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Article

Hierarchical CoSeS nanostructures assisted by Nb doping for enhanced hydrogen evolution reaction

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ABSTRACT

Metal doping for active sites exhibits remarkable potential for improving the hydrogen evolution reaction (HER). Multi-doping and the use of a conductive substrate can further modulate catalytic performance. Herein, Nb-CoSe well dispersed in N-doped carbon nanospheres (NCs, Nb-CoSe@NC) was synthesized to serve as a conductive substrate and facilitated good dispersion of active sites for the HER. Nb doping can also change the electronic structure of CoSe, which facilitates the activity for the HER. In order to further improve the conductivity and intrinsic activity of Nb-CoSe@NC, dual, nonmetal doping was realized through gas sulfurization to prepare hierarchical Nb-CoSeS@NC. The prepared Nb-CoSeS@NC, with a core-shell structure, exhibited a low overpotential of 115 mV at 10 mA cm⁻², which is smaller than that of the most doped catalysts. In addition, NCs not only improved the dispersion and conductivity of the catalyst but also prevented metal corrosion in an electrolyte, thus facilitating the long-term stability of Nb-CoSeS@NC. Moreover, the synergistic effect of the multi-doping of Nb, S, and Se was explained. This work provides a promising, multi-doping strategy for the large-scale application of transition-metal-based electrocatalysts for the HER.

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1. Introduction

The population growth and the current energy crisis necessitate the development a new, abundant energy source independent of fossil fuels. To this end, hydrogen is considered as ideal because it is a non-toxic, secondary energy source with the characteristics of high calorific value and rich content [1–3]. Water splitting is a green and potential method to produce hydrogen, and its realization paths, including photocatalysis and electrocatalysis, all have attractive properties [4–7]. Although the electrocatalytic process is remarkable for its high efficiency and environmental friendliness, it exhibits sluggishness and low efficiency of anode and cathode reactions [8,9]. Therefore, it is imperative to develop green and economical catalysts to improve the efficiency of the hydrogen evolution reaction (HER) as much as possible [10].

At present, Pt is advantageous under acidic conditions; however, considering its high price, the cost of hydrogen production would considerably increase, hindering any large-scale, industrial development [11]. Although scientists have been

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committed to the research and development of non-precious-metal-based electrocatalysts, the results are not satisfactory because of the corrosion and oxidation of metal catalysts, such as cobalt, iron, nickel, and molybdenum [12]. The conductive carbon shells may be an effective solution to this problem. In contrast, nonmetals, such as N, P, S, Se, and B, which can regulate the electronic configuration of catalysts on the atomic scale, have great potential as catalysts in the field of electrocatalysis. Moreover, considering that the co-doping of multiple heteroatoms with synergistic effects is superior to single-atom doping [13], attempts have been devoted to investigate bi-nonmetal-doped HER catalysts in recent years. For example, Wang's group generated pyrite-structured, cobalt sulfide nanoparticles on carbon nanotubes that exhibited high HER activity and stability [14]; S and P co-doping was key to the excellent catalytic performance. Similarly, the nanoscale Ni(Fe)PS₃ developed by Jin and colleagues showed high activity for hydrogen and oxygen evolution reactions [15].

Moreover, the doping of S and Se gradually manifested fascinating properties, which opened up a new, valuable strategy for the enhancement of HER efficiency. Suib *et al.* [16] performed selenization reactions on cobalt sulfide microspheres for an acidic HER, achieving an overpotential of 160 mV at 100 mA cm⁻². Furthermore, the peapod-like Co(S_xSe_{1-x})₂ reported by Wang *et al.* [17] showed persistent activity for water splitting, benefiting from the improved electron conductivity and enlarged surface areas. Moreover, S may offer more marginal active sites to CoSe_x and improve its HER performance. Considering its unique catalytic properties, cobalt selenide has not been extensively researched; thus, it is necessary to investigate CoSe to maximize its activity.

