

## Full Length Article

Direct growth of high-content 1T phase MoS<sub>2</sub> film by pulsed laser deposition for hydrogen evolution reaction

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## ABSTRACT

The modified MoS<sub>2</sub>-based material, with a higher conductivity and rich active sites, is promising one of a variety of nonprecious-metal electrocatalysts for hydrogen evolution reaction (HER). Here, the bulk MoS<sub>2</sub> is exfoliated to form small-size MoS<sub>2</sub> clusters by pulse laser, which are diluted in solid sulfur and further to form porous film. The 1T phase MoS<sub>2</sub> ratio in the prepared film was modulated by adding the different content of sulfur into MoS<sub>2</sub> target. Besides, this addition also has an effect on the pore structure of films. Finally, the obtained high-content 1T phase MoS<sub>2</sub> film provides the highly metallic conductivity and more active sites, which results in the more enhanced HER catalytic activity with a lower Tafel slope of 38 mV dec<sup>-1</sup>, a smaller overpotential of 151 mV at 10 mA cm<sup>-2</sup>, compared with the pure MoS<sub>2</sub> film.

## 1. Introduction

Transition metal dichalcogenides (TMDs) have been extensively focused because of their advanced applications in various fields [1–3]. Among TMDs, MoS<sub>2</sub> is abundant in nature as molybdenite, which is emphatically concerned due to its inherent activity for electrochemical hydrogen evolution reaction (HER) [4,5]. However, the intrinsic poor electrical conductivity and a limited density of active sites make bulk MoS<sub>2</sub> show an inferior HER performance. To improve the HER activity of MoS<sub>2</sub>, one route is to expose more active sites, such as the amorphization or the multihole of the MoS<sub>2</sub> [6–10]. For example, Hu et al. prepared a series of amorphous molybdenum sulfide catalysts, which showed the superior HER activity compared with the commercial MoS<sub>2</sub> micro-crystals and single crystalline MoS<sub>2</sub> [11–13]. The other way is to improve the conductivity of MoS<sub>2</sub> materials, which is usually realized by the hybridization of conductive materials with MoS<sub>2</sub>, such as the MoS<sub>2</sub>/graphene materials [14–18]. The 1T phase MoS<sub>2</sub> could combine these two optimized ways to improve the HER activity [19], because it has highly metallic conductivity and more active sites on basal planes than 2H phase [15,20]. But unfortunately, the metallic 1T phase MoS<sub>2</sub> is a metastable state on thermodynamics, and its synthesis is still challenging [21,22]. Top-down and bottom-up approaches have been adopted to obtain the 1T MoS<sub>2</sub> [23]. The bottom-up route usually utilizes the molecular precursors containing Mo and S to prepare the tetragonal MoS<sub>2</sub> [24], while in the top-down process the bulk MoS<sub>2</sub> is cut down to the nanoscale to synthesize 1T MoS<sub>2</sub> [25–27].

Currently, the preparation of nanostructured 1T MoS<sub>2</sub> films by top-down methods involves the exfoliation of bulk 2H-MoS<sub>2</sub> by the intercalation of alkali metal ions or the “broken down” process under foreign force and the stabilization of the formed 1T phase MoS<sub>2</sub> with the help of additive molecules [22]. Pulsed laser deposition (PLD) as one of the physically top-down methods has been demonstrated to be a useful technique for the synthesis of TMDs [28]. The high-energy laser knocks down the bulk MoS<sub>2</sub> target to form the plasma plume as a process of exfoliation, which contains the various small-size MoS<sub>2</sub> clusters and could further condense on the substrate [29–31]. For example, the mixed phase MoS<sub>2</sub> film on the substrate has been successfully prepared by the PLD [32,33]. However, how to stabilize metastable species well in the plasma plume is a problem in the PLD deposition of MoS<sub>2</sub> films.

