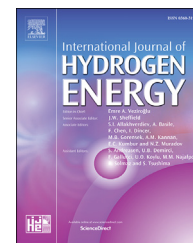


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Coupling molybdenum carbide nanoparticles with N-doped carbon nanosheets as a high-efficiency electrocatalyst for hydrogen evolution reaction

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ABSTRACT

Searching for earth-abundant and high-efficiency electrocatalysts for the hydrogen evolution reaction (HER) is of critical importance for future energy conversion devices. To facilitate the HER on a nonprecious metal-based catalyst, integration of catalytically active nanoparticles with highly conductive carbon supports represents a promising strategy since the formed nanohybrid can offer available active sites and improved electron transfer capability. Herein, we demonstrate a feasible and scalable approach to fabricate well-dispersed Mo₂C nanoparticles firmly anchored on 2D ultrathin N-doped carbon nanosheets (denoted as Mo₂C@N-C nanosheets) using inexpensive NaCl as recyclable templates. The adoption of NaCl template provides a 2D space for the one-step concurrent growth of Mo₂C nanoparticles and N-doped carbon nanosheets. Benefiting from the synergy between fine Mo₂C nanoparticles with high dispersity and N-doped C nanosheets, the resultant Mo₂C@N-C nanosheets exhibit an outstanding HER performance with a low overpotential, a small Tafel slope and excellent stability under acidic medium, making them a promising noble-metal-free HER catalyst.

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Introduction

With the ever-increasing energy crisis and environmental pollution, it is extremely urgent to explore alternative clean and sustainable energy sources to substitute traditional fossil fuels [1–4]. As an ideal renewable energy, hydrogen energy has attracted considerable attention due to its high energy density and environmental benignity [5–8]. Electrochemical water splitting has been recognized as one of the most attractive methods to produce hydrogen [9–11]. It has been well-documented that platinum group metals (PGMs) are the

most efficient electrocatalysts for the hydrogen evolution reaction (HER, $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) [12,13]. However, the prohibitive price, scarce reserves and poor electrochemical stability of PGMs have severely restricted their widespread applications in HER [14–16]. In this context, it is of paramount importance to develop cost-effective and high-efficiency HER electrocatalysts for the replacement of PGMs.

To date, great efforts have been made to pursue inexpensive alternative to Pt as the HER electrocatalyst. Fortunately, molybdenum-based compounds, such as dichalcogenides [17,18], carbides [19–21], nitrides [22,23], and phosphides

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[24,25], have been recently developed as promising and earth-abundant electrocatalysts towards the HER on account of their favorable electrocatalytic properties. Among them, Mo_2C has been identified as an appealing high-abundance HER electrocatalyst due to its Pt-like electronic structure and optimal hydrogen-adsorption capability [26–28]. However, synthesis of Mo_2C nanoparticles at a high reaction temperature ($>700^\circ\text{C}$) often suffers from inevitable agglomeration and excessive growth, which undoubtedly decreases their surface area severely and thus leads to unsatisfied electrocatalytic activities [29]. To address this issue, it is highly desirable to fabricate fine Mo_2C nanoparticles with small size and electrochemical accessibility. In order to circumvent the coarsening of crystallites and improve the HER performance, hybridization of fine Mo_2C nanoparticles with graphitic carbon support represents an efficient strategy due to the high electric conductivity, rapid electron transfer and superior chemical stability [30,31]. The intimate interaction between Mo_2C nanoparticles and carbon support could effectively prevent the agglomeration of Mo_2C nanoparticles. Moreover, the HER performance could be further optimized by delicate heteroatom (e.g., N and S) doping into carbon matrix due to the alternation of electronic structure of nanocarbon and creation of defects and more catalytically active sites [5,32,33]. Among various carbon supports, two dimensional (2D) carbon nanosheet represents an attractive catalyst support because of its large surface area, facilitated mass diffusion and electron transfer as well as highly mechanical strength [34,35]. Combined together, it is reasonable to envision that integration of fine Mo_2C nanoparticles with N-doped carbon nanosheets at nanoscale could afford a greatly enhanced HER performance. Nevertheless, it remains tremendous challenging to synthesize such nanohybrid *via* an economical and scalable approach at present.