In addition, Nb₂O₅ and NbS₂ have attracted research attention because of the absence of an electron in the D-band of Nb. For instance, Wang *et al.* [18] reported a highly active 2H-Nb_{1+x}S₂ catalyst for the HER, whose current density reached 5000 mA cm⁻² at 420 mV. However, because of limited synthesis conditions, poor chemical stability, and dense structure, the development of Nb catalysts has been considerably hindered [19]. Encouragingly, however, the integration of Nb and CoSeS may lead to promising results. It has been shown that catalytic performance can be significantly improved by combining catalysts with conductive substrates, such as carbon nanospheres, which can promote electron transport and catalyst dispersion [20–22]. At the same time, the synergistic electronic effect between them may improve intrinsic activity of the composite catalysts [23,24]. Therefore, Nb-doped CoSeS composite structures coupled with carbon nanospheres can effectively boost HER performance. However, the development of such catalysts has not been widely investigated thus far.

Herein, we have proposed a multi-doping strategy for hierarchical composites for the HER, encapsulating Nb and CoSeS into N-doped carbon nanospheres (NCs). Scheme 1 demonstrates the complete synthetic process for Nb-CoSeS@NC. Firstly, the well-defined NCs were synthesized from polymer nanospheres at high temperature, which can ensure effective contact between the active sites and the electrolyte. Secondly, well-dispersed Nb-CoSe@NC was realized by a hydrothermal

Scheme 1. Synthetic process for Nb-CoSeS@NC.

reaction. Thirdly, the nonmetal doping was achieved by subsequent gas sulfurization, yielding hierarchical Nb-CoSeS@NC electrocatalysts. The synergistic effect among the multi-doped elements as well as the presence of well-dispersed Nb-CoSeS and the carbon substrate, which can resist harsh conditions, facilitate high HER activity. The prepared catalyst showed a low overpotential and long-term stability under acidic conditions.

2. Experimental

2.1. Synthesis of polymer nanospheres

N-doped polymer nanospheres were synthesized according to previously reported methods [25]. The specific process was as follows. First, 0.76 mL of aniline and 0.6 mL of pyrrole were added to 120 mL of deionized water containing 0.2 g of TritonX-100, and then the mixture was stirred for 30 min followed by ultrasonic treatment. During this period, the 20 mL of aqueous solution containing 2.0 g of (NH₄)₂S₂O₈ was precooled at about 0 °C for 30 min, and then poured into the above solution at 0–2 °C for 12 h. Finally, the black polymer nanospheres were dried under vacuum at 60 °C after washing several times with deionized water.

2.2. Synthesis of NCs

The polymer nanoparticles were annealed at 900 °C for 6 h under an argon atmosphere with a heating rate of 5 °C min⁻¹. The resulting samples were denoted as NCs.

2.3. Synthesis of Nb-CoSe@NC

Nb-CoSe@NC was synthesized by a hydrothermal reaction. In a typical synthesis process, 15 mL of (CH₂OH)₂ and 15 mL of *N,N'*-dimethylformamide (DMF) were mixed thoroughly, and 0.25 g of Co(Ac)₂·4H₂O and 0.1 g of Nb powder were added sequentially. The liquid mixture was stirred for 30 min before adding 0.08 g of selenium powder and 0.035 g of NCs. After agitation and ultrasonic treatment, the obtained black solution was transferred to a 50 mL Teflon-lined autoclave and heated at 200 °C for 12 h. When the reaction kettle was cooled to room temperature, the solids were washed with ion water and ethanol and were dried at 60 °C.

2.4. Synthesis of Nb-CoSeS@NC

The dried Nb-CoSe@NC was cured under a H₂S atmosphere in an alumina combustion boat at 400 °C for 2 h with a heating rate of 2 °C min⁻¹.

2.5. Synthesis of CoSeS@NC

The synthesis of Nb-free CoSe@NC and CoSeS@NC were performed using the same method that produced Nb-CoSeS@NC but without the niobium source.

All characterization and electrochemical measurements can be seen in the supporting information.

