Exploring earth-abundant and noble metal-free catalysts for water electrolysis is pivotal in renewable hydrogen production. Herein, a highly active electrocatalyst of nitrogen-doped porous carbon nanosheets coupled with Mo$_2$C nanoparticles (Mo$_2$C/NPC) was synthesized by a novel method with high BET surface area of 1380 m$^2$ g$^{-1}$ using KOH to activate carbon composite materials. The KOH plays a key role in etching out MoS$_2$ to produce Mo precursor; simultaneously, it corrodes carbon to form porous structure and produce reducing gas such as H$_2$ and CO. The resulting Mo$_2$C/NPC hybrid demonstrated superior HER activity in acid solution, with the overpotential of 166 mV at current density of 10 mA cm$^{-2}$, onset overpotential of 93 mV, Tafel slope of 68 mV dec$^{-1}$, and remarkable long-term cycling stability. The present strategy may provide a promising strategy to fabricate other metal carbide/carbon hybrids for energy conversion and storage.

Keywords: Nitrogen-doped porous carbon nanosheet, β-Mo$_2$C, Electro catalyst, Hydrogen evolution reaction

Introduction

Nowadays, environmental pollution and energy crisis have become the key issues for sustainable development [1, 2]. The key to solving the problem is to achieve a clean and renewable energy source. Hydrogen produced through the decomposition of water by catalysts has been considered as a promising alternative to fossil fuels [3, 4]. Platinum-based catalysts are still the most efficient hydrogen evolution reaction (HER) catalysts to date, but the scarcity and high cost limit their large-scale applications. Therefore, the low-cost and earth-abundant transition metal compounds such as transition metal sulfides [5], oxides [6], nitrides [7], phosphides [8, 9], and carbides [10] appear as substitutions for the noble metal catalysts. Among these electrocatalysts, Mo$_2$C has attracted great interest as an efficient HER electrocatalysts since its d-band electronic structure is similar to that of Pt [11]. The catalytic properties of molybdenum carbide mainly rely on the exposure of more active sites and improving the conductivity of the catalysts. Researchers tend to the improvement of the composition and structure of Mo$_2$C hybrids; however, the current synthesis of Mo$_2$C hybrids mainly require high temperature, which will cause the particles to agglomerate, resulting in a decrease in active surfaces and reducing the HER catalytic performance [12]. In order to diminish the agglomeration of molybdenum carbide, conductive carbon supporting material is normally applied to increase the active surfaces and conductivity. Graphite with a two-dimensional structure proved to be an excellent supporting material for catalyst [13]. Otherwise, high surface area of the catalysts would provide more active sites exposed, thus improving the HER performance. Unfortunately, the recent method for improving the specific surface area of the catalyst is still limited, and researchers tend to make efforts to reduce the size...
of the catalyst, rarely focusing on increasing the porosity of the material [14, 15]. Therefore, the increase in the specific surface area of Mo2C/C composite is restricted. The preparation of porous carbon with high specific surface area (4196 m2 g−1) from potassium hydroxide activated polymer hydrogel [16] provides a new idea to synthesize the supporting conductive graphite substrate with a porous structure which would provide open space and short diffusion channels for reactants during HER [17]. Previous report has demonstrated that the synergistic effects between Mo2C and N dopants in carbon materials would lead to high HER electrocatalytic performance [18].

The controlled synthesis of N-doped porous carbon nanosheets as supporting substrate would possess high surface area, excellent conductivity, high durability, N dopants to enhance electron transfer, and porous structure to promote mass/charge transmission. Moreover, reports have proved that the β-Mo2C with a hexagonal structure is the most active phase of the four phases of molybdenum carbide since it has a valence band shape similar to Pt [19]. Thus, it is a challenge to synthesize the nitrogen-doped porous carbon nanosheets coupled with β-Mo2C nanoparticles for high-efficiency catalytic hydrogen production.

