Edge-rich MoS2 Naonosheets Rooting into Polyaniline Nanofibers as Effective Catalyst for Electrochemical Hydrogen Evolution

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\textbf{ABSTRACT}
Conductive polymer polyaniline (PANI) with abundant protonated sites which are beneficial to hydrogen evolution reaction (HER), was applied as the support of MoS\textsubscript{2} for enhanced HER performance for the first time. The novel three dimensional (3D) HER catalyst (MoS\textsubscript{2}/PANI) was constructed with two dimensional (2D) MoS\textsubscript{2} building blocks rooting into the integrative nanowires. PANI nanofibers acted as excellent substrates for the uniform, dense and approximate vertical growth of MoS\textsubscript{2} nanosheets exposing abundant active edges. Consequently, excellent HER performance has been achieved with a low onset overpotential of 100 mV and a small Tafel slope of 45 mV dec\textsuperscript{-1}. Most importantly, it only needed 200 and 247 mV overpotential to reach the current density of 30 and 100 mA/cm\textsuperscript{2} respectively. Additionally, MoS\textsubscript{2}/PANI has achieved superior stability over other MoS\textsubscript{2}-polymer-based HER electrocatalyst. In general, for the first time, employing PANI for the construction of the edge-rich integrative hybrid has successfully achieved an outstanding HER performance.

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1. Introduction

Hydrogen is a promising clean and sustainable energy carrier to substitute the traditional fossil fuels, then alleviate the energy crisis and environmental pollution [1–3]. Electrochemical splitting water is an efficient and clean technology [4]. Although the most efficient electrocatalysts for hydrogen evolution reaction (HER) are Pt-group metals, their high cost and resource scarcity hinder the practical application [5,6].

The hydrogen binding energy of MoS\textsubscript{2} has been identified to be close to that of Pt-group metals by density functional theory calculations [7–9], and MoS\textsubscript{2} has been confirmed to be the talented alternative for Pt as active, acid-stable and non-noble HER electrocatalyst [10,11]. By experimental together with computational studies [12,13] and direct experimental comparison reported recently [14], the catalytic activity of MoS\textsubscript{2} has been verified to stem mainly from the edges rather than the basal surface. In consequence, many investigations with the aim of exposing more active edges have been reported [15–18]. Unfortunately, MoS\textsubscript{2} appears to be stacking due to the unstable thermos-dynamically and van der Waals interactions therefore the number of active sites should be decreased [19,20]. To obstacle the agglomeration and disperse MoS\textsubscript{2} nanosheets for maximum edges exposure, kinds of substrates have been utilized, such as (carbon nanotubes) CNTs [21], graphene [22,23], amorphous carbon [24], carbon cloth [25,26] etc.

Conducting polymers have been widely used as matrix in relative electrochemical fields [27–33] due to their low cost, easy preparation, large electrochemical surface area as well as good stability [34,35]. Furthermore, unlike most materials with fixed morphology such as graphene, CNT and carbon fiber, conducting polymers have kinds of variable morphologies, which implies further regulation for enhanced performances for different applications [36–40]. In this work, we employed polyaniline (PANI) with the morphology of nanowire to construct the hierarchical integrative hybrid with MoS\textsubscript{2} (MoS\textsubscript{2}/PANI). A novel three dimensional (3D) HER catalyst with MoS\textsubscript{2} nanosheets rooting into PANI has been fabricated. And PANI nanofibers as excellent substrates have successfully realized the dense, uniform and approximate vertical growth of MoS\textsubscript{2} nanosheets with great exposure of active edges. On the other hand, effective proton adsorption facilitates the overall HER kinetics [41,42]. Herein PANI was chosen for its abundant protonated sites [43,44] and excellent adsorption ability [45,46]. The presence of numerous protons in close vicinity of active sites contribute significantly to the superior HER performance. Finally, a low onset overpotential of 100 mV and
a small Tafel slope of 45 mV dec\(^{-1}\) have been achieved. Most importantly, it only needed 200 and 247 mV overpotential to reach the current density of 30 and 100 mA/cm\(^2\) respectively. Additionally, excellent stability has been acquired by this 3D HER catalyst.

