Y. F. Yan, Metal–Organic Framework-Derived CoWP@C Composite Nanowire Electro catalyst for Efficient Water Splitting, *ACS Energy Lett.*, 2018, 3, 1434–1442; (c) W. Q. Liu, Y. M. Zhou, J. H. Bao, J. Q. Wang, Y. W. Zhang, X. L. Sheng, Y. Xue, C. Guo and X. X. Chen, Co-CoO-ZnFe2O4 encapsulated in carbon nanowires derived from MOFs as electrocatalysts for hydrogen evolution, *J. Colloid Interface Sci.*, 2020, 561, 620–628; (d) Y. J. Lei, L. Wei, S. L. Zhai, Y. Q. Wang, H. E. Karahan, X. C. Chen, Z. Zhou, C. J. Wang, X. Sui and
Y. Chen, Metal-free bifunctional carbon electrocatalysts derived from zeolitic imidazolate frameworks for efficient water splitting, Mater. Chem. Front., 2018, 2, 102–111; (e) Y. L. Li, B. M. Jia, B. Y. Chen, Q. L. Liu, M. K. Cai, Z. Q. Xue, Y. A. Fan, H. P. Wang, C. Y. Su and G. Q. Li, MOF-derived Mn doped porous CoP nanosheets as efficient and stable bifunctional electrocatalysts for water splitting, Dalton Trans., 2018, 47, 14679–14685.

18 H. Y. Ma, Y. Z. Zhang, H. Yan, W. J. Zhang, Y. W. Li, S. N. Wang, D. C. Li, J. M. Dou and J. R. Li, Two Microporous Co9S8-MOFs with Dual Active Sites for Highly Selective Adsorption of CO2/CH4 and CO2/N2, Dalton Trans., 2019, 48, 13541–13545.

19 (a) A. C. Ferrari and D. M. Basko, Raman spectroscopy as a versatile tool for studying the properties of graphene, Nat. Nanotechnol., 2013, 8, 235–246; (b) N. Sikdar, B. Konkena, J. Masa, W. Schuhmann and T. K. Maji, Co3O4@Co/NCNT Nanostructure Derived from a Dicyanamid-Based Metal–Organic Framework as an Efficient Bi-functional Electro catalyst for Oxygen Reduction and Evolution Reactions, Chem.–Eur. J., 2017, 23, 18049–18056; (c) D. N. Ding, K. Shen, X. D. Chen, H. R. Chen, J. Y. Chen, T. Fan, R. F. Wu and Y. W. Li, Multi-Level Architecture Optimization of MOF-templated Co-Based Nanoparticles Embedded in Hollow N-Doped Carbon Polyhedra for Efficient OER and ORR, ACS Catal., 2018, 8, 7879–7888; (d) S. M Alshehri, J. Ahmed, A. Khan, M. Naushad and T. Ahamad, Bifunctional Electrocatalysts (CoNCS@NSC) Derived from a Polymer-metal Complex for the Oxygen Reduction and Oxygen Evolution Reactions, ChemElectroChem, 2018, 5, 355–361.

20 (a) Y. W. Li, J. Xu, D. C. Li, J. M. Dou, H. Yan, T. L. Hu and X. H. Bu, Two microporous MOFs constructed from different metal cluster SBUs for selective gas adsorption, Chem. Commun., 2015, 51, 14211–14214; (b) Y. W. Li, H. Yan, T. L. Hu, H. Y. Ma, D. C. Li, S. N. Wang, Q. X. Yao, J. M. Dou, J. Xu and X. H. Bu, Two microporous Fe-based MOFs with multiple active sites for selective gas adsorption, Chem. Commun., 2017, 53, 2394–2397; (c) D. S. Zhang, Y. Z. Zhang, X. L. Zhang, F. Wang, J. Zhang, H. Hu, J. Gao, H. Yan, H. L. Liu, H. Y. Ma, L. L. Geng and Y. W. Li, Nanocage-Based Porous Metal–Organic Frameworks Constructed from Icosahedrons and Tetrahedrons for Selective Gas Adsorption, ACS Appl. Mater. Interfaces, 2019, 11, 20104–20109.