3. Results and discussion

The phase composition and crystal structure of the catalyst samples, including CoSe@NC, CoSeS@NC, Nb-CoSe@NC, and Nb-CoSeS@NC, were characterized by X-ray diffraction (XRD). The peaks of amorphous carbon can be observed at approximately 26° in the diffraction pattern of the NCs (Fig. S1(a)). The amorphous carbon guaranteed the presence of defects, which have been reported to regulate the charge of carbon materials and exhibit unusual electronic properties compared to ordered graphite carbon atoms [26]. As shown in Fig. 1, the characteristic peaks of Co₉Se₈ and CoSe were observed in all four catalyst samples. Moreover, the incorporation of Nb caused a peak shift to higher angles, indicating the reduction of the unit cell volume and the successful doping of Nb. After sulfurization, there were significant, new peaks at 35.1°, 46.6°, and 54° that can be well indexed to the (101), (102), and (110) planes of CoS (JCPDS 01-070-2864), respectively. The low electronegativity of S may change the electronic structure of the active center and increase the utilization of the metal atoms. In addition, the synergistic effect between the active center and S can significantly improve the catalytic performance [27]. Another interesting phenomenon was that the corresponding diffraction peaks after Nb doping or sulfurization became diffused and their intensity decreased, especially for Co₉Se₈. Furthermore, Raman spectra (Fig. S1(b)) demonstrated the disordered state of the NCs. The ratio of the strength of the D-band (1350 cm⁻¹) to that of the G-band (1580 cm⁻¹) of graphite carbon was about 1.05,

Fig. 1. XRD patterns of CoSe@NC, CoSeS@NC, Nb-CoSe@NC, and Nb-CoSeS@NC.

which indicates that the NCs possess considerable defects that are favorable for electron transfer [28]. Hence, the carbon substrate and the subsequent Nb and S dual-doping are crucial for achieving high conductivity.

X-ray photoelectron spectroscopy (XPS) revealed the surface chemical properties of Nb-CoSeS@NC, including elemental composition and chemical states. As shown in Fig. S2(a), the full XPS spectrum further indicates the presence of Nb, Co, Se, S, N, C, and O, in accordance with the energy-dispersive X-ray spectroscopy (EDS) mapping. Specifically, in the Nb 3d region spectrum (Fig. 2(a)), the peaks at 207.6 and 210.3 eV are assigned to Nb⁵⁺ 3d_{5/2} and Nb⁵⁺ 3d_{3/2} of Nb₂O₅, respectively, which is due to the oxidation on the catalyst surface. The peaks at 207.1 and 203.6 eV are derived from Nb⁴⁺ 3d_{5/2} and Nb⁴⁺ 3d_{3/2} [29]. Furthermore, the S 2p_{1/2} signal at 163 eV indicates that the sample surface contains some S²⁻, confirming the formation of a metal-sulfide phase. The additional peak of S–O at 168.2 eV may also be due to oxidation (Fig. 2(b)). The XPS spectrum of Co (Fig. S2(b)) contains six peaks, including two satellite peaks at 803.3 and 774.5 eV. The Co 2p electrons yield a peak at 778.6 eV that is consistent with that by the Co metal. Meanwhile, the peak located around 781.0 eV can be assigned to the Co–S band in the hybrid Nb-CoSeS@NC [30–32]. In addition, with the doping of Nb, the Co 2p peak shifted to a lower binding energy (Fig. 2(c)), indicating that the electron cloud density of Co increased. Moreover, the Se 3d_{5/2} and Se 3d_{3/2} peaks shifted to higher binding energies, which was related to the increase in the Se valence state (Fig. 2(d)). These changes in the oxidation states of Co and Se result from the electronegativity difference. Reasonably, it can be concluded that the incorporation of Nb leads to stronger electron interactions [33]. Figure S2(d) shows the C 1s spectrum, where the peak at 285.1 eV is attributed to sp²-hybridized graphitic carbon atoms [34], indicating that most of the carbon atoms are in a conjugated, honeycomb lattice [35]. The other peaks at 286 and 284.6 eV correspond to C–N and carbide species, respectively. In the N 1s region (Fig. S2(e)), the peaks at 397.9, 400.9, and 401.9 eV belong to graphitic N, pyrrolic N, and pyridinic N, respectively [36]. Nitrogen atoms, especially pyrrolic N, have high affinity potential for Co and Nb; thus, they produce significant synergistic effects at the interface, which is crucial to the elevation of the electrocatalytic performance [37]. The peaks in the O 1s region at 531.5 and 532.3 eV are attributed to Nb–O and Nb–N–O, respectively (Fig. S2(f)). The O signal may be caused by oxygen contamination of the sample owing to the calcination-hydrothermal reaction [38,39].