Herein, a series of mixed targets comprising the sulfur and MoS<sub>2</sub> powder are designed to solve this challenge, in which the labile MoS<sub>2</sub> clusters in PLD process could be stabilized by the vaporized sulfur solvent. The fragmentation of the 2H MoS<sub>2</sub> and more capture of 1T phase MoS<sub>2</sub> are achieved in the obtained MoS<sub>2</sub> film, showing the positive effects of sulfur species on the stabilization of the metastable state. In addition, this operation also introduces the regular pore structure on the films. Finally, the high-content 1T phase MoS<sub>2</sub> film gives the lower overpotential of 151 mV at 10 mA cm<sup>-2</sup> and a small Tafel slope of 38 mV dec<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

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# Pulsed laser deposition of amorphous molybdenum disulfide films for efficient hydrogen evolution reaction

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## ABSTRACT

At high current density during the hydrogen evolution reaction (HER) process, the active layer for most of MoS<sub>2</sub>-based electrocatalysts suffers from pulverizations and easily drops-off due to a high rate of bubble formation and strong stirring. Herein, a facile pulsed laser deposition (PLD) method is used to fabricate amorphous molybdenum disulfide (MoS<sub>2</sub>) films on gold-coated carbon cloth (Au/CC) for HER test. Because of the strong anchoring interaction between MoS<sub>2</sub> catalysts and the Au/CC substrate during the underlying laser ablation process, remarkable stability with 5000 continuous HER cycles has been achieved in the acid media. Furthermore, the as-obtained MoS<sub>2</sub> catalyst shows a small Tafel slope of 48 mV decade<sup>-1</sup>, an onset overpotential of 132 mV and the overpotential of 180 mV at a current density of 10 mA cm<sup>-2</sup>. These results demonstrate that PLD is a very promising technique for making the film electrodes for application in electrocatalytic process.

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## 1. Introduction

Electrochemical or photo-electrochemical water splitting is a sustainable process for the hydrogen production. In electrocatalytic process, the application of efficient catalyst is important to minimize the overpotential and to obtain the higher hydrogen evolution reaction (HER) efficiency [1,2]. Platinum is the best catalysts for the HER, but its scarcity and high cost hinder the large-scale deployment. Therefore, it is necessary to develop the inexpensive HER catalysts with highly active and acid-stable properties. Transition metal dichalcogenides, especially like the molybdenum disulfide (MoS<sub>2</sub>), have emerged as efficient catalysts for the HER in acidic media. The first work about the MoS<sub>2</sub> HER catalyst could be dated to 2005, and the authors used the graphite to support the nano-scale MoS<sub>2</sub> [3]. Two years later, Jaramillo et al. proved that the edge site provided the active site for 2H MoS<sub>2</sub> [4]. After that, substantially excellent work has been devoted to increase the concentration of exposed edges of MoS<sub>2</sub> catalysts [5–7]. Even so, the understanding and optimization of the MoS<sub>2</sub> catalytic properties are still attractive from theoretical prediction to experimental

investigation [8]. To obtain the higher HER catalytic activity of MoS<sub>2</sub>, some important aspects are focused currently, including 1) increasing the active sites, 2) improving the conductivity, 3) tuning the crystals structure [9].

Pulsed laser deposition (PLD), a way of patterning a very diverse range of materials, is widely used in the areas of thin film deposition and multi-layer research [10]. By ablating various target materials and altering the deposition condition, a stoichiometric and high quality film could be obtained [11]. Using this method, various materials, such as iron oxide, cobalt oxide and porous nitrogen doped-carbon supported cobalt thin films, have been prepared and demonstrated the excellent catalytic activity in different aspects due to the more exposed active sites of the catalysts [12–15]. In addition, the crystal few-layer MoS<sub>2</sub> films grown on different substrates have also been achieved in literature, which shows many advantages in various applications [16–18]. Because the PLD process is non-equilibrium in thermodynamics, the amorphous MoS<sub>2</sub> film obtained by this technique is promising to expose more active sites and further shows high HER performance. Moreover, as the physical deposition technique, the PLD also has the superiority to achieve the multilayer deposition with different species in the same substrate, which is very useful to engineer the interface structure.