21 (a) N. Yao, P. Li, Z. R. Zhou, Y. M. Zhao, G. Z. Cheng, S. L. Chen and W. Luo, Synergistically Tuning Water and Hydrogen Binding Abilities Over Co,N by Cr Doping for Exceptional Alkaline Hydrogen Evolution Electrocatalysis, Adv. Energy Mater., 2019, 9, 1902449; (b) Z. Y. Chen, Y. Song, J. Y. Cai, X. S. Zheng, D. D. Han, Y. S. Wu, Y. P. Zhang, S. W. Niu, Y. Liu, J. F. Zhu, X. J. Liu and G. M. Wang, Tailoring the d-Band Centers Enables Co,N Nanosheets To Be Highly Active for Hydrogen Evolution Catalysis, Angew. Chem., Int. Ed., 2018, 57, 5076–5080; (c) Y. P. Wu, W. Zhou, J. Zhao, W. W. Dong, Y. Q. Lan, D. S. Li, C. H. Sun and X. H. Bu, Surfactant-Assisted-Phase Selective Synthesis of New Cobalt MOFs and Their Efficient Electrocatalytic Hydrogen Evolution Reaction, Angew. Chem., Int. Ed., 2017, 56, 13001–13005; (d) H. Li, P. Wen, D. S. Itanze, M. W. Kim, S. Adhikari, C. Lu, L. Jiang, Y. J. Qiu and S. M. Geyer, Phosphorus-Rich Colloidal Cobalt Diphosphide [CoP2] Nanocrystals for Electrochemical and Photoelectrochemical Hydrogen Evolution, Adv. Mater., 2019, 31, 1900813; (e) H. P. Feng, L. Tang, G. M. Zeng, J. F. Yu, Y. C. Deng, Y. Y. Zhou, J. J. Wang, C. Y. Feng, T. Luo and B. B. Shao, Electron density modulation of Fe1-xCo,P nanosheet arrays by iron incorporation for highly efficient water splitting, Nano Energy, 2020, 67, 104174.

22 (a) E. P. Cao, Z. M. Chen, H. Wu, P. Yu, Y. Wang, F. Xiao, S. Chen, S. C. Du, Y. Xie, Y. Q. Wu and Z. Y. Ren, Boron-Induced Electronic-Structure Reformation of CoP Nanoparticles Drives Enhanced pH-Universal Hydrogen Evolution, Angew. Chem., Int. Ed., 2020, 59, 4154–4160; (b) Y. Tong, X. W. Yu, H. Y. Wang, B. W. Yao, C. Li and G. Q. Shi, Trace Level Co-N Doped Graphite Foams as High-Performance Self-Standing Electrocatalytic Electrodes for Hydrogen and Oxygen Evolution, ACS Catal., 2018, 8, 4637–4644; (c) X. Q. Wang, J. R. He, B. Yu, B. C. Sun, D. X. Yang, X. J. Zhang, Q. H. Zhang, W. L. Zhang, L. Gu and Y. F. Chen, CoSe2 nanoparticles embedded MOF-derived Co-N-C nanoflake arrays as efficient and stable electrocatalyst for hydrogen evolution reaction, Appl. Catal., B, 2019, 238, 117996; (d) Y. J. Zhang, W. F. Li, L. H. Lu, W. G. Song, C. R. Wang, L. S. Zhou, J. H. Liu, Y. Chen, H. Y. Jin and Y. G. Zhang, Tuning active sites on cobalt/nitrogen doped graphene for electrocatalytic hydrogen and oxygen evolution, Electrochim. Acta, 2018, 265, 497–506; (e) S. M. Wang, L. Zhang, Y. Qin, D. Ding, Y. F. Bu, F. Q. Chu, Y. Kong and M. L. Liu, Co,N-codoped graphene as efficient electrocatalyst for hydrogen evolution reaction: Insight into the active centre, J. Power Sources, 2017, 363, 260–268; (f) X. Z. Ma, K. Y. Li, X. Zhang, B. Wei, H. Yang, L. N. Liu, M. Y. Zhang, X. T. Zhang and Y. J. Chen, The surface engineering of cobalt carbide hollow nanowall arrays grown on Celgard separator as a multifunctional polysulfide separator for high-performance Li-S batteries, Energy Environ. Sci., 2018, 11, 2560–2568; (b) W. Xiong, K. Hu, Z. Li, Y. X. Jiang, Z. G. Li, Z. Li and X. W. Wang, A wearable system based on core-shell structured peptide-Co,N-S supercapacitor and triboelectric nanogenerator, Nano Energy, 2019, 66, 104149.