Introduction

With the ever increasing demand of energy and environmental protection on the global scale, development of technologies for clean and sustainable energy has been attracting great attention. As an alternative and renewable energy source, hydrogen has been hailed as a promising candidate to ameliorate the climate change and environmental problems associated with the combustion of fossil fuels. Toward this end, one effective approach is the production of hydrogen by environmentally friendly (photo)electrochemical water-splitting.\(^1\) In these studies, advanced catalysts for the electrochemical hydrogen evolution reaction (HER) are necessary to reduce overpotential and increase energy efficiency.\(^2\) To date, the most effective HER electrocatalysts are the Pt-group metals, which are known to catalyze HER at a significant rate with almost no overpotential.\(^7\) However, the high costs and scarcity of Pt severely limit its widespread applications in HER, and it remains a great challenge to develop highly active HER catalysts based on abundant materials with a low overpotential.\(^10\)–\(^12\)

Towards this end, it has been found that MoS\(_2\)-based materials are the most effective non-Pt electrocatalysts for hydrogen production at low overpotentials.\(^13\)–\(^15\) Since the report by Hinnemann et al.\(^13\) that MoS\(_2\) nanoparticles are active HER catalysts, the interest in using MoS\(_2\) and related metal sulfides as water-splitting electrocatalysts has intensified.\(^16\)–\(^18\) Computational studies confirm that the HER activity stems largely from the molybdenum edges of MoS\(_2\);\(^14\) the activity can be modified by nanostructure morphologies (e.g., nanowires and nanosheets),\(^19\)–\(^20\) or by supporting substrates (e.g., Si wires, graphene-protected 3D nickel foams, and graphene nanosheets).\(^21\)–\(^23\) For instance, Dai et al.\(^22\) synthesized MoS\(_2\) nanoparticles on reduced graphene nanosheets via a facile solvothermal procedure, which exhibited excellent HER activity with a small overpotential of \(~\)100 mV, large cathodic currents, and a Tafel slope as small as 41 mV dec\(^{-1}\). They attributed the
good HER performance to the highly exposed edges of MoS$_2$ and excellent electronic coupling to the underlying graphene sheets. However, further enhancement of the exposure of active edge sites and improvement in electronic conductivity have remained great challenges for MoS$_2$-based HER electrocatalysts. This is the primary motivation of the present study.

Herein, deliberate doping with nitrogen was employed to enhance the HER activity of MoS$_2$ electrocatalysts. Doping treatments with non-metals (e.g., N, S, B, and P)\cite{24-27} and metals (e.g., Fe and Zn)\cite{28,29} have been used rather extensively to enhance the electrocatalytic activity in oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Yet, to our knowledge, there has been no report on the enhancement of the HER performance of MoS$_2$ nanosheets by doping with either metallic or nonmetallic elements. In the present study, MoS$_2$ nanobelts were prepared via a hydrothermal reaction between thiourea and MoO$_3$ nanobelts, and the structures were characterized by a variety of experimental techniques. Electrochemical studies showed that the obtained N-doped heterostructures exhibited a remarkable electrocatalytic activity for HER, where the onset potential (−156 mV vs. RHE) was markedly more positive than those of MoS$_2$, Mo$_2$N, and MoO$_3$. This was accounted for by the nitrogen doping that led to the enhanced electronic conductivity of the heterostructures as well as a high density of spinning electron states around the N and Mo atoms in MoS$_2$ nanosheets that were the active sites for HER, as manifested in density functional theory studies of a N-doped MoS$_2$ monolayer.

**Experimental section**

**Materials**

All reagents were of analytical grade and used without further purification. Molybdenum powders (Mo), hydrogen peroxide (H$_2$O$_2$), cyanamide (C$_2$H$_4$N$_4$), thioacetamide (C$_2$H$_5$NS, TAA), and 10 wt% Pt/C were obtained from Sinopharm Chemical Reagents Beijing Co. Water was supplied by a Barnstead Nanopure Water System (18.3 MΩ cm).

**Synthesis of MoO$_3$ nanobelts**

MoO$_3$ nanobelts were synthesized by a simple hydrothermal procedure.\cite{28,29} In a typical reaction, 0.1 g of Mo metal powders was slowly added to 16 mL of 35% H$_2$O$_2$ under vigorous stirring in an ice-water bath, forming a yellow solution of the precursor compound MoO$_2$(OH)(OOH), which was then loaded into a 20 mL Teflon-lined autoclave and heated at 200 °C for 24 h. After cooling to room temperature, the white precipitates were then centrifuged and washed with deionized water several times. After drying in vacuum at 70 °C for 12 h, MoO$_3$ nanobelts were collected as white powders.

