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### S-rich single-layered MoS<sub>2</sub> nanoplates embedded in N-doped carbon nanofibers: efficient co-electrocatalysts for the hydrogen evolution reaction<sup>†</sup>

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S-rich  $MoS_2$ -NCNF hybrid nanomaterials exhibiting extraordinary HER activity, with a very low onset potential of 30 mV and a small Tafel slope of 38 mV per decade, were successfully fabricated by combining N-doped carbon nanofibers and single-layered  $MoS_2$ nanostructures with abundant edge active sites.

With the growing scientific and societal interest in energy and environmental protection on the global scale, the development of technologies for clean and sustainable hydrogen energy production has been attracting great attention.<sup>1,2</sup> With the aim of producing hydrogen by environmentally friendly means, the electrocatalytic hydrogen evolution reaction (HER) has been considered as one of the most sustainable and efficient approaches to generate hydrogen, in which Pt-based materials always serve as the catalysts in order to reduce overpotential and increase energy efficiency.<sup>3-5</sup> Until now, Pt-based catalysts have been generally considered as the most effective HER electrocatalysts,<sup>6</sup> while their large scale application is largely hindered by the low abundance and high cost of Pt. Hence, employment of a low-cost and highly efficient electrocatalyst to replace Pt-based catalysts for the HER has attracted increasing interest in the area of renewable energy research.<sup>7,8</sup>

Many efforts have been devoted to the search for nonprecious-metal based HER catalysts in recent decades. Various noble-metal-free catalyst materials, such as transition metal sulfides,<sup>3,4,9</sup> cobalt compounds<sup>5</sup> and N-doped carbon materials,<sup>5,9,10</sup> have been creatively developed to partially substitute the role of Pt in HER. As a typical two-dimensional (2D) material with rich

physical and chemical properties and broad applications, molybdenum disulfide (MoS<sub>2</sub>) is an exciting HER catalyst that exhibits promising HER activity in crystalline or amorphous materials and molecular mimics.<sup>3,9,10</sup> In the hydrogen evolution process, based on density functional theory (DFT) calculations, the sulfur atoms of the MoS<sub>2</sub> edges are easily bound to hydrogen atoms, which are 2-fold coordinated to molybdenum.<sup>11</sup> Theoretical and experimental studies both indicate that the edges of MoS<sub>2</sub> are catalytically active while the basal plane remains inert.<sup>4</sup> However, its catalytic HER performance is currently limited by the density and reactivity of the active sites and poor electrical transport. To improve the HER activity of MoS<sub>2</sub>, two aspects should be considered. The strong van der Waals interactions existing among the lamellar crystals will inevitably result in the aggregation phenomenon, which decreases the number of active sites as well as the whole electrocatalytic activity.<sup>4</sup> This means that larger sized MoS<sub>2</sub> nanosheets with multilayers could not generate enough active sites. The other aspect is the poor conductivity of MoS<sub>2</sub> due to the lateral transfer of electrons along the lamella structure of the MoS<sub>2</sub> nanosheets, which restricts efficient electron transfer as well as the related electrochemical kinetics.<sup>3,11</sup> Therefore, designing MoS<sub>2</sub> catalysts with few layers, a small size and rich in sulphur atoms would be an effective strategy to generate more active sites, enhancing their electrocatalytic activity in the HER.

A good electrocatalyst would be nanometer-large  $MoS_2$  crystallites supported on carbon-based materials, which are conducting but otherwise inert.<sup>11–13</sup> Recently, Rao *et al.*<sup>14</sup> prepared a  $MoS_2$ composite with nitrogen-doped reduced graphite oxide and it showed excellent HER activity, demonstrating that nitrogen incorporated graphene could be expected to improve the catalytic activity of a composite with  $MoS_2$  layers due to the enhanced electron donating ability of the N-doped graphene. N-doped carbon materials have high electrical conductivity, due to p-delocalization, and high thermal conductivity. In addition, they also exhibit promising HER activity together with a higher stability and a higher poisoning resistance than Pt/C.<sup>10,15</sup>

In the present investigation, we aim to fabricate nanoscale crystallites with single or few layers and rich in S atoms to

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generate more active sites for the HER. Meanwhile, N-doped carbon nanofibers (NCNFs) not only serve as a support to confine the growth of the MoS<sub>2</sub> nanoplates but also provide good conductivity and active sites for the generation of hydrogen. The Mo precursor,  $(NH_4)_2MOS_4$  was firstly dissolved with polyacrylonitrile (PAN) and then electrospun into PAN- $(NH_4)_2MOS_4$  precursor (PANMo) nanofibers. After treatment with S vapor at 400 °C for 2 h and graphitization at 1000 °C for 8 h, small and uniform MoS<sub>2</sub> nanoplates with single-layered structures and abundant exposed edges were formed in the NCNFs (experimental details can be found in the ESI†). The synergistic effects between the S-rich single-layered MoS<sub>2</sub> nanoplates and the NCNFs have shown extraordinary results in H<sub>2</sub> evolution, with a very low onset potential of 30 mV and a small Tafel slope of 38 mV per decade.

