Molybdenum Sulfide/N-Doped CNT Forest Hybrid Catalysts for High-Performance Hydrogen Evolution Reaction

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Supporting Information

ABSTRACT: Cost effective hydrogen evolution reaction (HER) catalyst without using precious metallic elements is a crucial demand for environment-benign energy production. Molybdenum sulfide is one of the promising candidates for such purpose, particularly in acidic condition, but its catalytic performance is inherently limited by the sparse catalytic edge sites and poor electrical conductivity. We report synthesis and HER catalysis of hybrid catalysts composed of amorphous molybdenum sulfide (MoS₂) layer directly bound at vertical N-doped carbon nanotube (NCNT) forest surface. Owing to the high wettability of N-doped graphitic surface and electrostatic attraction between thiomolybdate precursor anion and N-doped sites, ~2 nm scale thick amorphous MoS₂ layers are specifically deposited at NCNT surface under low-temperature wet chemical process. The synergistic effect from the dense catalytic sites at amorphous MoS₂ surface and fluent charge transport along NCNT forest attains the excellent HER catalysis with onset overpotential as low as ~75 mV and small potential of 110 mV for 10 mA/cm² current density, which is the highest HER activity of molybdenum sulfide-based catalyst ever reported thus far.

KEYWORDS: Molybdenum sulfide, carbon nanotubes, hydrogen evolution, catalyst, doping

Hydrogen is a promising alternative energy carrier that holds great promise for clean and sustainable energy technology.¹ Electrochemical water splitting by clean energy source or direct photoelectrolysis is attracting enormous research attention for efficient and eco-friendly generation of hydrogen.²⁻⁴ Unfortunately, relatively large thermodynamic overpotential for HER inherently deteriorates the overall energy conversion efficiency. In this regard, various catalyst materials, including Pt and noble analogues, have been exploited to minimize the energy barrier. However, those expensive rare earth materials are generally inappropriate for conventional energy conversion devices.⁵

Recently, molybdenum sulfide featuring unique electronic and optical properties⁶⁻¹⁰ is found to be an active nonmetallic HER catalyst, which is potentially useful for acidic HER condition with abundant protons.¹¹⁻¹⁵ While crystalline MoS₂ features HER catalytic sites along the edge of two-dimensional sheet,¹⁶ amorphous MoS₂ shows catalytic activity at the unsaturated sulfur atoms existing over the entire surface.¹⁴,¹⁷ For the further progress of molybdenum sulfide-based HER catalysts, the foremost issue is how to expose and stabilize more catalytic active sites at external surface.¹⁸⁻²¹ Previous research efforts have revealed that two-dimensional crystalline MoS₂ platelets readily stack parallel at catalytic support surfaces. Consequently, the effective catalytic sites located along platelet edges are hardly exposed externally. By contrast, amorphous MoS₂ possesses abundant catalytic sites over entire surface consisting of uncoordinated sulfur atoms with negative charges, which facilitate proton adsorption and conversion into H₂. Nonetheless, due to the intrinsic low electrical conductivity, amorphous MoS₂ catalysts suffer from retarded electron transport while undergoing HER reaction, which may severely deteriorate the overall electrocatalytic performance.²²⁻²⁹

In this work, we report highly HER active MoS₂/NCNT forest hybrid catalysts via straightforward low-temperature precursor decomposition. Our hybrid catalyst has an ideal morphology that ~2 nm scale thick amorphous MoS₂ catalysts are densely bound at electro-conductive NCNT forest, vertically standing on glassy carbon substrate. Unlike widely used oxygen functionalization, which severely damages the electrical properties of graphitic carbons, electron-rich N-doping provides additional electrons to graphitic carbons to maintain high electroconductivity. Moreover, while pristine graphitic carbon surface has a low surface energy and chemical inertness, the N-doped graphitic plane³⁰⁻³⁴ with electro-negative, readily protonated N shows greatly improved surface energy and intrigues favorable reaction affinity for MoS₂ precursor molecules without any intermediate adhesive layer.³⁵,³⁶ Besides, vertical NCNTs robustly bound at the
bottom glassy carbon substrate offer fluent charge transport pathway directly connecting MoS$_x$ catalyst and external electrochemical electrodes. Taking advantage of the synergistic structure our hybrid catalyst exhibits outstanding HER catalytic activity with a low overpotential of $\sim 75$ mV.