**Synthesis of MoO$_3$@Mo$_2$N nanobelts**

In a typical experiment, 50 mg of the MoO$_3$ nanobelts prepared above was dispersed into 50 mL of ethanol with 20 mg of cyanamide under continuous stirring. The products were heated at 450 °C for 1 h, then 650 °C for 2 h under an argon atmosphere to convert the single-crystalline MoO$_3$ nanobelts into porous MoO$_3$ core@Mo$_2$N shell nanobelts.

**Synthesis of MoO$_3$ nanobelts@nitrogen self-doped MoS$_2$ nanosheets**

MoO$_3$ nanobelts@nitrogen self-doped MoS$_2$ nanosheets were synthesized as follows. In a typical reaction, 20 mg of the MoO$_3$@Mo$_2$N nanobelts obtained above and 80 mg of thioacetamide (C$_2$H$_5$NS) were dissolved in 20 mL of deionized water. The solution was transferred to a Teflon-lined stainless steel autoclave and then heated in an electric oven at 200 °C for 24 h. The black product, MoO$_3$@N-doped MoS$_2$, was harvested after centrifugation and dried at 70 °C for 12 h. For comparison, powders of pure MoS$_2$ nanosheets were synthesized under the same conditions by using MoO$_3$ nanobelts instead of MoO$_3$@Mo$_2$N nanobelts as the precursors.

**Characterization**

Field-emission scanning electron microscopic (FESEM, Model JSM-7600F) measurements were used to characterize the morphologies of the samples. Transmission electron microscopic (TEM) measurements were carried out with a JOEL JEM 2100F microscope. Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance powder X-ray diffractometer with Cu K$_\alpha$ (λ = 0.15406 nm) radiation. X-ray photoelectron spectroscopic (XPS) measurements were performed using an ESCALAB 250 instrument. Raman spectra were recorded on a RENISHAW inVia instrument with an Ar laser source of 488 nm in a macroscopic configuration.

**Electrochemistry**

Electrochemical measurements were performed with an electrochemical workstation (CHI 760C, CH Instruments Inc.) in a 0.5 M H$_2$SO$_4$ aqueous solution. A Ag/AgCl electrode (saturated KCl) and platinum wire were used as the reference and counter electrode, respectively. 4 mg of the catalyst powders was dispersed in 1 mL of 4 : 1 (v/v) water–ethanol mixed solvent along with 80 μL of Nafion solution, and the mixture was ultrasonicated for 30 min. Then, 5 μL of the solution prepared above was dropcast onto the surface of a glassy carbon (GC) disk electrode at a catalyst loading of 0.285 mg cm$^{-2}$. The as-prepared catalyst film was dried at room temperature. The polarization curves were obtained by sweeping the potential from 0 to −0.8 V (vs. Ag/AgCl) at a potential sweep rate of 5 mV s$^{-1}$. The accelerated stability tests were performed in 0.5 M H$_2$SO$_4$ at room temperature by potential cycling between 0 and −0.6 V (vs. Ag/AgCl) at a sweep rate of 100 mV s$^{-1}$ for a given number of cycles. Current–time responses were monitored by chronoaamperometric measurements for 12 h.

In all measurements, the Ag/AgCl reference electrode was calibrated with respect to a reversible hydrogen electrode (RHE). The calibration was performed in a high-purity H$_2$ (99.999%) saturated electrolyte with a Pt wire as the working electrode and counter electrode. Cyclic voltammograms (CVs) were collected at a scan rate of 1 mV s$^{-1}$, and the average of the two potentials
at which the current crossed zero was taken as the thermodynamic potential for the hydrogen electrode reactions. In 0.5 M H₂SO₄, E[Ag/AgCl] = E[RHE] + 0.246 V (Fig. S1†).