Fig. 1a displays the typical morphology of the S-rich  $MoS_2$  nanoplates embedded in NCNFs. Compared with the pure CNFs and  $MoS_2$ -CNFs (Fig. S1, ESI<sup>†</sup>), the S-rich  $MoS_2$ -NCNFs possess abundant pores caused by the S vapor, leaving a notable space inside, which is beneficial for allowing the access of electrolytes to the  $MoS_2$  nanoplates. The average diameter of the S-rich  $MoS_2$ -NCNFs decreases to  $210 \pm 50$  nm, as compared with the PANMo nanofibers (Fig. S2, ESI<sup>†</sup>), indicating a high aspect ratio. Fig. 1b shows the unique morphology of the extremely thin and small wave-like  $MoS_2$  nanostructures that are uniformly embedded in the NCNFs, without any stacking layers.

The lateral dimension of the single-layered  $MoS_2$  nanostructure is around 8 nm, as verified by high resolution transmission electron microscopy (HRTEM) images (Fig. 1c). In addition, the thickness of the  $MoS_2$  is 0.4 nm (Fig. 1c), which is in accordance with the spacing between the two S layers (sandwiching the Mo layer), hence indicating the presence of single-layered  $MoS_2$ .<sup>14</sup> More images are shown in Fig. S3 (ESI†). From Fig. 1d and the inset, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images indicate that the irregular platelike morphology of  $MoS_2$  can be clearly seen and that no visible aggregated nanoplates occur because of the space-confined growth. Approximately, the  $MoS_2$  nanoplates stacked perpendicularly on the underlying substrates and possess highly exposed edges with



Fig. 1 (a) FE-SEM, (b) TEM, (c) HRTEM and (d) HAADF-STEM images of the S-rich MoS<sub>2</sub>–NCNFs hybrid nanomaterial; (e–i) STEM-EDS mapping images and (j) line scan EDX spectra of selected areas of the S-rich MoS<sub>2</sub>–NCNFs.

slightly folded dentations on the rim, significantly increasing the exposure of active edge sites. In addition, the NCNFs can not only confine the growth and dispersion of the MoS<sub>2</sub> nanoplates to guarantee the exposure of active edge sites but also can facilitate electron transfer during the electrocatalysis, leading to highly improved conductivity of the composite.<sup>12,13</sup> The drastic morphological difference highlights the important role of NCNFs as a novel support material for the design of new MoS<sub>2</sub> nanostructures with highly active sites. As illustrated in Fig. 1e to i, the STEM-EDS mapping clearly confirms the formation of S-rich MoS<sub>2</sub> nanoplates embedded in NCNFs. Fig. 1f and g exhibit the nitrogen and carbon elements, which are in accordance with the mapping area, demonstrating the presence of N-doped CNFs. The Mo and S elemental images reveal an even distribution across the whole CNFs, confirming the presence of S-rich MoS<sub>2</sub> nanostructures. The line-scan energy dispersive X-ray (EDX) spectra (Fig. 1j) display the relative intensity of the C, N, Mo and S elements, also confirming the successful fabrication of S-rich MoS<sub>2</sub> nanoplates.

As shown in Fig. 2a, the X-ray diffraction (XRD) pattern of the original PANMo has a sharp intense peak at 16.8°, corresponding to the (100) diffraction of the PAN crystalline phase. The NCNFs exhibit a representative diffraction peak (002) of the stacked graphite layers (JCPDS 75-1621) at  $2\theta = 23.5^{\circ}$ , demonstrating the crystalline structures of the graphitic carbon in the NCNFs.<sup>16</sup> For the S-rich MoS<sub>2</sub>-NCNFs, only two new peaks appeared, at  $42.6^{\circ}$  (103) and  $64.2^{\circ}$  (110), revealing a single phase of MoS<sub>2</sub> in the hybrid. Previous literature<sup>4,9</sup> has reported that the distinctive strong (002) peak of pure  $MoS_2$ at  $2\theta = 14.8^{\circ}$  signifies a well-stacked layered structure, while the disappearance of the (002) peak indicates that stacking of the single layers does not take place. In the present investigation, the S-rich  $MoS_2$ -NCNFs does not show any (002) peaks and therefore, together with the TEM and HAADF-STEM results we can infer that the MoS<sub>2</sub> nanoplates should have a single-layered or few-layer structure with abundant catalytically active sites. Raman spectra are shown in Fig. S4 (ESI<sup>†</sup>).