Vertical NCNT forest were grown on SiO$_2$/Si substrate by plasma-enhanced chemical vapor deposition (PECVD) under NH$_3$ environment (see Supporting Information for synthetic details) and transferred onto glassy carbon electrode substrates (Supporting Information Figure S1). The mirror-polished glassy carbon was chosen as the substrate material considering its inertness to HER activity as well as strong chemical resistance to corrosion. The electrical contact between NCNT forest and glassy carbon substrate was confirmed to be ohmic by conduction AFM measurement (Supporting Information Figure S2). For MoS$_x$ deposition, the template NCNT forest were immersed in aqueous HCl solution (pH = 5) for 30 min and ammonium tetrathiomolybdate ((NH$_4$)$_2$MoS$_4$) precursor solution was injected into the solution. The mixture solution was kept at 90°C for precursor decomposition. The hybrid catalyst formation process is schematically illustrated in Figure 1a. Thiomolybdate anions are adsorbed on the NCNT wall by electrostatic interaction and decomposed into amorphous MoS$_x$ at the elevated temperature. Notably, the mechanical contact between NCNT root and bottom glassy carbon substrate is strong enough to withstand the wet chemical reaction. Field-emission scanning electron microscopy (FE-SEM) images in Figure 1b,d contrast the morphological change of NCNT forest before and after MoS$_x$ deposition. Smooth NCNT surfaces are roughened with MoS$_x$ catalyst layer with $\sim 2$ nm thickness. Vertical NCNT forest retains the large surface area during MoS$_x$ deposition without any collapse or aggregation of NCNT strands (Figure 1c). As such, this three-dimensional catalyst/electrode hybrid structure demonstrates an ideal morphology with maximum catalytic surface area and fluent charge transport pathway to external electrode. Moreover, its nanoscale morphology ensures fluent transport of reactants and products among individually separated vertical catalyst strands.

Figure 1e,f shows transmission electron microscopy (TEM) images of pure NCNT and typical MoS$_x$/NCNT hybrid catalyst, respectively. Amorphous MoS$_x$ catalysts are uniformly distributed along NCNT strand. Interestingly, tiny crystal domains with typical size of less than 5 nm are observed in the amorphous MoS$_x$ layer (Figure 1f inset). Fringe lattice spacing of the crystal is 0.27 nm, which is consistent with lattice spacing of (100) plane of crystalline MoS$_2$ (Supporting Information Figure S3a). The TEM observation clarifies that the NCNT strands are coated with amorphous MoS$_x$ embedded with tiny MoS$_2$ crystalline domains. Significantly, such an amorphous MoS$_x$ with dense unsaturated S atoms expose dense catalytic sites over entire surface. However, amorphous MoS$_x$ has an intrinsic low electrical conductivity, which may bottleneck the charge transport during electrocatalysis. TEM observation also reveals that the nanoscale MoS$_x$ catalysts are intimately
contacted with NCNT surface, which is highly desired for direct charge transfer from NCNTs to catalytic sites.

We also carried out thermal annealing of the hybrid catalysts at 600 °C under H2/Ar environment. As shown in TEM image of Figure 1g, MoS2 layer is transformed into few-layer stacked MoS2 nanosheets. MoS2 formation could be also confirmed by Raman spectroscopy (Supporting Information Figure S4). Fast Fourier transform (FFT) pattern (the upper inset of Figure 1g) taken from selected area verifies the MoS2 crystal structure. The lattice spacing of 0.67 and 0.27 nm is measured, which is consistent with the interlayer spacing of MoS2 sheets and crystal lattice spacing within MoS2 plane, respectively (Supporting Information Figure S3b,c). Additionally, X-ray diffraction (XRD) illustrates typical diffraction peaks for (002) and (100) planes of MoS2. Because of the limited number of layer stacking, the diffraction peak intensity for (200) is much weaker than that of (100) plane (Supporting Information Figure S5). TEM observation (Figure 1g) confirms that double layer stacking is dominant.