2. Experimental Section

2.1. Reagent

Commercial Pt/C (20 wt%), (NH\(_4\))\(_6\)Mo\(_7\)O\(_24\) \(\cdot\) 4H\(_2\)O and Nafion (5 wt%) were purchased from Alfa-Aesar. Aniline was obtained from Xilong Chemicals (Guangdong, China) and distilled before use. HCl, (NH\(_4\))\(_2\)S\(_2\)O\(_8\), H\(_2\)SO\(_4\) and thiourea were purchased from Beijing Chemicals, China. Unless otherwise stated, reagents were of analytical grade and used as received. All aqueous solutions were prepared with doubly distilled water from a Millipore system (>18 M\(\Omega\) cm).

2.2. Synthesis of Mo\(_2\)S\(_2\)/PANI

1.3 g (NH\(_4\))\(_6\)Mo\(_7\)O\(_24\) \(\cdot\) 4H\(_2\)O and 3.34 g aniline were dissolved in 40 mL water, and aqueous HCl (1 M) was dropwise added to adjust pH to 4-5 until white precipitate appeared. After stirring at 50 °C for 2 hours, the white product of Mo\(_3\)O\(_{10}\)\(\cdot\)(C\(_6\)H\(_8\)N\(_2\))\(_2\) \(\cdot\) 2H\(_2\)O was collected by centrifugation and dried at 50 °C subsequently. Then 0.34 g Mo\(_3\)O\(_{10}\)\(\cdot\)(C\(_6\)H\(_8\)N\(_2\))\(_2\) \(\cdot\) 2H\(_2\)O and 0.50 g (NH\(_4\))\(_6\)Mo\(_7\)O\(_24\) \(\cdot\) 4H\(_2\)O were mixed with 0.57 g (NH\(_4\))\(_2\)S\(_2\)O\(_8\) in 40 mL water and 1 M HCl was added to adjust pH to about 2. After stirring vigorously for

Fig. 1. (a) SEM image of Mo\(_2\)S\(_2\)/PANI, inset: high-magnification SEM image of Mo\(_2\)S\(_2\)/PANI; (b) SEM image of pure Mo\(_2\)S\(_2\); (c) TEM image of Mo\(_2\)S\(_2\)/PANI (inset: the corresponding HRTEM image); (d) TEM image of pure Mo\(_2\)S\(_2\); (e) STEM image of Mo\(_2\)S\(_2\)/PANI and the corresponding elemental mapping images of C, N, Mo, and S.
6 hours, dark green MoO$_3$/PANI was collected by centrifugation and then dried at 50°C. After this, 0.40 g MoO$_3$/PANI nanowires were dispersed in 20 mL water containing 0.30 g thiourea, then transferred to a 40 mL Teflon-lined stainless-steel autoclave and treated at 200°C for 48 h. The product hierarchical MoS$_2$/PANI nanowires were collected by centrifugation then thoroughly washed with water and ethanol several times and finally dried at 50°C overnight.

Pure MoS$_2$ for contrast experiments was synthesized as following. 0.40 g (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O was introduced in 20 mL water containing 0.50 g thiourea, then transferred to a 40 mL Teflon-lined stainless-steel autoclave and treated at 200°C for 48 h. Pure MoS$_2$ was collected by centrifugation, thoroughly wash and finally drying at 50°C overnight.

Pure PANI for contrast experiments was synthesized as following. 0.3 mL aniline and 0.18 g of (NH$_4$)$_2$S$_2$O$_8$ were added in 10 mL aqueous HCl (1 M). After stirring vigorously for 6 hours, pure PANI was collected by centrifugation, thoroughly wash and finally drying at 50°C overnight.

2.3. Apparatus

Scanning electron microscope (SEM) images were taken on an XL30 ESEM FEG field emission scanning electron microscope. Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM), scanning transmission electron microscopy (STEM) and elemental mapping images were all carried out on a Fei Tecnai G2 F20 S-TWIN transmission electron microscope operating at 200 kV. X-Ray diffraction pattern (XRD) was obtained with a Siemens D5005 diffractometer with Cu Kα radiation, and was applied to investigate the crystallographic structure of the as-fabricated products. X-Ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB MKII X-ray photoelectron spectrometer with Al Kα X-ray radiation as the X-ray source for excitation. Fourier-transform infrared (FTIR) spectra of KBr powder-pressed pellets were recorded on a Bruker Vector 22 Spectrometer. The average percentage of MoS$_2$ in hybrid was determined by measuring the concentration of Mo using an inductive coupled plasma emission spectrometer (ICP, PerkinElmer OPTIMA 3300DV). The average percentages of C, H, N were measured by the combustion elemental analysis (Vario EL cube, Elementar, Germany).