Herein, we report a novel method of self-template to achieve a highly active and stable noble metal-free electrocatalyst with great porosity. Commercial MoS2 was used as Mo source and self-template and dopamine was applied as C and N source, respectively. Since dopamine can easily self-polymerize on the surface of Mo source to form poly-dopamine (PDA) microspheres, it is essential to synthesize catalysts with more active surface exposed to air [20]. Reporters tend to use templates such as SiO2 [21] and NaCl [22] to avoid aggregation and form structures with high specific surface area. However, dissolving silica requires hydrofluoric acid, which is a high-risk chemical, and removing the salt template involves more steps. We chose commercial MoS2 as Mo source and self-templates since MoS2 can react with KOH at high temperature. The removal of the template and the activation of KOH which lead to porous carbon and reducing gas synthesized the final Mo2C/NPC hybrid with high catalytic activity. Our synthesis method suggests a promising strategy to fabricate noble metal-free high performance HER catalysts.

**Methods**

**Preparation of Mo2C/NPC Hybrid and the Reference NPC**

In a typical synthesis, 500 mg of commercial MoS2 was first dispersed in 100 ml deionized water via sonication process. Then, 120 mg of Trizma® base and 200 mg of dopamine hydrochloride were added into the suspension. The mixture was stirred for 24 h at room temperature, and the product was collected by filter after washed with deionized water. After placing it in oven overnight, the resulting MoS2@PDA was carbonized in a tube furnace at 600 °C for 2 h to form MoS2@NC. The carbonized MoS2@NC was soaked in 4 ml of 7 M KOH, with a KOH to MoS2@NC mass ratio of 3:1. The dried KOH/MoS2@NC mixture was heated under N2 at 800 °C for 1 h. After cooling, the sample was filtered and washed with dilute hydrochloric acid solution and deionized water. It was then dried at 60 °C overnight. The final product was Mo2C/NPC, and N-doped porous carbon (NPC) was obtained following a similar procedure except that no commercial MoS2 was added.

**Characterization**

X-ray diffraction (XRD) was performed on a PANalytical X’Pert3 Powder using Cu Kα radiation (λ = 1.54056 Å). The morphology was characterized using a field-emission scanning electron microscopy (SEM, Hitachi S-8020). Transmission electron microscopy (TEM) images and corresponding energy-dispersive X-ray (EDX) elemental mapping images were performed with a FEI Tecnai G2 F20 S-TWIN TMP. Raman spectrum was recorded with a confocal Raman spectrometer (HORIBA LabRAM HR Evolution). X-ray photoelectron spectra (XPS) were carried out on a PHI Quantera-II scanning X-ray microprobe spectrometer with Al Kα radiation (1486.6 eV) as an excitation source. TGA/DSC curve was measured by a TGA/DSCi Mettler-Toledo thermal analyzer. Specific surface area of the sample was measured with a Micromeritics ASAP 2020 HD88.

**Electrochemical Measurements**

All electrochemical tests are conducted with a standard three-electrode system on a CHI660E potentiostat (CH Instruments, China), and all potentials in this paper are referred to reversible hydrogen electrode (RHE) according to E(RHE) = E(Ag/AgCl) + 0.059 pH + 0.197 V. Graphite rod was used as the counter electrode and Ag/AgCl (saturated KCl-filled) as the reference electrode, respectively. A glassy carbon electrode with a diameter of 5 mm covered by 15 μL catalyst ink was used as the working electrode. Typically, in preparation of a working electrode, 4 mg of the Mo2C/NPC and 20 μL of Nafion solution are dispersed in 1 mL of 3:1 v/v water/ethanol by ultrasonication for 1 h to form a homogeneous ink. Before the electrochemical tests, the fresh working electrode is cycled 50 times to stabilize the current, and linear sweep voltammetry (LSV) is tested in 0.5 M H2SO4 at a scan rate of 5 mV s−1 without IR compensation. Additionally, cyclic voltammograms (CV) are obtained from 0 to 0.2 V (versus RHE, in 0.5 M H2SO4) with sweep rates of 20, 40, 60, 80, 100, 120, and 140 mV s−1, respectively.