The detailed morphology of all obtained samples was further characterized by scanning electronic microscopy (SEM). As shown in Figs. 3(a)–(b), the spherical structure of the polymer did not collapse after high-temperature carbonization, and no obvious agglomeration or fragmentation was observed throughout the hydrothermal treatment. As the substrate, the robust NCs caused the metal particles to more evenly dispersed and significantly reduced metal corrosion in the electrolyte. Obviously, the Nb-CoSe@NC and Nb-CoSeS@NC composites were both uniform spheres with diameters of about 120 nm (Figs. 3(c)–(d)). Constructing NC nanostructures was an effec-

Fig. 2. Characterization of Nb-CoSeS@NC. XPS spectra of Nb 3d (a) and S 2p (b) regions of Nb-CoSeS@NC and Co 2p (c) and Se 3d (d) regions of CoSeS@NC and Nb-CoSeS@NC.

tive method for increasing the areal density of the active sites [40]. In contrast, the wrinkles on the sample surface also increased the number of available sites, thus improving the overall electrocatalytic performance. The surfaces of CoSeS@NC and Nb-CoSeS@NC were rougher after sulfurization, which may explain their increased catalytic activity for the HER. More details will be described below.

Transmission electron microscopy (TEM) images more clearly showed the hierarchical, hollow, rough, and spherical morphology of Nb-CoSe@NC and Nb-CoSeS@NC with shell

layers of around 30 nm (Figs. 4(a)–(c)). The well-dispersed Nb and CoSeS were encapsulated in the NC substrate, facilitating a large electrochemical contact area and inducing rapid mass transfer. In the supporting information, Fig. S4 revealed the slight agglomeration of metal nanocrystals in CoSe@NC, CoSeS@NC, and Nb-CoSe@NC. More details about the crystal phase of the samples were provided by high-resolution TEM images. For CoSeS@NC, in Fig. S4(g), the crystal lattice fringe can be observed with a lattice spacing of 0.169 nm, corresponding to the lattice distance of the (110) planes of CoS. As

Fig. 3. Scanning electron microscopy images of polymer nanospheres (a), NCs (b), Nb-CoSe@NC (c), and Nb-CoSeS@NC (d).

Fig. 4. TEM images of Nb-CoSe@NC (a), Nb-CoSeS@NC (b,c); (d) HRTEM images of Nb-CoSeS@NC.

Fig. 5. SEM mapping of Nb-CoSeS@NC.

shown in Fig. 4(d), Nb-CoSeS@NC was composed of four main crystal phases, consisting of the (101) crystal plane (0.254 nm) of CoSe, the (440) crystal plane (0.184 nm) of Co₉Se₈, the (110) crystal plane of CoS (0.169 nm), and the (220) crystal plane (0.239 nm) of NbCo₂, which are consistent with the XRD patterns. Moreover, compared with Nb-CoSe@NC (Fig. S4), the CoSe lattice spacing of Nb-CoSeS@NC remained unchanged, while the (222) plane of Co₉Se₈ decreased from 0.301 to 0.184 nm [37], which may be more evidence of the reduction of the Nb-CoSeS@NC cell volume. Combined with above results, specific defects and disorder caused by multi-doping may facilitate the adsorption of H and promote the HER.

Further, SEM mapping and EDS of Nb-CoSeS@NC showed the homogenous distribution of Nb, Co, Se, S, N, C, and O elements, as well as their corresponding content (Figs. 5 and S5), revealing the successful doping and good dispersion of Nb.

In order to evaluate the HER activity of all the catalysts, electrochemical measurements were carried out with a standard three-electrode cell configuration in 0.5 M H₂SO₄ under the same conditions. The linear sweep voltammetry (LSV) curves in Fig. 6 showed that 20% Pt/C exhibited extremely low overpotentials of 48 mV at 10 mA cm⁻² and 66 mV at 200 mA cm⁻². The higher overpotential of Nb-CoSe@NC illustrated that the introduction of the S source was beneficial to HER activity. This

Fig. 6. HER performance of NC, CoSe@NC, CoSeS@NC, Nb-CoSe@NC, and Nb-CoSeS@NC. (a) IR-corrected LSV curves; (b) Tafel plots; (c) Nyquist plots (d) determined double-layer capacitance values.

