

Regular Article

Nitrogen, phosphorus dual-doped molybdenum-carbide/molybdenum-phosphide-@-carbon nanospheres for efficient hydrogen evolution over the whole pH range

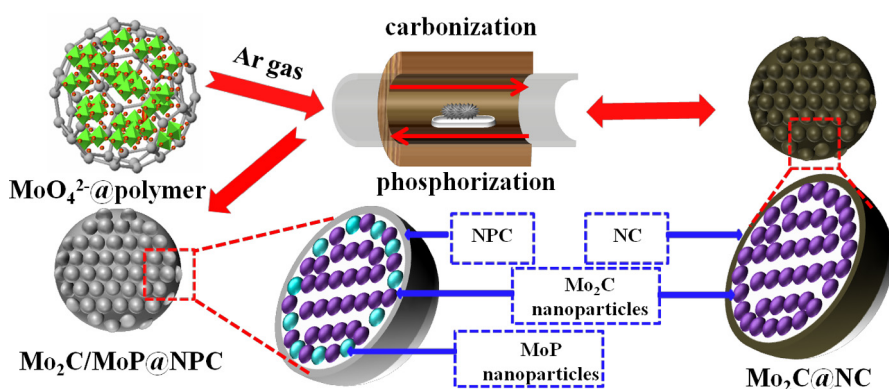


Jing-Qi Chi^a, Wen-Kun Gao^{a,b}, Jia-Hui Lin^{a,b}, Bin Dong^{a,b,*}, Kai-Li Yan^a, Jun-Feng Qin^a, Zi-Zhang Liu^{a,b}, Yong-Ming Chai^a, Chen-Guang Liu^{a,*}

^a State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao 266580, PR China

^b College of Science, China University of Petroleum (East China), Qingdao 266580, PR China

GRAPHICAL ABSTRACT



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ABSTRACT

MoO₄²⁻@aniline-pyrrole (MoO₄²⁻@polymer) spheres as precursors have been used to synthesize unique core-shell nanostructure consisting of molybdenum carbide and molybdenum phosphide composites encapsulated into uniformly dual N, P-doped carbon shells (Mo₂C/MoP@NPC) through a facile two-step strategy. Firstly, porous core-shell N-doped Mo₂C@C (Mo₂C@NC) nanospheres have been synthesized with ultrafine Mo₂C nanoparticles as core and ultrathin NC as shell by an annealing route. Secondly, Mo₂C/MoP@NPC has been obtained maintaining intact spherical-like morphology through a phosphidation reaction in high temperature. The synergistic effect of Mo₂C and MoP may reduce the strong Mo–H bonding energy of pure Mo₂C and provide a fast hydrogen release process. In addition, the dual N, P-doped carbon matrix as shell can not only improve the electroconductivity of catalysts but also prevent the corrosion of Mo₂C/MoP nanoparticles during the electrocatalytic process. When used as HER cathode in acids, the resulting Mo₂C/MoP@NPC shows excellent catalytic activity and durability, which only needs an overpotential of 160 mV to drive 10 mA cm⁻². Moreover, it also exhibits better HER performance in basic and neutral media with the need for overpotentials of only 169 and 228 mV to achieve 10 mA cm⁻², respectively. This inorganic-organic combination of Mo-based catalysts may open up a new way for water-splitting to produce large-scale hydrogen.

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* Corresponding authors at: State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao 266580, PR China (B. Dong).

E-mail addresses: dongbin@upc.edu.cn (B. Dong), cgliu@upc.edu.cn (C.-G. Liu).

1. Introduction

The widespread use of Hydrogen (H_2) has been considered as a promising substitute as energy carrier to replace non-renewable fossil fuels due to its renewability, zero carbon emission and high energy density [1–5]. Water splitting is an effective strategy for the production of highly pure hydrogen, in which highly active electrocatalyst that can decrease the overpotential is demanded to obtain high efficiency [6–11]. As we know, Pt-based electrocatalysts have been considered as the most efficient catalysts because it can produce large cathodic current densities with a nearly zero overpotential. However, the low abundance and high cost of Pt noble metal severely limit its global-scale applications on earth [12–15]. Motivated by this aspect of challenge, developing low-cost and earth-abundant catalysts to replace Pt is urgently needed for large-scale application [16,17].

Transition metal Mo-based alternatives, including Mo_2C [18,19], MoP [20,21], MoN [22] and MoS_2 [23–26] as well as a series of nonmetal N, P-doped carbon materials have been widely developed as effective HER electrocatalyst. To improve the intrinsic activity of Mo-based electrocatalysts especially for representative high active Mo_2C and MoP, two strategies usually has been adopted including designing uniform nanostructures and tuning chemical composition by doping metal or non-metal element [27,28]. To expose more density of surface reactive sites and improve the conductivity of Mo-based electrocatalysts, many efforts have been devoted to construct various nanostructures like nanowires [29], nanosheets [30] and nanoparticles [31] with rich porosity. However, controllable synthesis of nanostructured metal carbides or phosphides with small nanoparticles and rich porosity towards high HER performance still keeps a great challenge, because carbonization or phosphorization at high temperature during synthesis process may lead to inevitable aggregation of Mo-based-compound nanoparticles, thus reducing their exposed active sites and specific surface area [19]. So it is desirable to synthesize well-defined Mo-based-compound nanostructures to avoid sintering and aggregating at high temperature and to expose sufficient active sites for improving the intrinsic HER activity.