### Theoretical calculations

The geometric and electronic properties of N-doped MoS₂ were calculated by density functional theory studies in the generalized gradient approximation implemented in the Vienna **Ab initio** Simulation Package (VASP), which projected the augmented wave method and Perdew-Burke-Ernzerhof exchange correlation were used. The plane-wave cutoff energy was 520 eV throughout the calculations. The Brillouin zone integrations were performed with a (3 × 3 × 1) $\Gamma$-center $k$-point mesh and the Gaussian smearing width was 0.05 eV. In order to simulate the N-doped MoS₂, we constructed a (4 × 4 × 1) supercell and the Gaussian smearing width was 0.05 eV. In order to simulate the N-doped MoS₂, we constructed a (4 × 4 × 1) supercell based on the primitive cell of a MoS₂ monolayer, in which an S atom is replaced by an N atom. Then the atomic positions were relaxed by using the conjugate-gradient algorithm until the residual forces of all atoms were less than 0.02 eV Å⁻¹.

### Results and discussion

Fig. 1 describes the procedure for a typical synthesis of MoO₂@N-doped MoS₂ nanobelts, which involves three major steps: (a) the surface of MoO₃ nanobelts was coated with a thin film of cyanamide; (b) the cyanamide/MoO₃ nanobelts were calcined at 650 °C under an argon atmosphere to obtain MoO₂@Mo₂N nanobelts by the decomposition of the cyanamide polymer; and (c) the resulting products were hydrothermally treated with thioacetamide (TAA) to produce nitrogen-doping MoS₂ nanosheets on MoO₂ nanobelts. The morphologies of the as-prepared MoO₂ nanobelts@nitrogen-doped MoS₂ nanosheets were firstly examined by using field-emission scanning electron microscopic (FE-SEM) measurements. Fig. 2a presents an overview of the smooth MoO₃ nanobelts which are 80–400 nm in width and 5–10 μm in length. After calcination at 650 °C under an argon atmosphere, porous nanobelts composed of MoO₂ and Mo₂N were obtained (Fig. 2b), which was confirmed by XRD measurements (Fig. S2†). The obtained porous MoO₂@Mo₂N nanobelts were then used as Mo and N sources to synthesize N-doped MoS₂. From Fig. 2c and d, it can be seen that after hydrothermal treatment with TAA, the nanobelts surfaces were homogeneously decorated with a number of curvy nanosheets. XRD studies show that the diffraction peaks of Mo₂N disappeared and the remaining diffraction features were primarily due to MoO₂ (Fig. S2†). While no diffraction peaks were identified for MoS₂ in XRD measurements (Fig. S2†), Raman spectroscopic studies (Fig. S3†) did show that MoS₂ was formed with a characteristic vibrational band at 377.8 cm⁻¹. This suggests that the nanosheets observed in Fig. 2d was most likely composed of MoS₂ leading to the formation of a MoO₂@N-doped MoS₂ core-shell heterostructure.

XPS measurements were then carried out to further investigate the chemical composition and valence states of the samples, which were depicted in Fig. 3 and summarized in Table 1. From the survey spectra in panel (a), the element of Mo can be clearly identified in all samples, with S found only in MoO₂@N-doped MoS₂ (curve 3). Fig. 3b depicts the high-resolution scans of the Mo 3d electrons, where one can see two peaks at 236.2 eV and 233.2 eV in the starting MoO₃ nanobelts (curve 1), consistent with Mo 3d₃/₂ and 3d₅/₂ of Mo⁶⁺. After calcination reactions of MoO₂ nanobelts and cyanamide (curve 2), both Mo³⁺ (located at 229.5 and 232.5 eV, blue and aqua-blue peaks) and Mo⁵⁺ (located at 231.5 eV, magenta peak) can be identified, as a result of the formation of MoO₂ and Mo₂N, respectively, which is consistent with the XRD results in Fig. S2b. After the hydrothermal reaction with TAA (curve 3), only Mo⁴⁺ was observed (blue and aqua-blue peaks), but with different covalent bonds of MoS₂ (227.2 eV) and MoO₂ (232.7 and 229.5 eV). Meanwhile, the S 2p electrons exhibited various bonding energies for S²⁻ (162.2 eV, 163.2 eV, 164.1 eV, 165.1 eV) and S⁴⁺ (168.5 eV) (curve 3 in panel c). This is likely due to the different
environments of S caused by nitrogen-doping in MoS₂.\cite{37} Note that the S signals were totally absent in the MoO₃ and MoO₂@Mo₂N nanobelts (curves 1 and 2 in Fig. 3c). The formation of N-doped MoS₂ nanosheets was further manifested in the measurements of the N1s electrons as depicted in Fig. 3d. For MoO₂@Mo₂N (curve 2), the Mo3p₃/₂ and N1s electrons can be identified at 395.5 eV (aqua-blue peak) and 397.5 eV (blue peak), respectively, consistent with the formation of Mo–N bonding linkages;\cite{38} and after hydrothermal treatments, the N1s peak in curve (3) was found to blue-shift to 398.5 eV, likely because of the formation of MoS₂ nanosheets where Mo carried a higher oxidation state and N was embedded into the nanosheet matrix (Fig. 1). Similar self-doping reactions have also been carried out to synthesize N-doped TiO₂ from TiN₂.\cite{39,40} One may notice that there is a substantial overlap between the Mo3p₃/₂ and N1s electrons, which renders it difficult to have an accurate quantitative analysis of the elements.