**Results and Discussions**

The synthetic procedure of Mo2C/NPC hybrid was illustrated in Fig. 1. We chose dopamine as carbon and nitrogen source. Commercial bulk MoS2 was selected as
Mo source and self-template, by which the size is \( \sim 2 \mu m \) (Additional file 1: Figure S1a). Firstly, the dopamine self-polymerized on the surface of bulk MoS\(_2\) to form a MoS\(_2@\)PDA core-shell structure (Additional file 1: Figure S1b). Then, the core-shell structure MoS\(_2@\)PDA was carbonized to form N-doped carbon film wrapped on the surface of MoS\(_2\), which was signed as MoS\(_2@\)NC (Additional file 1: Figure S1c) [23, 24]. Finally, the mixture of the as-prepared MoS\(_2@\)NC and KOH was placed into a tube furnace and reacted to acquire the final product: nitrogen-doped porous carbon nanosheets coupled with Mo\(_2\)C nanoparticles (donated as Mo\(_2\)C/NPC) (Additional file 1: Figure S1d). When MoS\(_2\) was severed as Mo source, dopamine forms a PDA film on the surface of MoS\(_2\), the MoS\(_2\) served as a self-template to avoid dopamine to form microspheres, and a PDA film was generated. This is because the conversion from PDA to N-doped C will continue to maintain its morphology [15]; when MoS\(_2\) react with KOH, we can get carbon nanosheets about 2 \( \mu m \) in length. The carbon in MoS\(_2@\)NC can also be activated by KOH to get the porous C nanosheets. The formation of Mo\(_2\)C/NPC can be proposed based on a series of reactions. The process of KOH insert and react with carbon can be summarized as KOH activation reaction, the chemical reaction equation is described as \( 6\text{KOH} + 2\text{C} \leftrightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3 \).
and the K₂CO₃ can be further decomposed into K₂O, CO₂, and CO. The process of KOH activation reaction can not only corrode carbon units to produce porous structure of carbon, but also promote the formation of graphitic carbon. Meanwhile, KOH could etch MoS₂ template to produce Mo₂C nanoparticles with the diffusion of sulfur vapor and the formation of K₂S. Thus, the reactions lead to the formation of Mo₂C/NPC hybrid.

The crystalline phase composition of the product was examined by X-ray diffraction (Fig. 2a). A broad peak near 26°and the peak at 46.3°can be attributed to the (003) and (012) planes of graphitic carbon. The other X-ray diffraction peaks at 34.3, 37.9, 39.39, 52.1, 61.5, 69.5, 74.6, and 75.5° are attributed to the diffractions of the (100), (002), (101), (102), (110), (103), (112), and (201) faces of hexagonal β-Mo₂C (JCPDS 35-0708), respectively. In addition, there are no discernible impurities such as molybdenum metal, oxides, sulfides, or other carbides, indicating the full conversion of commercial MoS₂ to Mo₂C. The results of Raman spectroscopy in Fig. 2b further confirmed that the as-prepared catalyst is a mixture of molybdenum carbide and graphite. The intensity ratio of G band to D band, I_G/I_D > 1, suggests that the carbon is basically graphitic [26]. The amount of Mo₂C in the final product is found to be ~44 wt% based on the thermogravimetric analysis (TGA) in air (Additional file 1: Figure S2). Nitrogen adsorption-desorption isotherms were measured at 77 K to evaluate the Brunauer-Emmett-Teller (BET) specific surface area. As shown in Fig. 2c, the nitrogen adsorption-desorption isotherms of Mo₂C/NPC showed an H₄ type hysteresis loop, which was suitable for materials with micro-meso pores. Moreover, the BJH desorption average pore size is calculated to be 3.23 nm and the specific BET surface area is 1380 m² g⁻¹, which revealed the successful synthesis of the porous structure. Such a micro-meso-porous structure of carbon matrix with ultrahigh surface area is supposed to be an ideal electrode material, which
not only can provide open space and short diffusion channels for reactants but can also facilitate the absorption of $\text{H}^+$ and desorption of $\text{H}_2$, thus leading to good mass/charge transfer ability.

Then, the morphology and structure of the hierarchical Mo$_2$C/NPC hybrid was investigated by SEM and TEM. As shown in Fig. 2d, the low-magnification SEM image presents that numerous well-dispersed nanosheet-like structure with the average size of 2 $\mu$m, which is consistent with the size of the template MoS$_2$. The TEM images in Fig. 3a and c revealed that the $\beta$-Mo$_2$C nanoparticles with the size from various several nanometers to 50 nm were anchored on nitrogen-doped carbon nanosheets. The porous nature of carbon nanosheets can be seen from TEM images in Fig. 3b [27]. In addition, high-resolution TEM image in Fig. 3d showed the lattice fringes with d-spacing of 0.23 nm and 0.24 nm which correspond to the (101) and (002) planes of $\beta$-Mo$_2$C. The porous structure of supporting carbon and the coupling of Mo$_2$C nanoparticles with N-doped porous C nanosheets would facilitate the transfer of electrons from molybdenum carbide to carbon, thereby increasing the efficiency of the catalyst. As exemplified in Fig. 3e, the energy dispersive spectroscopy (EDS) analysis demonstrated that the nanosheets were comprised of Mo, C, and N elements, confirming the successful synthesis of Mo$_2$C/NPC hybrid.