Fig. 2 (a) XRD pattern of the PANMo nanofibers, pure NCNFs and the S-rich MoS<sub>2</sub>–NCNFs hybrid. High-resolution XPS of the (b) N 1s, (c) Mo 3d and (d) S 2p spectra of the S-rich MoS<sub>2</sub>–NCNFs.

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The chemical state of the S-rich MoS<sub>2</sub>-NCNFs was further confirmed by XPS analysis. The C 1s spectra demonstrate a significant amount of charge transfer from the graphitic carbon to the MoS<sub>2</sub> nanoplates, which are shown in Fig. S5 (ESI<sup>+</sup>). The N1s spectra of the S-rich MoS<sub>2</sub>-NCNFs revealed three N characteristic peaks, as shown in Fig. 2b. The two peaks at lower binding energies (about 398.4 and 400.5 eV) correspond to pyridinic and pyrrolic N, respectively, which contribute electron density to the p-conjugated system with a pair of p-electrons in the graphitic carbon layers.<sup>18</sup> The peak at 401.1 eV was due to N atoms substituted for C within the graphene, referred to as graphitic N. Previous research reported that pyridinic N and graphitic N at higher concentrations were more effective than pyrrolic N at improving the electrochemical performance of N-doped carbon materials.<sup>18</sup> In addition, Li<sup>19</sup> et al. reported the positive effects of pyridinic and graphitic N on the hydrogen evolution reaction. Compared with pyrrolic N, the pyridinic and graphitic N have the dominant concentrations (calculated by XPS spectra) and hence, it could benefit the HER activity due to the positive synergistic effect between S-rich MoS<sub>2</sub> and NCNFs. As shown in Fig. 2c, three characteristic peaks emerged at 232.3, 229.1 and 225.4 eV, corresponding to Mo  $3d_{3/2}$ , Mo  $3d_{5/2}$  and S 2s binding energies, respectively. According to the literature,<sup>9,17</sup> the binding energies of the Mo 3d are close to the 1T phase of MoS<sub>2</sub>, and the 1T phase of MoS<sub>2</sub> is meta-stable, providing a prediction of better HER performance. The S 2p spectra (Fig. 2c) can be deconvoluted to three main peaks located at about 163.7, 164.4 and 165.1 eV, which relate to S  $2p_{3/2}$  and S  $2p_{1/2}$  for S<sup>2-</sup> and S<sub>2</sub><sup>2-</sup> binding energies, respectively. The atomic ratio of S to Mo for MoS<sub>2</sub>-NCNFs is calculated to be 2.32:1 by XPS spectra, which is much larger than commonly reported for MoS<sub>2</sub>.<sup>4,9</sup> The existence of bridging  $S_2^{2-}$  and/or apical  $S^{2-}$  and terminal  $S_2^{2-}$  and/or  $S^{2-}$ , suggests that a S-rich MoS<sub>2</sub> structure has been formed in the NCNFs hybrid. It is reported that MoS<sub>2</sub> with more active S edge sites is highly active for HER.4,9

To evaluate the electrochemical performance of the S-rich MoS<sub>2</sub>-NCNFs, linear sweep voltammetry (LSV) of various electrocatalysts was investigated in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution using a typical three-electrode system. Pure MoS<sub>2</sub>, N-doped CNFs, S and N co-doped CNFs, MoS<sub>2</sub>-CNFs prepared without S vapor, and Pt/C were investigated for reference. As shown in Fig. 3a, the Pt/C catalyst exhibits extremely high HER catalytic activity with a near zero overpotential. Pure MoS<sub>2</sub> displays negligible HER performance and a high onset potential (about 210 mV), as well as a low cathodic current density. The NCNFs and S-NCNFs both exhibit small HER activities with onset potentials of about 180 and 170 mV, indicating that the N- and S-doped CNFs indeed have catalytic activity for the generation of H<sub>2</sub>. It has been observed that the incorporation of nitrogen and sulphur enhances the electron-donor or basic capacities of the carbon material, thereby enhancing the HER activity. The as-prepared MoS<sub>2</sub> without S vapor treatment also has a nanoplate morphology (Fig. S2, ESI<sup>+</sup>). The MoS<sub>2</sub>-NCNFs obtain a low onset potential of about 98 mV, as well as a relatively high cathodic current density, indicating a synergistic effect between the N-doped CNFs and MoS2 nanostructures that improves the



**Fig. 3** (a) Polarization curves of a GCE electrode recorded in N<sub>2</sub> purged 0.5 M  $H_2SO_4$  for various electrocatalysts. Scan rate: 2 mV s<sup>-1</sup>. (b) The corresponding Tafel plots for various electrocatalysts. (c) Nyquist plots of EIS for various electrocatalysts at a modified GCE. (d) Stability test of the S-rich MoS<sub>2</sub>–NCNFs electrocatalyst. Negligible HER current was lost after 1000 cycles of cyclic voltammetry from -0.4 to 0.2 V vs. RHE.