Theoretical and experimental studies have suggested that the choice of substrate is crucial in determining the HER activity of MoS<sub>2</sub> [19,20]. Selecting the suitable support and engineering better

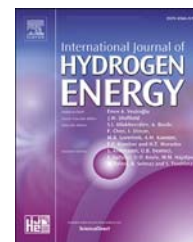
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# MOF-derived cobalt-embedded nitrogen-doped mesoporous carbon leaf for efficient hydrogen evolution reaction in both acidic and alkaline media

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## ABSTRACT

Metal-embedded nitrogen-doped carbon materials have been proposed as novel hydrogen evolution reaction (HER) catalysts to replace platinum-based materials, while these alternatives usually exhibit low activity and gradual deactivation during their use. Here, leaf-like cobalt-embedded nitrogen-doped porous carbon sheet (Co-NC) for the HER is obtained by simple pyrolysis of a two-dimensional metal organic framework. The Co-NC annealed at 800 °C exhibits large surface area and the active metallic cobalt species embedded in the N-doped carbon layers, which leads to the lower overpotential, higher current density, and superior durability in alkaline media. However, the Co-NC annealed at 600 °C shows abundant nitrogen-coordinated cobalt species, which favors the high HER activity under acidic condition. These structural properties of the Co-NC enable the efficient HER activity by increasing the active sites and enhancing mass transfer of water molecules or protons at the interface where the reaction takes place.

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## Introduction

Hydrogen, with the low weight and highest gravimetric energy density, has been recognized as a promising and sustainable fuel in the future [1,2]. Hydrogen evolution reaction (HER) is a clean and effective process to obtain the high-purity hydrogen fuel [3]. The Pt-group metals are the state-of-the-art electrocatalysts for HER. However, the high cost and low abundance of Pt metal severely impede their large-scale industrial application, and the low-cost catalysts with the high electrocatalytic activity are imperative to develop the hydrogen energy [4].

A variety of non-noble HER electrocatalysts, including heteroatom doped carbon materials [5–7], transition metal alloys [8], carbides [9,10], sulfides [11], and phosphide [12], have been extensively studied because of their high catalytic activity, selectivity, and excellent durability. Among them, the N-doped carbon materials combined with metal species (M-NC) have been regarded as a promising representative due to their low-cost, high efficiency and excellent chemical stability in both acidic and alkaline mediums [13]. For example, by annealing the mixture of dicyandiamide and  $\text{CoCl}_2$ , Asefa et al. obtained the cobalt embedded nitrogen-rich carbon nanotube (Co-NRCNT) as the HER catalyst. The N dopants or N

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# Tuning the active sites in the cobalt-based nitrogen-doped carbon by zinc for enhancing hydrogen evolution reaction



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## ABSTRACT

The cobalt-embedded nitrogen-doped carbon is an attractive alternative to platinum-based catalysts for hydrogen evolution reaction (HER) due to their abundant active sites and excellent durability. In the present paper, a leaf-like zinc and cobalt-based bimetallic metal-organic framework is used to prepare the nitrogen-doped porous carbon sheet (ZnCo-NC). The introduction of Zn in the metal organic framework precursors ensures the uniform and dense distribution of cobalt nanoparticles in the final carbon structure, which reserves the prime active sites, nitrogen-coordinated cobalt (Co-N<sub>x</sub>) and active metallic cobalt species embedded in the N-doped carbon layers (Co@NC), in the catalysts. The Co-N<sub>x</sub> and Co@NC sites are found to be enriched in the ZnCo-NC, and the larger surface area and abundant pores on it further accelerate the mass transfer process, which are beneficial for enhancing HER performance of catalysts in acidic and alkaline media.

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## 1. Introduction

Hydrogen, as a green energy carrier, is a promising alternative in the future energy supply system [1]. Hydrogen evolution reaction (HER) through the electrochemical water splitting is an attractive technology by developing highly efficient electrocatalysts [2]. Particularly, exploration of the non-precious catalysts is the main task due to the low-abundance and high-cost platinum-based catalysts [3].