Herein, for the first time, we report a facile pyrolysis approach to fabricate 2D ultrathin N-doped carbon nanosheets decorated with well-dispersed Mo_2C particles (denoted as $\text{Mo}_2\text{C}@N-C$ nanosheets) by using NaCl crystallites as templates. With the assistance of NaCl template, numerous ultra-fine Mo_2C particles could be *in-situ* generated on the ultrathin N-doped carbon nanosheets. The reduced size of Mo_2C particles and porous structure of N-doped carbon nanosheets offer a large surface area ($373.9\text{ m}^2\text{ g}^{-1}$) and abundant active sites. Benefiting from the unique structural and compositional advantages, the as-synthesized $\text{Mo}_2\text{C}@N-C$ nanosheets exhibit a low HER overpotential of 210 mV at a current density of 10 mA cm^{-2} , a small Tafel slope of 69 mV dec^{-1} and excellent stability under acidic condition. These findings manifest that the $\text{Mo}_2\text{C}@N-C$ nanosheets could serve as an economical yet high-efficiency HER electrocatalyst in the future.

Experimental section

Preparation of $\text{Mo}_2\text{C}@N-C$ nanosheets

In a standard synthesis, 6.0 g of NaCl, 0.35 g of chitosan (CS) and 1.0 mmol (0.177 g) of ammonium molybdate were initially dissolved in 15 mL of diluted HAc solution (1 wt%) to form a homogeneous solution, followed by drying in an oven at 60°C

for 12 h. Subsequently, the resultant mixture was transferred into a tube furnace and heated to 850°C for 3 h under Ar/H_2 ($V_{\text{Ar}}:V_{\text{H}_2} = 95:5$) atmosphere. Once cooled down to room temperature, the acquired product was washed with deionized water several times to remove NaCl, followed by drying at 60°C . Thus, $\text{Mo}_2\text{C}@N-C$ nanosheets could be harvested. For comparison, $\text{Mo}_2\text{C}@N-C$ nanosheets carbonized at 750 and 950°C were also synthesized through the similar protocol. Additionally, $\text{Mo}_2\text{C}@N-C$ nanosheets with different Mo_2C loading amount were also fabricated through the identical procedures, except varying the amount of ammonium molybdate. The samples derived from 0.5 to 1.5 mmol of ammonium molybdate are denoted as $\text{Mo}_2\text{C}(0.5)@N-C$ nanosheets and $\text{Mo}_2\text{C}(1.5)@N-C$ nanosheets, respectively.

Characterization

The crystallinity and phase purity of the products were identified by X-ray powder diffraction (XRD) on a Rigaku D/max-RC diffractometer with a $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406\text{ nm}$). The Raman spectrum was recorded on a Raman spectrometer (LabRAM HR800, $\lambda = 514\text{ nm}$). The morphology, structure and constituent of the samples were investigated by transmission electron microscopy (TEM, JEOL JEM-2010F, 200 kV), scanning electron microscopy (SEM, Hitachi S5500) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F, 200 kV). The surface chemistry of product was carried out by X-ray photoelectron spectroscopy (XPS) on a Thermo VG Scientific ESCALAB 250 spectrometer with an $\text{Al K}\alpha$ light source. The BET specific surface area and pore size distribution were measured at 77 K using a Micromeritics ASAP 2050 system.

Electrochemical measurements

The electrochemical measurements were carried out in a three-electrode system with a glassy carbon electrode (GCE, $d = 3\text{ mm}$) as the working electrode, saturated calomel electrode (SCE) as the reference electrode and a graphite rod as the counter electrode at room temperature. For the preparation of catalyst ink, 5 mg of the catalyst and 0.1 mL neutralized Nafion (5 wt%, Sigma-Aldrich) were dispersed in 0.9 mL of ethanol solution (the volume ratio of water to ethanol is 3:1) by ultrasonication for 30 min to form a homogeneous suspension. Then 6 μL of the resultant ink was dropped onto the polished GCE and dried at 40°C (loading density of $\sim 0.42\text{ mg cm}^{-2}$). The HER tests were performed by linear sweep voltammetry (LSV) in N_2 -saturated 0.5 M H_2SO_4 solution at a scan rate of 5 mV s^{-1} . A series of cyclic voltammetry (CV) measurement were carried out at various scan rates ($20\text{--}180\text{ mV s}^{-1}$) under the potential window from 0.1 to 0.2 V vs. reversible hydrogen electrode (RHE). The electrochemical stability was investigated by continuous CV scanning from -0.2 to 0.2 V vs. RHE at a scan rate of 0.1 V s^{-1} . In the work, all potentials have been referenced to RHE.

Results and discussion

For the standard synthesis of $\text{Mo}_2\text{C}@N-C$ nanosheets, NaCl crystallites are employed as removal templates. The judicious

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