2.4. Electrochemical Measurements

Catalyst inks for electrochemical testing were respectively prepared by adding 5 mg prepared sample and 20 μL Nafion solution (5 wt%) into 490 μL ethanol and 500 μL water, then treated by sonication until a homogeneous ink was obtained. After that, 5 μL catalyst ink was deposited onto a well-polished glassy carbon electrode (GCE, 3 mm in diameter) as the working electrode and dried at room temperature. All the electrochemical measurements were performed in electrolyte of 0.5 M H$_2$SO$_4$ with a three electrodes system. Apart from the decorated GCE as working

![Fig. 2](image-url) (a) XRD pattern of MoS$_2$/PANI; (b) FTIR spectrum of MoS$_2$/PANI; (c) XPS survey spectrum of MoS$_2$/PANI (inset: S 2p spectrum); (d) Mo 3d spectrum and its deconvolution.
electrode, a saturated calomel electrode (SCE) and a carbon rod were employed as the reference electrode and counter electrode, respectively.

Linear Sweep Voltammetry (LSV) was operated with a scan rate of 5 mV/s. While cyclic voltammetry (CV) was conducted with a scan rate of 100 mV/s in potential ranging from -0.2 V to 0.2 V and performed from 1000 cycles to 3000 cycles. Amperometric i-t curve was obtained at a static overpotential of 220 mV for 50000 s. The measurements above mentioned were all conducted by an electrochemical CHI 920c workstation (CH Instruments, Inc., Shanghai). All data were iR corrected determined by CHI 920c via the resistance test.

Electrochemical impedance spectroscopy (EIS) measurements were carried out with Solartron 1255B Frequency Response Analyzer (Solartron Inc., UK) with frequencies ranging from 100 kHz to 0.1 Hz at various overpotentials from 165 mV to 200 mV.

All the experiments were conducted after bubbling nitrogen for 10 min at room temperature and without activation progress. All the potentials are given with respect to RHE.

3. Results and Discussions

3.1. Characterization of MoS2/PANI

Firstly, MoO3 (C6H12N2)0.2H2O integrative hybrid nanowires were fabricated (Fig. S1). Then the 1D precursor converted to MoOx/PANI nanowires with a tougher surface and larger diameter after polymerization (Fig. S2). Finally, hierarchical MoS2/PANI nanowires were achieved by the treatment of thiourea to MoOx/PANI in hydrothermal process. SEM image of MoS2/PANI nanowires with uniform length and diameter is shown in Fig. 1a. Moreover, the uniform and dense growth of MoS2 nanosheets exhibits an outstanding edge-rich morphology. Approximately, MoS2 nanosheets root into PANI with a vertical direction (inset of Fig. 1a), which further increases the active edges exposure as reported [23–26]. Compared with the pure MoS2 nanoclusters folding themselves with lots of active edges buried inside (Fig. 1b), more active edges exposure has been achieved by PANI as excellent substrate to enfold MoS2 nanoclusters against their trend of curling up. In addition, pure PANI nanofibers synthesized without hybridization with Mo precursor have much smaller length and diameter compared with MoS2/PANI (Fig. 5a). And pure MoS2 physically mixed with pure PANI (MoS2-PANI) with the same percentage of MoS2/PANI maintains their separate nanocluster and nanofiber morphologies (Fig. 5b). Compared with the physical mix, the chemical synthesis for integrative hybridization of MoS2/PANI is essential for edge-rich MoS2 nanosheets rooting into PANI nanofibers. Furthermore, in contrast with pure MoS2 (Fig. 1d), MoS2/PANI (Fig. 1c) is confirmed to have a superior configuration accumulating thin MoS2 nanosheets into the edge-rich morphology. It’s worth noticing that two dimensional (2D) MoS2 building blocks are assembled into the nanowires forming 3D integrative hybrid. The interlayer distance of 0.62 nm between parallel lines in HRTEM image of MoS2/PANI (inset of Fig. 1c) is attributed to the (0 0 2) lattice of MoS2. The elemental mapping images of C, N, Mo, S corresponding to scanning transmission electron microscopy (STEM) image (Fig. 1e) substantiate that Mo and S elements are uniformly and intensively distributed on each PANI nanofiber.