The surface composition of the as-synthesized Mo$_2$C/NPC nanosheets was further elucidated by XPS. From the survey spectrum displayed in Fig. 4a, elements of Mo, C, N, and O can be clearly identified. The C 1s XPS peak can be fitted into three peaks centered at 284.6, 285.6, and 288.8 eV (Fig. 4b), which can be attributed to C-C/C=, C-N, and C=O species, respectively [28, 29]. The Mo 3d XPS peak can be deconvoluted into two doublets (Fig. 4c). One is centered at binding energy of 228.6/231.6 eV and the other is 232.9/235.9 eV, which can be ascribed to Mo$_2$C and surface-oxidized MoO$_3$, respectively [14, 26, 29]. The unavoidable abundance of a significant amount of molybdenum oxide is coming from the slow oxidation at the surface of molybdenum carbide when exposed to air [30]. Moreover, it has been

![Fig. 4 XPS survey spectrum (a) and high-resolution XPS scan of C 1s (b), Mo 3d (c), and N 1s (d) of Mo$_2$C/NPC](image-url)
reported that the oxide formed on the surface of carbide may retain the activity of the carbide. The N 1s peak (Fig. 4d) at binding energy of 398.4, 400.2, and 401.4 eV can be ascribed to pyridine, pyrrolic, and quaternary N atoms, respectively [24, 29]. Previous report has proved that the N dopants in carbon could induce the electron-transfer process (\(\text{Mo}_2\text{C} \rightarrow \text{C} \rightarrow \text{N}\)), resulting in a reinforcement of the synergy between \(\text{Mo}_2\text{C}\) and N dopants in carbon [18].

The electrocatalytic HER activity of the \(\text{Mo}_2\text{C}/\text{NPC}\) was first evaluated in 0.5 M H\(_2\)SO\(_4\). For comparison, the original commercial MoS\(_2\) (c-MoS\(_2\)), N-doped porous C (NPC), and 20 wt% Pt/C were also tested by using the same loading amount. Figure 5a compares the corresponding polarization curves. As expected, both the NPC and commercial MoS\(_2\) showed very limited HER activity, with an onset overpotential of 354 mV and 289 mV, respectively, whereas the \(\text{Mo}_2\text{C}/\text{NPC}\) had an onset overpotential of 93 mV, much lower than that of NPC and c-MoS\(_2\). The overpotential of the \(\text{Mo}_2\text{C}/\text{NPC}\) at a current density of 10 mA cm\(^{-2}\) is 166 mV, much lower than that of NPC and the original c-MoS\(_2\) and comparable to that of the \(\text{Mo}_2\text{C}/\text{C}\) hybrids in other works [20, 31]. To explore the HER kinetics of the catalysts, Tafel plots were fitted to the Tafel equation (\(\eta = a + b \log(j)\)), where \(b\) is the Tafel slope. As shown in Fig. 5b, the Tafel slope of \(\text{Mo}_2\text{C}/\text{NPC}\) was calculated to be 68 mV dec\(^{-1}\), much lower than those of c-MoS\(_2\) (184 mV dec\(^{-1}\)) and NPC (296 mV dec\(^{-1}\)), suggesting that the desorption step was efficient on the surfaces of the \(\text{Mo}_2\text{C}/\text{NPC}\) catalysts. The Tafel slope of the \(\text{Mo}_2\text{C}/\text{NPC}\) hybrid falls within the range of 40–120 mV dec\(^{-1}\), implying that the HER occurred on the \(\text{Mo}_2\text{C}/\text{NPC}\) surface follows a Volmer-Heyrovsky mechanism [32]. Based on the Tafel analysis, the exchange current density \((j_0)\) of \(\text{Mo}_2\text{C}/\text{NPC}\) was calculated to be 37.4 μA cm\(^{-2}\), which outperforms many non-precious HER.