Fig. 7. Stability results of Nb-CoSeS@NC in 0.5 M H₂SO₄. (a) Chronoamperometry at a constant potential of -0.16 V vs RHE; (b) polarization curves before and after 1000 CV sweeps.

can be attributed to the fact that S would change the spin density, charge distribution, and valence orbital energy level of nearby carbon atoms, thereby activating the carbon atoms and making them active sites [41]. For comparison, CoSeS@NC was also synthesized, and after the introduction of Nb, its HER performance considerably elevated, which was possibly because Nb re-regulated the distribution of the electron cloud, thus enhancing electron interactions and intrinsic conductivity. Notably, Nb-CoSeS@NC showed the lowest overpotential of all samples, 115 mV at 10 mA cm^{-2} and 240 mV at 200 mA cm^{-2} , which are also higher than those of the majority of other doped electrocatalysts (Table S1). S and Se anions are good proton-acceptor sites, while Nb and Co cations can form hydride-acceptor centers, which perhaps weaken S and Se hydrogen bonds and promote the formation of H–H bonds. Therefore, the multi-doped elements synergistically boost the HER process.

It is difficult to elucidate the exact working mechanism of different HER electrocatalysts. However, the Tafel slope can often be used as an indicator of the rate-determining step and can provide some valuable insight into possible reaction pathways. The Tafel slope of 20% Pt/C was 29 mV dec^{-1} (Fig. 6(b)), consistent with previous reports [42]. The Tafel slope of 43 mV dec^{-1} for Nb-CoSeS@NC shows that the electrocatalytic process conforms to the Volmer-Heyrovsky mechanism in which the rate-determining step is electrochemical desorption [43]. Electrochemical impedance spectroscopy is recommended to determine the charge transmission characteristics of electrocatalysts during the reaction (the equivalent circuit is illustrated in Fig. 6(c)). Compared with all other samples, Nb-CoSeS@NC had the lowest R_{ct} value, suggesting that it had higher conductivity and faster electron transmission. The acceptable reason may be that the electron interactions between sulfide and the NCs facilitated the charge transfer and accelerated hydrogen production. In addition, the modified NC substrate's conductivity and active sites benefited from the electronegativity difference between N and C. The double-layer capacitance (C_{dl}) values were calculated from cyclic voltammetry (CV) curves with different scanning rates, which served as an effective method for measuring the electrochemically active surface area. The C_{dl} of Nb-CoSeS@NC was 5.7 mF cm^{-2} , higher than that of the other

samples (Fig. 6(d)). The large active surface area resulted from the well-defined, porous core-shell structure and the rough surface of Nb-CoSeS@NC. It is necessary to assess the stability of catalysts to further evaluate their performance. The chronoamperometry results in Fig. 7(a) showed no obvious reduction in current density of Nb-CoSeS@NC over 12 h. Moreover, the overpotential at 200 mA cm^{-2} only increased by 4 mV with 1000 CV sweeps (Fig. 7(b)). Furthermore, after CV characterization, the morphology of Nb-CoSeS@NC was still well maintained (Fig. S7). These results all indicate the excellent HER activity and long-term durability of hierarchical Nb-CoSeS@NC, owing to the robust structure of the NC substrate together with multi-element doping.

4. Conclusions

In conclusion, through a simple hydrothermal reaction followed by gas sulfurization, Nb-assisted hierarchical Nb-CoSeS@NC nanostructures encapsulated in NCs were successfully synthesized. The characterization and property tests indicated that Nb-CoSeS@NC was a highly active and stable electrocatalyst with a rough surface. The high HER activity of Nb-CoSeS@NC was attributed to the synergistic effects between CoSeS and Nb metal, the reasonable, hierarchical structure design, and the strong binding force between the N-doped carbon substrate and the metal ions. This force endowed the Nb-CoSeS with higher dispersion, and the electron coupling between the substrate and metal ions synergistically improved the intrinsic catalyst activity. In particular, for Nb-CoSeS@NC, synergistic effects among Nb, S, and Se were observed and analyzed. This work provides a favorable platform and reference for future research on multi-doped, transition-metal-based electrocatalysts for HER processes.