Fig. 4 show the representative TEM images of the resulting MoO₃ nanobelts, MoO₂@Mo₂N nanobelts and MoO₂ nanobelts@N-doped MoS₂ nanosheets. The smooth nanobelt morphology for MoO₃ and porous nanobelt morphology for MoO₂@Mo₂N can be clearly seen in Fig. 4a and c, respectively, consistent with the SEM results in Fig. 2; and for the MoO₂ nanobelts@N-doped MoS₂ nanosheets, it can be seen that the MoO₂ nanobelts were uniformly decorated with MoS₂ nanosheets (Fig. 4e). Most of the MoS₂ nanosheets were aligned perpendicular to the surface of the nanobelts, which have been known to possess abundant folded edges with high catalytic activity for HER.\cite{3} From Fig. 4f, the (002) planes of MoS₂ can be clearly seen with a lattice spacing of 0.61 nm; and from the HRTEM images in Fig. 4b, d and f, the periodic fringe spacings of 0.35 nm, 0.34 nm, and 0.24 nm agree well with the interplanar spacings of (040) for MoO₃ (orthorhombic, \(a = 0.40\) nm, \(b = 1.38\) nm, \(c = 0.37\) nm), (011) for MoO₂ (monoclinic, \(a = 0.56\) nm, \(b = 0.48\) nm, \(c = 0.55\) nm), and (111) for Mo₂N (cubic, \(a = b = c = 0.416\) nm), respectively. Furthermore, elemental mapping based on energy dispersive X-ray (EDS) analysis clearly shows that the MoO₂@N-doped MoS₂ consists of Mo, N, and S elements (Fig. 4g), and the N element was distributed evenly in the heterostructured nanobelt. This again confirmed that the N element was indeed doped into the MoS₂ nanosheets.

The electrocatalytic activities for HER of the nanobelts prepared above were then examined by electrochemical measurements in 0.5 M H₂SO₄. From Fig. 5a, it can be seen that the bare GC electrode exhibited almost no catalytic activity for HER.

![Fig. 3](image-url) (a) XPS survey spectra and high-resolution scans of (b) Mo3d, (c) S2p and (d) N1s electrons of (1) MoO₃ nanobelts, (2) MoO₂@Mo₂N nanobelts and (3) MoO₂@N-doped MoS₂ heterostructures.

![Fig. 4](image-url) TEM images of (a and b) MoO₃ nanobelts, (c and d) MoO₂@Mo₂N nanobelts and (e and f) MoO₂ nanobelts@nitrogen self-doped MoS₂ nanosheets, and (g) EDS elemental maps for a MoO₂@N-doped MoS₂ heterostructure.

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**Table 1** Summary of elemental composition, binding energy, and valence state of different samples by XPS measurements

<table>
<thead>
<tr>
<th>Samples</th>
<th>Elements</th>
<th>Binding energy (eV)</th>
<th>Valence state</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO₃ nanobelts</td>
<td>Mo</td>
<td>389.5; 236.2, 233.2</td>
<td>+6</td>
</tr>
<tr>
<td>MoO₂@Mo₂N nanobelts</td>
<td>Mo</td>
<td>395.5; 232.5, 229.5, (Mo⁴⁺) and 231.5 (Mo²⁺)</td>
<td>+2, +4</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>397.5</td>
<td>+4</td>
</tr>
<tr>
<td>MoO₂@N-doped MoS₂</td>
<td>Mo</td>
<td>395.5; 232.7, 229.5, 227.2</td>
<td>+4</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>398.5</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>162.2, 163.2, 164.1, 165.1 (S²⁻), and 168.5 eV (S⁶⁺)</td>
<td>-2, +6</td>
</tr>
</tbody>
</table>

