



Porous core-shell N-doped Mo₂C@C nanospheres derived from inorganic-organic hybrid precursors for highly efficient hydrogen evolution



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ABSTRACT

Using inorganic-organic MoO₄²⁻/aniline-pyrrole (MoO₄²⁻-Polymer) hybrids nanospheres as precursors, we synthesize the porous core-shell N-doped Mo₂C@C nanospheres with the three advantages including porous nanostructures, conductive substrate and N-doping, which may maximize the activity of electrocatalysts for hydrogen evolution reaction (HER). The as-prepared Mo₂C@NC has the porous core-shell nanospherical structure with ultrafine Mo₂C nanoparticles as core and ultrathin N-doped carbon (NC) nanolayers as shell. The aniline-pyrrole in MoO₄²⁻-Polymer prevents fast growth and severe aggregation of Mo₂C and form porous structure composed of ultrafine Mo₂C, which implies the more exposed active sites. On the other hand, the carbonization of MoO₄²⁻-Polymer produces the ultrathin N-doped carbon shell on the surface of Mo₂C@NC nanospheres, which can optimize electronic structures and greatly improve charge transfer rate. Through varying MoO₄²⁻ content and carbonization temperature, the optimized Mo₂C@NC sample exhibits enhanced HER performance and long-time stability both in acidic and alkaline solution. It requires an onset potential of only 110 mV and 60 mV, striking kinetic metrics (Tafel slope: 83 mV dec⁻¹ and 70 mV dec⁻¹) in 0.5 M H₂SO₄ and in 1 M KOH, respectively. Therefore, designing unique inorganic-organic hybrid nanostructures may open up a new way for excellent electrocatalysts for HER.

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1. Introduction

The sustainable and clean alternative energy have accumulated wide interests all over the world due to the increasing severe environmental and energy crisis [1–6]. Hydrogen is considered as the most potential alternative to fossil fuel because of its high energy density, renewability and low environmental pollution with zero carbon emission [7–11]. In this regard, electrochemical water splitting (2H₂O → 2H₂ + O₂) utilizing renewable sources such as solar energy and wind provides an environmentally responsible and carbon free method for hydrogen evolution reaction (HER) [12–14]. However, to make this process energy efficient, the development of active and earth-abundant electrocatalysts is of critical importance to realize the mass production of hydrogen from water split-

ting [15–17]. As we all known, platinum (Pt) and its alloys are commonly considered as benchmark catalysts owing to their low overpotential and fast kinetics for HER, however, the prohibitive cost and scarcity of Pt hinders its adoption for large-scale application [18–20]. Therefore, it is highly desirable to design robust, cost-efficient HER and durable catalysts based on earth-abundant materials.

Very recently, Mo-based compounds, such as Mo₂C [21,22], MoN [23] and MoS₂ [24,25] have been adopted as highly-effective HER electrocatalysts owing to their Pt-like electrochemical behaviors with similar d-band states [26]. As one of the most representative carbides, Mo₂C has been highlighted in view of its wide pH applicability, tunable nanostructures and outstanding HER activity [27,28]. Further improving HER activity of pristine Mo₂C requires constructing of various structures such as nanowires [29,30], nanoparticles [31] and nanosheets [32] to expose higher density of surface reactive sites. However, it is not easy to obtain a well-defined porous nanostructure with large surface area because the high reaction temperature often induces extensive

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particle sintering and agglomeration [33,34]. Now most reported Mo_2C nanomaterials and their hybrids are irregular in shape and only limited progress has been made in the preparation of unique molybdenum carbide nanostructures with ultra small crystalline size [35]. For example, Girault et al. synthesized nanoporous molybdenum carbide nanowires as active and stable electrochemical catalyst for HER [29]. Despite the advantage, it is still a challenge to synthesize Mo_2C with small nanocrystallites and desirable porosity to increasingly expose its catalytically active sites and to mitigate aggregation during carbonization process for enhanced HER activity.

The HER electrochemical activity of Mo_2C is intrinsically limited by the large density of empty d-orbitals and the resulting strong H-binding energy, which severely restrict the desorption of adsorbed H to produce H_2 [12,36]. Introducing electron rich dopants is another feasible strategy to accomplish the improved HER activity intrinsically by downshifting the density empty of d-orbitals thus weaken Mo-H binding energy [37,38]. Nonmetallic elements such as N, P and S with low electronegativity as a suitable option has been confirmed to perform enhanced electrochemical activity compared with pristine active sites [32]. For example, Zou et al. reported that carbon atoms adjacent to the N dopants are found to be the most electrocatalytically active sites in $\text{Mo}_2\text{C}@\text{NC}$ [21]. However, it is still tough work to develop a new approach to integrate N source into active phase via a facile “one-pot” method for highly active HER performance.