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Graphical Abstract

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Hierarchical CoSeS nanostructures assisted by Nb doping for enhanced hydrogen evolution reaction

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Nb-CoSe well dispersed in NCs (Nb-CoSe@NC) was synthesized through a hydrothermal reaction and facilitated good dispersion of the active sites. Se and S doping further improved the excellent HER activity of Nb-CoSeS@NC.

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Nb掺杂调控CoSeS多级纳米结构用于增强析氢反应

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摘要: 电催化析氢(HER)是清洁制氢的一种有效途径, 对于氢经济和氢能产业的发展具有重要意义。金属掺杂是提高电催化剂本征活性的有效方法, 导电基底的采用也有利于电荷传输和催化性能的整体提高。尽管已有关于硒化物作为HER催化剂的相关报道, 但是合成条件有限、导电性、本征活性的影响, 其电催化性能仍有提升的空间。此外, 在酸性电解液中的腐蚀和氧化极大限制了催化剂性能的发挥。基于此, 本文以氮掺杂碳球为载体, 采用金属Nb掺杂、非金属硫硒化物协同以及表面碳包覆的三重策略, 将掺杂元素Nb和活性位中心元素Co封装到氮掺杂碳纳米球内并进行连续的硫化反应, 成功构筑多级纳米结构(Nb-CoSeS@NC)以提高其电催化析氢性能。碳球可为活性位的生长和分散提供足够的空间, 同时有效防止活性金属的腐蚀和分解, 并阻止金属纳米颗粒的团聚。硫化过程实现了非金属硫元素的掺杂, 对于提高硒化物的催化活性和导电性都有重要作用。通过扫描电镜(SEM)、透射电镜(TEM)、X射线衍射(XRD)、拉曼光谱、X射线光电子能谱(XPS)及电催化性能测试, 详细研究了Nb-CoSeS@NC独特的纳米结构和电催化制氢性能, 并分析了构效关系。

XRD结果发现, 引入Nb后Co₉Se₈和CoSe的特征峰移向更高的角度, 表明其晶格体积的减小, 有助于电荷传输。同时, 氮掺杂碳球(NC)在26°可以观察到无定型碳的峰, 而石墨碳的D带和G带强度比约为1.05, 均表明NC中缺陷的存在, 这可以进一步提高碳材料的导电性。SEM和TEM表征显示, 催化剂为直径120 nm的均匀的纳米核壳结构, 壳层约为30 nm, 无明显的团聚和破碎, 这是催化剂具有高稳定性的重要原因。表面的褶皱保证了大的活性比表面积, 可以大大增加活性位点的数量。同时, 催化剂与NC之间的紧密结合可以降低电子传输的阻抗进而改善其稳定性和析氢性能。分析高分辨率的TEM结果发现, Nb掺杂后, Nb-CoSeS@NC中Co₉Se₈的(222)晶面由0.301 nm减小至0.184 nm, 与XRD结果相符。XPS表征揭示了引入Nb之后的电子效应。与CoSeS@NC相比, Nb的掺杂使Co 2p向更低的结合能移动, 而Se 3d则移向高结合能移动, 这是由于Nb导致了更强的电子相互作用。在0.5 M的H₂SO₄中测试催化剂的析氢性能, Nb-CoSeS@NC仅需115 mV的过电位便可以实现10 mA cm⁻²的电流密度, Tafel斜率为43 mV dec⁻¹, 优于CoSeS@NC等其他对比样品, 且优于大多数掺杂型硒化物电催化剂。经过12 h稳定性测试, 电流密度未见明显降低, 表明该多级结构催化剂的优异稳定性。

Nb-CoSeS@NC提高活性可归因为Nb的掺杂增强了催化剂的电子相互作用, 有助于提高的本征导电性。Nb、Co正离子可以形成氢化物-受体中心, 可能会削弱S-H键和Se-H键, 并促进H-H键的形成, 因此, 多元掺杂产生的协同效应可以有效促进HER过程。此外, 坚固的氮掺杂纳米碳壳为活性位点的分散提供了足够的空间和优异的电荷传输性能, 同时降低了金属活性位腐蚀的可能性。

关键词: 铌; 硫硒化钴; 氮掺杂碳纳米球; 多掺杂; 析氢反应

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