HER activity. The S-rich  $MoS_2$ -NCNFs hybrid obtains the lowest onset potential, of about 30 mV. The onset potential of the S-rich  $MoS_2$ -NCNFs is about 30 mV, which is comparable to that of Pt/C and means low energy consumption occurs in the catalytic process.

Moreover, the S-rich MoS<sub>2</sub>-NCNFs also display the largest cathodic current density of all the tested samples, with 10 mA  $\rm cm^{-2}$ at an overpotential of 120 mV, which is larger than that of previously reported MoS<sub>2</sub> carbon systems and close to the values for commercial Pt/C.<sup>4,9,17</sup> The cathodic current density is proportional to the quantity of evolved hydrogen, and hence, the large current density here demonstrates prominent hydrogen evolution behaviour. Compared with the HER performance of MoS<sub>2</sub>-NCNFs, with a overpotential of 230 mV at 10 mA cm<sup>-2</sup>, the S-rich MoS<sub>2</sub> nanoplates possess a certain amount of bridging disulfides  $S_2^{2-}$  and apical  $S^{2-}$ , which are highly active edge sites for HER. The good catalytic behaviour of the S-rich MoS<sub>2</sub>-NCNFs hybrid may arise from the synergetic effect of major exposed active edge sites, N-doped carbon and excellent internal electrical conductivity. In addition, because of the porous structure of the nanofibers, the electrolyte can easily access the MoS<sub>2</sub> nanoplates embedded in the NCNFs, leading to enhanced HER activity.

To obtain further insight into the S-rich  $MoS_2$ -NCNFs, the corresponding Tafel plots of the various selected catalysts were investigated (Fig. 3b). The S-rich  $MoS_2$ -NCNFs obtain the smallest Tafel slope of 38 mV per decade, which is very close to that of the Pt/C catalyst (30 mV per decade).<sup>16</sup> Meanwhile, the Tafel plots of pure  $MoS_2$ , NCNFs, S-NCNFs and  $MoS_2$ -NCNFs are ~170, ~129, ~104, and ~55 mV per decade, respectively. The small Tafel slope of the S-rich  $MoS_2$ -NCNFs is advantageous for practical applications because it will lead to faster incrementation of the HER rate with increasing overpotential. The Tafel plots of S-rich  $MoS_2$ -NCNFs are higher than those reported for  $MoS_2$  based catalysts (~50<sup>4</sup> and 45<sup>17</sup> mV), suggesting the

interspatial-confinement growth method could be a promising way to prepare low-cost and highly efficient HER catalysts.

Fig. 3c shows the corresponding electrochemical impedance spectroscopy (EIS) spectra of various electrocatalysts, in order to further investigate the interface reactions and electrode kinetics of the catalysts in the HER. Nyquist plots reveal a dramatically decreased charge-transfer resistance  $(R_{ct})$  for S-rich MoS<sub>2</sub>-NCNFs (207  $\Omega$ ) relative to the MoS<sub>2</sub>-CNFs (596  $\Omega$ ), S-NCNFs (874  $\Omega$ ), NCNFs (987  $\Omega$ ) and pure MoS<sub>2</sub> (2.4 k $\Omega$ ). The small resistances observed for MoS2-NCNFs and S-rich MoS<sub>2</sub>-NCNFs indicate the importance of the synthesis of MoS<sub>2</sub> incorporated with conductive substrates, which enables simple and effective electrical integration that minimizes parasitic ohmic losses. After 1000 cycles of continuous operation, the S-rich MoS<sub>2</sub>-NCNFs catalyst shows almost negligible decay in the electrocatalytic current density (Fig. 3d), indicating excellent HER activity with reasonable long-term stability. The graphitic carbon protects the MoS<sub>2</sub> nanoplates from poisoning or delamination from the electrolyte, leading to only a slight loss in catalytic activity.

In summary, we developed a facile approach to design and fabricate S-rich small and single-layered  $MoS_2$  nanoplates grown in N-doped CNFs. It was shown that the S-rich  $MoS_2$ -NCNFs hybrid nanomaterial exhibited extraordinary HER activity, with a very low onset potential of 30 mV and a small Tafel slope of 38 mV per decade, due to synergistic effects. Graphitic carbon layers acted as a channel for transferring electrons to  $MoS_2$  in the  $MoS_2$ -NCNFs hybrid, this together with the abundant catalytic activity of the  $MoS_2$  nanoplates and pyridinic N and graphitic N, lead to excellent HER activity.

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