It is well known that the hydrogen-binding free energy (ΔG_{H^*}) can serve as a good symbol of the intrinsic activity for HER [32]. The intrinsic activity of pure Mo_2C or MoP is restricted by the strong interaction between active phase and H_{ads} [33]. Metal or non metal doping by tuning chemical composition to produce optimal ΔG_{H^*} is another paramount way to fabricate highly effective HER electrocatalysts [34]. Utilizing the synergistic effect among bimetal compounds, now many efforts have been devoted to the regulation of metal composition, such as NiMoS [35], CoMoS [36], CoMoN [37] and FeCoP [38]. While non metal elements such as N, P and S doping with low electronegativity as a ideal choice to weak Mo–H binding energy is also an alternative method to improve the intrinsic activity for HER, especially for the combination of catalytically active metal carbides and phosphides contributing to a synergistically excellent electrocatalytic activity [17,39]. For example, Li's group synthesized an electrocatalyst composed of MoP and Mo_2C composite coated by few-layer N-doped graphitic carbon shells exhibiting excellent HER performance over the whole range of pH [40]. Although limited progress has been made, such combination is still a great challenge because there exists difficulty to combine carbonization and phosphorization at high temperature. So it is highly desirable to design and fabricate hybrid of Mo_2C /MoP nanostructures to realize optimal Mo–H bonding energy for efficient HER.

Herein, we have designed and synthesized the first composite HER catalyst composed of hybrids of Mo_2C and MoP nanospheres encapsulated into dual N, P-doped carbon matrix by a facile two-

step method. Firstly, the $Mo_2C@NC$ is obtained by the first step of carbonization process with the ultrafine Mo_2C nanoparticles as core and ultrathin NC as shell. Secondly, a second step of phosphorization reaction is adopted to form mixture of Mo_2C and MoP coated by few-layer dual N, P-doped carbon shells. Such composite electrocatalyst exhibits excellent HER performance over the whole pH range with the low overpotential of 160, 169 and 228 mV achieved at a current density of 10 mA cm^{-2} in the acidic, basic and neutral media, respectively.

2. Experimental

2.1. Synthesis of $MoO_4^{2-}@polymer$ nanospheres

All chemicals were used as-obtained without further purification. The organic–inorganic hybrids of $MoO_4^{2-}@polymer$ nanospheres were synthesized in the presence of surfactant as template. In a typical synthesis, 1.98 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 0.12 g Triton X-100 were dispersed in 40 ml deionized water. Then 0.4 g aniline and 0.3 g pyrrole were dropped into the above mixed solution slowly with magnetic stirring for 0.5 h and ultrasonication for 0.5 h to form a homogeneous solution. After that, the aqueous solution of 2 g $(NH_4)_2S_2O_8$ precooled at 0–2 °C for 0.5 h was added into the above aqueous solution in one portion. Then the polymerization reaction was allowed to proceed for 12 h at 0–2 °C. Finally, the obtained sample was washed with ethanol and deionized water for several times and dried under vacuum at 60 °C for 12 h. The synergistic effect between aniline and pyrrole plays critical role for the formation of $MoO_4^{2-}@polymer$ nanospheres. As we know, pyrrole and aniline possess different hydrophobic properties, so aniline and pyrrole comonomers diffuse into different positions of the micelles after adding Triton X-100 template. When oxidation is added, polymerization of pyrrole and aniline occurs at the interface of water and micelle thus forming spherical-like nanostructures, and at the same time MoO_4^{2-} enters into various position of nanospheres to form homogeneous distributed $MoO_4^{2-}@polymer$.

2.2. Synthesis of $Mo_2C@NC$ nanospheres ($Mo_2C@NC$)

The cubic $Mo_2C@NC$ nanospheres were prepared by pyrolyzing above obtained $MoO_4^{2-}@polymer$ nanospheres under argon atmosphere at 650 °C for 3 h with a temperature ramp of 5 °C min^{-1} .

2.3. Synthesis of hybrids of $Mo_2C/MoP@NPC$ nanospheres ($Mo_2C/MoP@NPC$)

To obtain $Mo_2C/MoP@NPC$, the as-prepared $Mo_2C@NC$ (0.1 g) and 2 g of NaH_2PO_2 were put into a porcelain boat and calcined at 750 °C under argon atmosphere for 2 h. During the process of phosphorization, partial Mo_2C or MoO_2 species may be converted into high active MoP, which may be favorable for enhanced HER performance.

2.4. Synthesis of hybrids of N, P co-doped carbon nanospheres (NPC)

To obtain NPC, the polymer nanospheres without adding $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.1 g) and 2 g of NaH_2PO_2 were put into a porcelain boat and calcined at 750 °C under argon atmosphere for 2 h.

2.5. Characterizations

X-ray diffraction (XRD) patterns were collected on a X'Pert PRO MPD system equipped with a $Cu K\alpha$ radiation source ($\lambda = 0.154 \text{ \AA}$).

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