**Fig. 5** Electrochemical measurements of \(\text{Mo}_2\text{C}/\text{NPC}\) hybrid for HER electrocatalysis in 0.5 M H\(_2\)SO\(_4\). a Polarization curves and b Tafel plots of \(\text{Mo}_2\text{C}/\text{NPC}\) in comparison with Pt/C benchmark, c-MoS\(_2\), and NPC. c CV curves of \(\text{Mo}_2\text{C}/\text{NPC}\) under different scan rates from 20 to 140 mV/s. The inset illustrates the plot of capacitive current at 0.1 V against the scan rate. d Polarization curves of \(\text{Mo}_2\text{C}/\text{NPC}\) before and after 3000 potential cycles.
and it is consistent with the specific BET surface area, thus

commercial MoS2 was used as Mo source and self-

analyzer was etched out by KOH to produce Mo precursor, and the

MoS 2@PDA, (c) MoS2@NPC and (d) Mo 2C/NPC. Figure S2. TGA curve of the as-prepared

Mo 2C/NPC hybrid with the overpotential of 166 mV at 10 mA cm−2, the

onset overpotential of 93 mV, Tafel slope of 68 mV dec−1,

and outstanding long-term cycling stability is attributed to the

nitrogen doping content, the porous conductive substrate, the abundance of active sites, and the strong

testify that Mo 2C/NPC is a highly efficient catalyst.

Conclusions

In summary, a novel strategy for preparing hierarchical

Mo 2C/NPC hybrid was developed through a KOH activation

method. Commercial MoS 2 was used as Mo source and self-

template while dopamine was used as C and N source. MoS 2

was etching out by KOH to produce Mo precursor, and the

carbonized PDA was corroded by KOH to form porous

graphite substrate. The excellent HER activity of Mo 2C/NPC

hybrid under the working conditions, we calculated the double-
layer capacitance (Cdl) from cyclic voltammetry (CV) curves

at different scan rates in Fig. 5c. As shown in the inset of

Fig. 5c, the linear correlation of the current density at 0.1 V

against the scan rate indicated that the Cdl of Mo 2C/NPC is

102.4 mF cm−2. If we assume a standard value of 60 μF/

cm2, the ECSA of Mo 2C/NPC is estimated to be ∼ 558 m2/g

(the calculation is shown in Additional file 1: Figure S3).

Such a high ECSA is contributed from both Mo 2C and the

carbon support. Since carbon is much lighter, the N-doped porous C is estimated to account for the most ECSA [26]

and it is consistent with the specific BET surface area, thus

supports that most of the active Mo 2C surface is electro-

chemically accessible.

Besides the HER activity, the stability is another de-

cissive factor to evaluate a catalyst. Long-term cyclic volt-

ammetry was conducted to measure the stability of the

Mo 2C/NPC in 0.5 M H 2SO 4. The HER polarization

curves in Fig. 5d for the Mo 2C/NPC show only 2 mV

loss after 3000 cycles, indicating the negligible stability

of the catalyst. The chronoamperometric response curve

of Mo 2C/NPC at the overpotential of −0.166 V vs. the

RHE was illustrated in the Additional file 1: Figure S4.

Based on the above electrochemical study, the remarkable electrocatalytic performance of Mo 2C/NPC

nanosheets can be ascribed to the following factors: (1) the high specific surface area of the catalysts would lead to more active sites for H+ absorption, and the good conductivity of the supporting substrate would improve the electron transmission; (2) the coupling of β-Mo 2C nanoparticles and N-doped porous C nanosheets would enlarge the contact of the catalyst with the electrolyte, facilitating the charge and mass transfer; and (3) the doping N atoms can not only better interact with H+ than C atoms but also modify the electronic structures of adjacent Mo and C atoms, making Mo 2C/NPC a highly efficient catalyst.

Competing Interests

The authors declare that they have no competing interests.