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H$_2$O$^+$ + e$^-$M $\leftrightarrow$ H$^-$M + H$_2$O (discharge reaction)  

2H$^-$M $\leftrightarrow$ H$_2$M + M (combination reaction)  

H$_2$O$^+$ + e$^-$M $\leftrightarrow$ H$^-$M + H$_2$O (ion + atom reaction)  

where e$^-$M denotes metal-bound electrons, while H$^-$M and H$_2$M represent a hydrogen atom and molecule adsorbed onto a surface metal atom, respectively. Various Tafel slopes have been predicted and observed. For instance, a slope of 30 mV dec$^{-1}$ has been found to correspond to a fast discharge reaction (1) followed by a rate-determining combination reaction (2); whereas a high slope of 40 mV dec$^{-1}$ is proposed to signify a fast discharge reaction (1) followed by the ion + atom reaction (3), corresponding to a transfer coefficient ($\alpha$) of ~0.5. From Fig. 5b, linear regressions of the linear portions by the Tafel equation, $\eta = b \log j + a$, yield a slope of 49.8, 47.5, and 77.7 mV dec$^{-1}$ for 10 wt% Pt/C (curve 5), MoO$_2$@N-doped MoS$_2$ (curve 4) and pure MoS$_2$ (curve 3), respectively. Note that in a previous study of HER with MoS$_2$ nanoparticles supported on graphene,$^{22}$ a Tafel slope of 41 mV dec$^{-1}$ was observed, which suggested that the rate-determining step of HER was the electrochemical desorption of hydrogen. In the present study, the fact that the Tafel slopes for commercial Pt/C and MoO$_2$@N-doped MoS$_2$ were almost identical indicates that the reaction pathways for HER were likely similar on these two catalysts at rather comparable electron-transfer kinetics. This may account for the low overpotential (and hence enhanced performance) observed for MoO$_2$@N-doped MoS$_2$, with electrochemical desorption of hydrogen being the rate-determining step, in comparison to pure MoS$_2$.

In addition to good catalytic activity, the MoO$_2$@N-doped MoS$_2$ electrode also exhibited good stability for HER. Fig. 5c shows that, even after 2000 potential cycles, the j-V curve of the MoO$_2$@N-doped MoS$_2$ electrode remained almost unchanged. The reverse scans also confirmed the good HER stability of the MoO$_2$@N-doped MoS$_2$ electrode (Fig. S4†). To further investigate the stability of MoO$_2$@N-doped MoS$_2$ in HER, the current-time plots at the applied potential of ~0.25 V (vs. RHE) was depicted in Fig. 5d. It can be seen that commercial Pt/C catalysts (red curve) exhibited a much higher initial current than MoS$_2$ (blue curve) and MoO$_2$@N-doped MoS$_2$ (black curve); yet the steady-state current of MoO$_2$@N-doped MoS$_2$ was the highest among the three. For instance, the current density of MoO$_2$@N-doped MoS$_2$ at 2 h is 8.1 times and 2.2 times higher than those of pure MoS$_2$ and 10 wt% Pt/C, respectively. Notably, the current remained steady over 12 h of continuous operation (black curve), indicating excellent durability of the MoO$_2$@N-doped MoS$_2$ electrode for HER in 0.5 M H$_2$SO$_4$.

It should be noted that while the overpotential and Tafel slope of MoO$_2$@N-doped MoS$_2$ in HER were somewhat higher than those reported previously,$^{22,42}$ the enhancement of the HER performance by the nitrogen-doping procedure above is markedly more pronounced than by other mechanisms. For instance, the overpotential for HER was reduced by 105 mV with MoO$_2$@N-doped MoS$_2$, as compared to that of pure (unsupported) MoS$_2$ (Fig. 5). In comparison, the overpotential was reduced by only about 60 mV with defect-rich MoS$_2$, relative to that of defect-free MoS$_2$; and for MoS$_2$ nanoparticles supported on reduced graphene nanosheets, the overpotential was reduced by only 50 mV as compared to that of unsupported MoS$_2$ nanoparticles (Table S1†). It should be noted that in the present study, the remarkable performance of MoO$_2$@N-doped MoS$_2$ in HER was observed despite a low content of MoS$_2$ (not detectable in XRD measurements, Fig. S2†). Thus, further research...
is required to examine the effects of nitrogen doping and MoS$_2$ loading on the electrocatalytic activity for HER.