Fig. 3. (a) Polarization curves of Pt/C, MoS2/PANI, MoS2-PANI, MoS2 and PANI (b) the polarization curves in the magnified version; (c) Tafel plots of Pt/C, MoS2/PANI, MoS2-PANI, MoS2; (d) Polarization curves of MoS2/PANI with different percentages of MoS2 in the hybrid.
To further characterize the identity and structure of MoS$_2$/PANI, XRD was measured. As shown in Fig. 2a, the characteristic peaks at 2θ = 13.62, 33.10, 57.48° correspond to the (0 0 2), (1 0 0) and (1 1 0) planes of MoS$_2$, which confirms the well-defined and hexagonally symmetric structure of MoS$_2$. Moreover, MoS$_2$/PANI composition was confirmed by FTIR spectrum in Fig. 2b. The bands at 1585 and 1498 cm$^{-1}$ are associated with the stretching vibration of quinonoid (Q) and benzenoid (B) rings, respectively [47,48]. The peaks at 1293 and 1220 cm$^{-1}$ are assigned to vC-N in Q-B-Q and B units, and those at 1128 and 815 cm$^{-1}$ are attributed to δC-H in Q and B rings. To further confirm the chemical states of PANI and MoS$_2$ in MoS$_2$/PANI, XPS was conducted. The peaks at about 395 and 285 eV in survey spectrum (Fig. 2c) are related to N 1s and C 1s, which are the characteristic peaks of PANI as reported [49–51]. Peaks in S 2p spectrum (inset of Fig. 2c) at 161.8 and 162.9 eV attributed to S 2p$_{3/2}$ and S 2p$_{1/2}$ indicate the domain oxidation state of $S^{2-}$ [52]. As shown in Mo 3d spectrum (Fig. 2d), peaks at 228.9 and 232.1 eV are assigned to Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ respectively [53–56]. Furthermore, according to the deconvolution, Mo 3d spectrum exclusively consists of Mo$^{4+}$ peaks with the co-existence of 2H and a small portion of 1T phase [57]. As reported, the presence of 1T phase plays a crucial role for the catalytic activity [58,59], therefore the coexistence of 1T phase provides a prediction of the better HER performance.

3.2. HER electrocatalytic activities of MoS$_2$/PANI

The HER catalytic activity of MoS$_2$/PANI has been evaluated by LSV measurements. Meanwhile, pure MoS$_2$, pure PANI and MoS$_2$/PANI have also been measured as comparisons. As Fig. 3a shown, the polarization curve of Pt/C exhibits the highest HER catalytic performance with a near zero onset overpotential as expected, while PANI hardly shows any HER activity. A pretty large onset overpotential of pure MoS$_2$ (190 mV) as reported has been achieved [22,24,54,60]. Compared with the onset overpotential of pure MoS$_2$ and MoS$_2$/PANI (160 mV), MoS$_2$/PANI shows a much smaller one of 100 mV, which is clearly shown by the polarization curves in the magnified version (Fig. 3b). Moreover, further negative potential leads to rapidly increased cathodic current density. To afford current density of 30 and 100 mA/cm$^2$, MoS$_2$/PANI only needs overpotential of 200 and 247 mV, respectively. Much higher catalytic activity of MoS$_2$/PANI has been achieved in contrast with that of MoS$_2$ and other transition metal dichalogenides (TMDs) [61–63], which can be ascribed to the great active edges exposure configuration with the participation of PANI. The onset overpotential of MoS$_2$/PANI as well as the overpotentials to reach the particular current densities are quite low compared with those of other MoS$_2$-based HER electrocatalysts (MoS$_2$ on varied conductive substrates) as shown in Table 1. It substantiates that PANI as support can rival high conductive substrates applied in HER, such as graphene [23,36,64,65], CNTs [18,21], carbon nano- [60,66], carbon cloth [26], even metals like nanoporous gold [55] and molybdenum [67]. In addition, the efficient hydrogen generation is presented by the photograph of Fig. 5a.