Author details

1. Yu F, Zhou H, Huang Y, Sun J, Qin F, Bao J, Goddard WA 3rd, Chen S, Ren Z

(2018) High-performance bifunctional porous non-noble metal phosphide
catalyst for overall water splitting. Nat Commun 9:2551

Additional file 1: Figure S1. SEM images of (a) c-MoS 2, (b) MoS 2@PDA,

c-MoS2: Commercial MoS2; HER: Hydrogen evolution reaction; HRTEM: High-

resolution transmission electron microscopy; Mo 2C/NPC: Nitrogen-doped porous

carbon nanosheets coupled with Mo 2C nanoparticles; c-MoS2: Commercial MoS 2; HER: Hydrogen evolution reaction; HRTEM: High-

resolution transmission electron microscopy; Mo 2C/NPC: Nitrogen-doped porous

carbon nanosheets coupled with Mo 2C nanoparticles; PDA: Poly-dopamine; Pt/C: Platinum/ carbon catalyst; RHE: Reversible hydrogen electrode; TGA: Thermogravimetric analysis


catalysts reported in the literature (as illustrated in

Additional file 1: Table S1) [33–35]. To estimate the electrochemically active surface area (ECSA) of Mo 2C/NPC

under the working conditions, we calculated the double-
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at different scan rates in Fig. 5c. As shown in the inset of

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In summary, a novel strategy for preparing hierarchical

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and outstanding long-term cycling stability is attributed to the

nitrogen doping content, the porous conductive substrate, the abundance of active sites, and the strong

interaction between Mo 2C and graphitic carbon. This effective method may be applied to the design and preparation of other carbide compounds with high specific surface area for various electrocatalytic applications.

Supplementary information

Supplementary information accompanies this paper at https://doi.org/10.1186/s11671-019-3147-z.

Abbreviations
c-MoS2: Commercial MoS 2; HER: Hydrogen evolution reaction; HRTEM: High-

resolution transmission electron microscopy; Mo 2C/NPC: Nitrogen-doped porous

carbon nanosheets coupled with Mo 2C nanoparticles; c-MoS 2: Commercial MoS 2; HER: Hydrogen evolution reaction; HRTEM: High-

resolution transmission electron microscopy; Mo 2C/NPC: Nitrogen-doped porous

carbon nanosheets coupled with Mo 2C nanoparticles; PDA: Poly-dopamine; Pt/C: Platinum/ carbon catalyst; RHE: Reversible hydrogen electrode; TGA: Thermogravimetric analysis

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Not applicable.

Authors’ Contributions

YL designed the experiments, carried out the experiments, and prepared and edited the manuscript. JYZ and JL supervised the work, guaranteed the integrity of the study, and finalized the manuscript. YY and JZ revised the manuscript. YL, YKZ, MJ, YZ, KZ, and AY participated in the experimental discussion. All authors read and approved the final manuscript.

Authors’ Information

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Availability of Data and Materials

All data are fully available without restriction.

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References

1. Yu F, Zhou H, Huang Y, Sun J, Qin F, Bao J, Goddard WA 3rd, Chen S, Ren Z

(2018) High-performance bifunctional porous non-noble metal phosphide
catalyst for overall water splitting. Nat Commun 9:2551
2. Tan C, Luo Z, Chaturvedi A, Cai Y, Du Y, Gong Y, Huang Y, Lai Z, Zhang X, Zheng L, Qi X, Goh MH, Wang J, Han S, Wu Xi, Gu L, Kbc C, Zhang H (2018) Preparation of high-percentage 1 T-phase transition metal dichalcogenide nanodots for electrochemical hydrogen evolution. Adv Mater 30

3. Kibsgaard J, Chen Z, Reinecke BN, Jaramillo TF (2012) Engineering the surface structure of MoS2 to preferentially expose active edge sites for electrocatalysis. Nat Mater 11:963–969

4. Chen Z, Duan X, Wei W, Wang S, Ni B-J (2019) Recent advances in transition metal-based electrocatalysts for alkaline hydrogen evolution. J Mater Chem A 7:14971–15005

5. Deng J, Li H, Wang S, Deng D, Chen M, Liu C, Tian Z, Novoselov KS, Ma C, Deng D, Bao X (2017) Multiscale structural and electronic control of molybdenum disulfide foam for highly efficient hydrogen production. Nat Commun 8:14430

6. Zhang T, Wu M-Y, Yao D-Y, Mao J, Liu H, Hu Wu-B, Du X-W, Ling T, Qiao S-Z (2018) Engineering oxygen vacancy on NiO nanotrod arrays for alkaline hydrogen evolution. Nano Energy 43:103–109