The aforementioned enhancement of the HER performance of MoO$_3$@N-doped MoS$_2$ can be attributed to the following factors. The first is the high electronic conductivity of MoO$_3$@N-doped MoS$_2$. Indeed, electrochemical impedance spectroscopic measurements of MoS$_2$ and MoO$_3$@N-doped MoS$_2$ showed that the charge-transfer resistance of MoO$_3$@N-doped MoS$_2$ for HER is markedly smaller than that for the bare MoS$_2$ nanosheets (Fig. S7†). This low resistivity may also be facilitated by the aligned perpendicular growth of MoS$_2$ nanosheets on the MoO$_2$ nanobelt surface. MoS$_2$ with a sandwiched layer structure is composed of Mo atoms situated between two layers of hexagonally close-packed sulfur atoms, and the MoS$_2$ layers are stacked together by van der Waals interactions. In this configuration, the electronic conductivity parallel to the layered structure of the MoS$_2$ nanosheets is much higher than that along the vertical direction.\(^1\) Therefore, the perpendicular growth of MoS$_2$ nanosheets on the conductive substrates is advantageous for electron transport between MoS$_2$ and MoO$_2$ nanobelts.\(^2\) Second, N doping in MoS$_2$ nanosheets synthesized from Mo$_2$N most likely results in the exposure of additional active edge sites, as depicted in the schematic representation in Fig. S6.\(^1\) The S atoms in MoS$_2$ are partially replaced by N atoms, leading to a high density of defects and exposure of Mo edges that are known for high HER activity. In fact, defect-rich MoS$_2$ nanosheets can be identified in HRTEM studies of MoO$_3$@N-doped MoS$_2$ (Fig. S7†). Notably, whereas controlled growth of MoS$_2$ nanomaterials with exposed Mo edges has been reported before,\(^3\) to our knowledge this is the first ever report of nitrogen self-doping treatment of MoS$_2$ nanosheets to further enhance the HER activity.

The mechanistic interpretations above were also consistent with results from theoretical calculations. Fig. 6 and S8† depict the spin polarized density of states (DOS) and spin polarized charge density of a nitrogen-doped MoS$_2$ nanosheet. It can be clearly seen that there are two peaks near the Fermi energy (Fig. S8†). The spin-up peak is totally occupied, while the spin-down peak is totally vacant. This spin split in DOS leads to a 1.0 $\mu_B$ magnetic moment in the supercell. In Fig. 6, the spin polarized charge density indicates that the magnetic moment mostly arises from the N atoms and spreads to the nearby Mo and S atoms. Therefore the doped N atoms likely provide a localized state near the Fermi energy in the band gap of the semiconducting MoS$_2$. That is, there is a high density of electronic states around the N and Mo atoms, which is consistent with the enhanced electronic conductivity of the MoO$_3$@N-doped MoS$_2$ heterostructures (Fig. S5†). Furthermore, such electron-rich sites are critical and beneficial for HER where the negative charge is anticipated to help attract and chemisorb H\(^+\) to the catalyst surface, a critical first step in HER, ultimately leading to improved HER performance.

**Conclusion**

In this study, an effective electrocatalyst based on earth-abundant and inexpensive components was developed for hydrogen evolution reaction. MoO$_3$ nanobelts@nitrogen self-doped MoS$_2$ nanosheets were produced by nitridation and sulfuration treatments of MoO$_3$ nanobelts. The MoS$_2$ nanosheets were found to grow perpendicular on the MoO$_2$ nanobelt surface such that the heterostructures possessed high electronic conductivity and abundant exposed active edges. Electrochemical studies showed that the obtained electrocatalysts exhibited excellent HER activity with an onset potential of $\sim$156 mV (vs. RHE), a large current density, a small Tafel slope of 47.5 mV dec$^{-1}$ and prominent electrochemical durability, in comparison with commercial Pt/C catalysts. DFT calculations suggested a high density of electronic states around the N and Mo atoms which was likely responsible for the enhanced electronic conductivity as well as apparent HER performance of the MoS$_2$ nanosheets. Such a strategy based on doping engineering of HER catalysts with N, P and B elements may pave the way towards the design and preparation of highly efficient catalysts for water splitting.

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**Notes and references**