The Tafel plots, which are recorded with the linear regions fitted into the Tafel equation, yielding Tafel slopes of 30 mV dec$^{-1}$ for Pt/C, 45 mV dec$^{-1}$ for MoS$_2$/PANI, 82 mV dec$^{-1}$ for MoS$_2$/PANI and 121 mV dec$^{-1}$ for pure MoS$_2$ as previously reported [22,24,54,60] (Fig. 3c). The drastically reduced Tafel slope of the integrative hybrid indicates the significant improvement of the electrocatalytic activity. As reported, Tafel slope value can also imply the mechanism of hydrogen reduction on cathodes [68]. In acid solutions, three principal reaction steps as following, Eq. (1) to (3) are involved with Tafel slopes of 120, 40, 30 mV dec$^{-1}$ respectively [56,69]. Based on this point, Tafel slope of 45 mV dec$^{-1}$ obtained by MoS$_2$/PANI corresponds to the Volmer-Heyrovsky mechanism with Heyrovsky reaction as the rate limiting step [68]. Besides, the numerous protonated sites [43,44] and excellent proton adsorption ability [45,46] of PANI not only indicate the fast formation of catalyst-H therefore the rate limiting role of Heyrovsky step, but also accelerate the Heyrovsky reaction which greatly contributed to the small Tafel slope of MoS$_2$/PANI.

Volmer reaction: H$_2$O$^+ + e$ + catalyst $\rightarrow$ catalyst-H$^+$ + H$_2$O

Heyrovsky reaction: H$_2$O$^+ + e$ + catalyst-H$^+$ $\rightarrow$ catalyst$^-$ + H$_2$ + H$_2$O

Tafel reaction: catalyst-H$^+$ + catalyst-H$^-$ $\rightarrow$ 2catalyst + H$_2$

Table 1

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Onset $\eta$ (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>Current density (j, mA cm$^{-2}$)</th>
<th>$\eta$ at the corresponding j (mV)</th>
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<td>MoS$_2$/MoS$_2$ core-shell nanowires</td>
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<td>272</td>
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<td>200</td>
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<td>MoS$_2$ nanosheets/CNTs composite</td>
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<td>44.4</td>
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<td>95</td>
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<td>10</td>
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<td>MoS$_2$ nanoplates within carbon nanofibers</td>
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<td>$\sim$230</td>
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This work
Moreover, the effect of the percentage of MoS$_2$ in MoS$_2$/PANI on the HER performance was explored. The percentage of MoS$_2$ in MoS$_2$/PANI was determined to be 79.6% by ICP with the C, H, N percentage of 15.1%, 1.5%, and 3.4% respectively measured by the combustion elemental analysis. MoS$_2$ hybrid with other percentages of 62.6%, 72.3% and 82.9% present inferior HER performances as shown in Fig. 3d, suggesting 79.6% is the optimal percentage in our experiment. Increased percentage with more MoS$_2$ nanosheets brought more exposed active edges, which can enhance the HER performance. However, too many MoS$_2$ nanosheets may hinder the edge exposure therefore draw back the HER activity.