7. Wei B, Tang G, Liang H, Qi Z, Zhang D, Wu H, Shen H, Wang Z (2018) Bimetallic vanadium-molybdenum nitrides using magnetron co-sputtering as alkaline hydrogen evolution catalyst. Electrochem Commun 93:166–170

8. Yang J, Zhang F, Wang X, He D, Wu G, Yang Q, Hong X, Wu Y, Li Y (2016) Porous molybdenum phosphate nano-octahedrons derived from confined phosphorization in UiO-66 for efficient hydrogen evolution. Angew Chem Int Ed 55:12854–12858

9. Xu H, Wei J, Zhang K, Shihaith Y, Du Y (2018) Hierarchical NiMo phosphide nanospheres strongly anchored on carbon nanotubes as robust electrocatalysts for overall water splitting. ACS Appl Mater Interfaces 10:29647–29655

10. Fan X, Liu Y, Peng Z, Zhang Z, Zhou H, Zhang X, Yakobson BI, Goddard WA, Guo X, Hauge RH, Tour JM (2017) Atomic H-induced Mo2C hybrid as an active and stable bifunctional electrocatalyst. ACS nano 11:384–394

11. Chen WF, Wang CH, Sasaki K, Marinkovic N, Xu W, Muckerman JT, Zhu Y, Adzić RR (2013) Highly active and durable nanostructured molybdenum carbide electrocatalysts for hydrogen production. Energy Environ Sci 6:943–951

12. Alhajri N, Anjum D, Takahata K (2014) Molybdenum carbide-carbon nanocomposites synthesized from a reactive template for electrochemical hydrogen evolution. J Mater Chem A 2:10548–10556

13. Deng D, Novoselov KS, Qiang F, Zheng N, Tian Z, Bao X (2016) Catalysis with two-dimensional materials and their heterostructures. Nat Nanotechn 11:2128

14. Chen YY, Zhang Y, Jiang W, Zhang X, Dai Z, Wang Li, Hu JS (2016) Pomegranate-like N,P-Doped Mo2C@C nanospheres as highly active electrocatalysts for alkaline hydrogen evolution. ACS nano 10:8851–8860

15. Chen L, Jiang H, Jiang H, Zhang H, Guo S, Hu Y, Li C (2017) Mo-based ultrasmall nanoparticles on hierarchical carbon nanosheets for superior lithium ion storage and hydrogen generation catalysis. Advanced Energy Materials 7:1602782

16. He J, To J, Mf, Piaras PC, Han H, Atkinson T, Holmes RT, Nordlund D, Bao Z, Wilcox J (2016) Tunable polyaniline-based porous carbon with ultrahigh surface area for CO2 capture at elevated pressure. Adv Energy Mater 6:1602782

17. Fu J, Hassan FM, Zhong C, Lu J, Liu H, Yu A, Chen Z (2017) Defect engineering of chalcogen-tailed oxygen electrocatalysts for rechargeable quasi-solid-state zinc-air batteries. Adv Mater 29

18. Li Y, Yu G, Li GD, Sun Y, Asefa T, Chen W, Zou X (2015) Coupling Mo2C with nitrogen-rich nanocarbon leads to efficient hydrogen-evolution electrocatalytic sites. Angew Chem Int Ed 54:10752

19. Wang C, Regmi YN, Leonard BM (2014) Multiple phases of molybdenum carbide as electrocatalysts for the hydrogen evolution reaction. Angew Chem Int Ed 53:6407–6410

20. Wang C, Sun L, Zhang F, Wang X, Sun Q, Cheng Y, Wang L (2017) Formation of Mo-polypyridine hollow spheres and their conversions to Mo2C/C and Mo2C/C for efficient electrochemical energy storage and catalyst. Small 13

21. Chen W, Pei J, He CT, Wan J, Ren H, Zhu Y, Wang Y, Dong J, Tian S, Cheong WC, Lu S, Zheng L, Yang X, Wu Z, Zhang Z, Chen C, Peng Q, Wang D, Li Y (2017) Rational design of single molybdenum atoms anchored on N-doped carbon for effective hydrogen evolution reaction. Angew Chem Int Ed 56:16086–16090