Based on the above analysis, we herein designed and synthesized porous core-shell-structured N-doped $\text{Mo}_2\text{C}@\text{C}$ nanospheres as highly active electrocatalysts for HER both in acidic and alkaline solution by employing inorganic-organic MoO_4^{2-} -Polymer hybrids with tunable composition as precursors (Fig. 1). The introduction of guest metal species into the polymer host as co-precursor enables easy synthesis of ultrafine Mo_2C nanocrystallites, which are difficult to obtain from a single polymer source. Ultrathin carbon nanolayers formed at high temperature and rich nitrogen sources deriving from aniline and pyrrole prevent the

agglomeration and coalescence of in situ-generated Mo_2C nanocrystallites and improve HER performance intrinsically. Benefiting from the synergistic effect between Mo_2C and N dopants, the as-prepared Mo_2C nanospheres exhibit remarkable electrocatalytic activity for HER in both acidic and alkaline conditions. We investigate the HER performance systemically by varying the MoO_4^{2-} content and carbonization temperature. Remarkably, the as-prepared $\text{Mo}_2\text{C}@\text{NC}$ is in a cubic phase, which is unexpected at a relatively low carbonization temperature of 750 °C exhibiting the best HER performance. It requires a low onset potential of 110 mV and Tafel slope of 83 mV dec^{-1} in 0.5 M H_2SO_4 and onset potential of 60 mV and Tafel slope of 70 mV dec^{-1} in 1 M KOH electrolytes, respectively. The mechanisms of enhancement of $\text{Mo}_2\text{C}@\text{NC}$ -2-750 have been discussed in detail.

2. Experimental section

2.1. Synthesis of MoO_4^{2-} -Polymer spheres

To prepare MoO_4^{2-} -Polymer spheres, 2 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ were dissolved in 60 ml deionized water containing 0.10 g Triton X-100. Then 388 g aniline and 0.290 g pyrrole was slowly dropped into the above mixed solution under stirring for 0.5 h and a strong ultrasonication bath for 0.5 h to form a homogeneous solution. After that, the mixture was maintained at 0 °C for 0.5 h. Then the aqueous solution of containing $(\text{NH}_4)_2\text{S}_2\text{O}_8$ cooled at 0 °C for 0.5 h was added to the above mixture for polymerization for 12 h at 0 °C. Finally, the obtained green product was washed with deionized water and ethanol for several times and dried under vacuum at 60 °C for 24 h. The pyrolyzed spherical-like product was denoted as MoO_4^{2-} -Polymer-2. The coexistence of both aniline and pyrrole in micelles was critical to form the porous spheres. The formation mechanism of spherical-like MoO_4^{2-} -Polymer nanostructures can be explained as follows: firstly, aniline, pyrrole and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ entered into Triton X-100 micelles, and remained at different position of the micelles

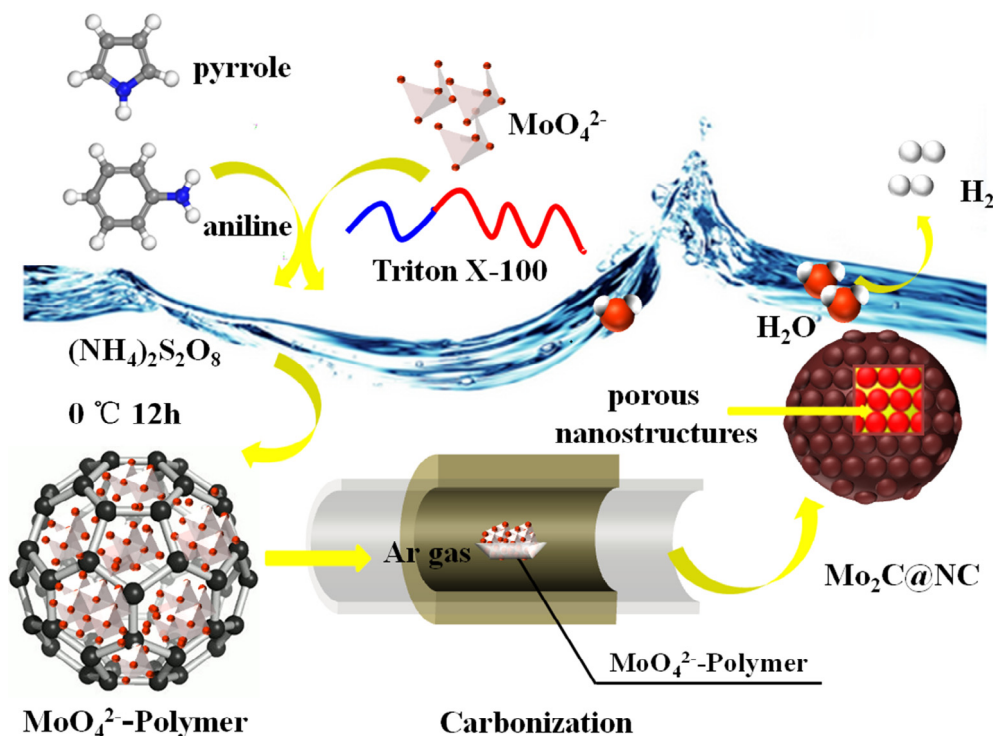


Fig. 1. Schematic illustration of the synthesis process for $\text{Mo}_2\text{C}@\text{NC}$ -2-750.

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