The electrode kinetics of HER catalyzed by the MoS$_2$/PANI was investigated by the electrochemical impedance spectroscopy (EIS). Experimental data were fitted using an equivalent circuit model shown in Fig. 4a. It consists of a resistor (R$_s$) in series with two parallel units of resistor and capacitor [70–72], in which R$_1$ represents the uncompensated solution resistance while R$_ct$ corresponds to charge transfer resistance arisen from HER. The constant unit, R$_s$ and CPE$_1$, is probably related to the contact between the GCE and the catalyst [73]. In Nyquist plots shown in Fig. 4b and c, empty patterns represent the experiment data and solid line for fitted curve. As the Nyquist plots in Fig. 4b shown, R$_s$, R$_ct$ of MoS$_2$, MoS$_2$/PANI and MoS$_2$/PANI under 200 mV overpotential are 421.65, 228.71 and 70.92 Ω, respectively. Under the proton reduction potential, lower R$_ct$ value reflects more efficient electron transfer at the interface between MoS$_2$/PANI and electrolyte, therefore more efficient hydrogen generation. The effect of PANI is presented by the lower R$_ct$ of MoS$_2$/PANI compared with that of MoS$_2$. As is well known, PANI acted as protonated emeraldine salts with numerous protonated sites [43,44]. Moreover, nitrogen sites with electron donating ability as basic sites [74,75] has excellent adsorption capacity [45,46]. Nitrogen has been involved to facilitate the proton adsorption for enhanced HER performance recently [76]. Herein, numerous protonated basic sites and protons effectively and continuously adsorbed by nitrogen sites in the non-catalytic PANI contributed to the effect electron transfer and the efficient hydrogen generation reaction. Furthermore, the much lower R$_ct$ of MoS$_2$/PANI compared with that of MoS$_2$–PANI and pure MoS$_2$ should result from the hybrid’s morphology exposing abundant active edges which fully contacted with the electrolyte and make the electron transfer between the catalyst and electrolyte more efficiently. Besides, the Nyquist plots of MoS$_2$/PANI at different overpotentials are shown in Fig. 4b. The R$_ct$ are 404.48, 323.19, 193.90, 109.64 and 70.92 Ω corresponding to overpotential of 165, 170, 180, 190 and 200 mV, respectively. It indicates that at increased overpotential, more rapid electron transfer and more efficient hydrogen generation took place, as illustrated by the polarization curve of MoS$_2$/PANI (Fig. 3a). Moreover, the Tafel slope can be derived from the plot of overpotential versus log (R$_ct$) (Fig. 4d, inset) [70–72], and determined to be 45.28 mV dec$^{-1}$ which agrees well with that obtained from polarization curve. It worth noticing that the Tafel slope obtained this way reflects the electrode kinetics better than those obtained from the polarization curve.

Additionally, stability is an essential issue for evaluating an advanced electrocatalyst considering the practical application. First, we employed CV measurement for this investigation. Fig. 3a shows the polarization curves of MoS$_2$/PANI initial and after 1000,
2000 and 3000 CV cycles. The slight decays and the gradually reduced deterioration (inset of Fig. 5a) in current density suggest the high stability of MoS$_2$/PANI. In addition, the time-dependent current density curve of MoS$_2$/PANI (Fig. 5b) at a cathodic current density of 50 mA/cm$^2$ shows slight degradation during this 50000 s. It confirms the strong binding between MoS$_2$ nanosheets and PANI under a long-term bubbles-generation-release condition. Herein, MoS$_2$/PANI exhibits superior stability over the previously reported polypyrrole/MoS$_2$ [33]. It mainly ascribes to the strong mechanical interaction between MoS$_2$ nanosheets and PANI, which were assembled together integrally.

4. Conclusions

PANI with numerous protonated sites which are beneficial to HER has been first applied as the support of MoS$_2$ for enhanced HER performance in this work. Novel 3D HER catalyst MoS$_2$/PANI is constructed with MoS$_2$ nanosheets rooting into the PANI nanowires integrally. With the participation of PANI as substrate, the hierarchical integrative hybrid has realized the edge-rich morphology of uniform, dense and approximate vertical alignment of MoS$_2$ nanosheets. Consequently, MoS$_2$/PANI has achieved an excellent HER activity with a low onset overpotential of 100 mV and a small Tafel slope of 45 mV dec$^{-1}$. It’s worth to note that it only needed 200 and 247 mV overpotential to reach the current density of 30 and 100 mA/cm$^2$ respectively. The outstanding HER catalytic activity of MoS$_2$/PANI confirmed the successful application of PANI in HER electrocatalyst, which can rival other high conductive substrates like graphene, CNTs, carbon cloth, carbon nanofiber, even metals like gold or molybdenum etc. Furthermore, MoS$_2$/PANI has achieved superior stability over other MoS$_2$-polymer-based HER electrocatalyst.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2015.08.108.

Fig. 5. (a) Polarization curves for MoS$_2$/PANI initially and after 1000, 2000 and 3000 cycles (inset: the polarization curves in the magnified version); (b) Time-dependence of cathodic current density curve for MoS$_2$/PANI under 220 mV static overpotential for 50000 s.

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