Metal embedded nitrogen-doped carbon material, derived from the metal organic frameworks (MOFs), is an ideal one in various non-precious catalysts because of their structural controllability and designability [4–7]. More specifically, the cobalt embedded nitrogen-doped carbon material (Co-NC) with plentiful active sites by the pyrolysis of the cobalt-based MOFs has shown the intrinsic electrochemical activity [8–10]. In the Co-NC catalyst, the Co-N<sub>x</sub> site [11–13], metallic cobalt nanoparticle coated by the carbon shell [14–18], and the N-doped carbon layer [19,20] have been validated as the active sites for the formation of adsorption hydrogen atom. The precise construction of Co-NC structure provides us an opportunity to obtain these sites [21]. In general, the regular morphology and the larger surface area with the uniform pore

distribution could guarantee the more exposure of the active sites and more fluent diffusion of the reaction species [22–24]. Unfortunately, the control of Co-NC structure seems to have some difficulties. For example, the collapse of the physical structure usually happens in the high-temperature pyrolysis of the single metal MOFs precursors, which inevitably hinders the improvement of the catalytic performance of the final catalysts [25]. In addition, the uncertain change of the pore structure also decreases the advantages of the Co-NC [26,27].

The introduction of inactive Zn into Co-based MOFs is an effective method to adjust the structure of Co-NC. The Zn-based imidazole frameworks with a similar topology as that of Co-based one could afford a high surface area and high N content for the final carbon, having been utilized to design the Co-NC structures in oxygen evolution/reduction systems [28,29]. Furthermore, the volatile Zn at high temperature is easily removed and could restrict the agglomeration of Co species, ensuring the uniformly spatial dispersion of metal-based active sites in NC matrices [30]. These inspired us to expand the potential roles of Zn in developing Co-NC catalysts with high HER activity.

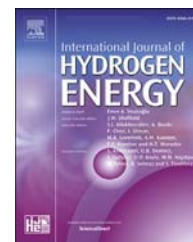
Herein, based on the leaf-like Co-MOFs, we explored the structure of the Co-NC catalysts on the HER process by introducing the zinc to the MOFs precursor. It could be found that the final ZnCo-NC has more cobalt nanoparticles on the N-doped carbon layers which provide abundant active sites, because the Zn species effectively inhibits the agglomeration of Co during high

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# Hierarchical molybdenum carbide/N-doped carbon as efficient electrocatalyst for hydrogen evolution reaction in alkaline solution

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## ABSTRACT

Development of highly-active and noble-metal-free electrocatalysts for hydrogen evolution reaction (HER) is of critical challenge for water splitting, and optimizing the structure and the composition of the relative materials is very necessary to obtain the high-quality catalysts. Herein, a novel molybdenum carbide/N-doped carbon (Mo<sub>2</sub>C/NC) hybrid is fabricated by using the hierarchical polyaniline tube network as a carbon source and a reactive template, and the as-fabricated Mo<sub>2</sub>C/NC hybrid possesses a uniform hierarchical tube structure. The coupling of the ultrafine Mo<sub>2</sub>C nanoparticles and the N-doped carbon substrate provides the abundant active sites and accelerates the charge transfer process. The final Mo<sub>2</sub>C/NC catalyst gives the excellent catalytic activity for HER in alkaline condition, which shows a lower overpotential of 142 mV at 10 mA cm<sup>-2</sup> and a small Tafel slope of 61 mV decade<sup>-1</sup> in 1 M KOH.

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## Introduction

Hydrogen (H<sub>2</sub>) is a sustainable and renewable energy resource because of its high energy density and the clean nature [1,2]. However, current industrial production of H<sub>2</sub> always involves fossil fuels, which inevitably produce greenhouse gases under most conditions [3]. Water splitting by electrolysis to generate hydrogen has attracted much attention since the production process of H<sub>2</sub> from water is relatively simple and environmental friendly [2,4,5]. Hydrogen evolution reaction (HER) is a half-reaction of water electrolysis, in which platinum is the most active and catalytically stable catalyst; however, its scarcity and high cost make it impractical for global-scale

applications [4]. Therefore, the search of platinum-free electrocatalysts, based on transition-metal elements (such as Fe, Co, Ni and Mo, W)-based materials, is particularly important for the development of hydrogen energy [6–10].

Transition-metal carbides are potential substitutes for platinum because of their low cost, high catalytic activity, selectivity, and good electrochemical stability under rigorous conditions [11]. Among carbide-based hydrogen evolution catalysts, molybdenum carbide is considered to be a promising one due to its “platinum-like” d-band structure and encouraging HER catalytic activity [12]. However, bare molybdenum carbide particles possess some drawbacks, such as poor process ability and easy aggregation. In order to enhance

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