22. Meng T, Zheng L, Qn J, Zhao D, Cao M (2017) A three-dimensional hierarchically porous Mo2C architecture: salt-template synthesis of a robust electrocatalyst and anode material towards the hydrogen evolution reaction and lithium storage. J Mater Chem A 5

23. Sun X, Jiang J, Yang Y, Shan Y, Gong L, Wang M (2019) Enhancing the performance of Si-based photocathodes for solar hydrogen production in alkaline solution by facilely intercalating a sandwich N-doped carbon nanolayer to the interface of Si and TiO2. ACS Appl Mater Interfaces 11: 19132–19140

24. Fan Z, Ding B, Guo H, Shi M, Zhang Y, Dong S, Zhang T, Dou H, Zhang X (2019) Dual dopamine derived polydopamine coated N-doped porous carbon spheres as a sulfur host for high-performance lithium-sulfur batteries. Chemistry 25:10710–10717

25. Zhang J, Zhang C, Zhao Y, Aminin IS, Zhou H, Liu X, Tang Y, Mu S (2017) Three dimensional few-layer porous carbon nanosheets towards oxygen reduction. Appl Catal B Environ 211:1448–1546

26. Huang Y, Gong Q, Song X, Feng K, Nie K, Zhao F, Wang Y, Zeng M, Zhong J, Li Y (2016) Mo2C nanoparticles dispersed on hierarchical carbon microflowers for efficient electrocatalytic hydrogen evolution. ACS nano 10: 11337–11343

27. Jia J, Xiong T, Zhao L, Wang F, Liu H, Ru Z, Jhou Z, Zhou W, Chen S (2017) Ultrathin N-doped Mo2C nanosheets with exposed active sites as efficient electrocatalyst for hydrogen evolution reactions. ACS nano 11:12509–12518

28. Wang C, Zhang K, Xu H, Du Y, Goh MC (2019) Anchoring gold nanoparticles on poly(3,4-ethylenedioxythiophene) (PEDOT) nanonet as three-dimensional electrocatalysts toward ethanol and 2-propanol oxidation. J Colloid Interface Sci 514:258–268

29. Lu C, Tianca D, Zhang J, Rodri Guez Hernandez FN, Yu Z, Zhuang X, Zhang F, Song Y, Feng X (2017) Molybdenum carbide-embedded nitrogen-doped porous carbon nanosheets as electrocatalysts for water splitting in alkaline media. ACS nano 11:3933–3942

30. Ma R, Zhou Y, Chen Y, Li P, Liu Q, Wang J (2015) Ultrathin molybdenum carbide nanoparticles compositied with carbon as a highly active hydrogen-evolution electrocatalyst. Angew Chem Int Ed 54:14723–14727

31. Wu Z-Y, Hu B-C, Wu P, Liang H-W, Yu Z-L, Lin Y, Zheng Y-R, Li U Z, Yu S-H (2016) Mo2C nanoparticles embedded within bacterial cellulose-derived 3D N-doped carbon fiber networks for efficient hydrogen evolution. NPG Asia Mater 8:e288–e288

32. Shi Z, Nie K, Shao Z-J, Gao B, Lin H, Zhang H, Liu B, Wang Y, Zhang Y, Sun X, Cao X-M, Hu P, Gao Q, Tang Y (2017) Phosphorus-Mo2C@carbon nanowires toward efficient electrochemical hydrogen evolution: composition, structural and electronic regulation. Energy Environ Sci 10: 1262–1271

33. Je D, Qiang W, Huang C, Yao W, Xu Q (2018) Cost Effective Mo Rich Mo2C Electrocatalysts for hydrogen evolution reaction. J Mater Chem A 10:12518–12523

34. Cui W, Cheng N, Liu Q, Ge C, Asiri AM, Sun X (2014) Mo2C nanoparticles decorated graphic carbon sheets: biopolymer-derived solid-state synthesis and application as an efficient electrocatalyst for hydrogen generation. ACS Catal 4:2658–2661

35. Wu HB, Xia BY, Yu L, Yu XY, Lou XW (2015) Porous molybdenum carbide nano-octahedrons synthesized via confined carburization in metal-organic frameworks for efficient hydrogen production. Nat Commun 6:6512

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