X-ray photoelectron spectroscopy (XPS) was utilized to characterize the chemical nature and bonding state of MoS2 at NCNT surfaces (Figure 2a). The binding energy of Mo S 2p2/3 = 162.0 and 163.3 eV.37 Our XPS result verifies amorphous MoS2 phase formation. Energy dispersive X-ray spectrometry (EDX) line scanning profile was performed to examine the elemental distribution (Figure 2b). S elements are principally distributed near two side walls of NCNT strand. Besides, Mo and N element signals are also detected. The comparison of the peak intensities between Mo and S shows that the S element is much more than two times the Mo element. This amorphous MoS2 formation results from the decomposition of ammonium tetrathiomolybdate precursor at the relatively low temperature of 90 °C. The precursor decomposition is also accompanied with the oxidation of S2− ligands, the reduction of Mo metal as well as the thermal decomposition of intermediates.37 In comparison to the as-synthesized MoS2, the thermally annealed one shows different XPS spectrum, as shown in Figure 2a. The S 2p peak is shifted to a lower binding energy while an additional peak grows at 163 eV. This is consistent with the typical XPS spectrum of crystalline MoS2.26

The crucial role of N-dopants for MoS2 deposition could be illustrated by control experiment employing pristine CNTs without heteroatom doping (experimental detail is described in Supporting Information). Figure 3a and its inset figures contrast the morphology change after molybdenum sulfide deposition at pristine CNT and NCNT surfaces, respectively. While small MoS2 patches are sparsely deposited at pristine CNT surface, nanoscale thick MoS2 layer is densely coated at NCNT surface. Figure 3b exhibits the difference of XPS profile between pristine CNT forest and NCNT forest. Owing to the N-doping, NCNT possesses not only better wettability but also more favorable interaction with precursor molecules.39–43 As illustrated in Figure 3c, the protonation of lone-pair electrons at pyridinic N-doping sites can attract thiomolybdate anions by straightforward electrostatic attraction. The attracted thiomolybdate anions can be subsequently decomposed into amorphous MoS2 while the nucleation barrier for molybdenum sulfide formation is significantly reduced at the slightly elevated reaction temperature of 90 °C.

The electrochemical HER tests are performed using three-electrode setup in the acidic condition of 0.5 M H2SO4 solution (see Supporting Information for details). We note that all polarization curves are not corrected for iR loss. Typical polarization curve (I−V plot) demonstrates that MoS2/NCNT forest hybrid electrode presents a low onset overpotential (η) of ∼75 mV versus RHE for taking off HER activity (Figure 4b). Further negative potential induces rapid rise of cathodic current. The HER performances of commercial Pt/C catalyst, amorphous MoS2, and bare NCNT forest are compared in the same experimental setup (see Supporting Information for synthesis approach). Commercial Pt/C catalyst shows the highest HER activity with negligible overpotential. Amorphous MoS2 exhibits HER activity but the low electrical conductivity limit the HER performance particularly in terms of current density. As a typical reference metric for electrochemical catalytic performance, the potential value for 10 mA/cm2 current density is frequently employed, while applying less than 200 mV overpotential.17 Our hybrid catalysts only require ∼110 mV to achieve 10 mA/cm2, which is far better than any other molybdenum sulfide-based HER catalysts ever reported so far.14,17,22–27,39

To understand the detailed underlying mechanism of HER activity, Tafel plots based on polarization curves are acquired, as shown in Figure 4c. The linear regions of Tafel plots were fit to
The Tafel equation \( \eta = b \log j + a \), where \( j \) is the current density and \( b \) is the Tafel slope, is used to obtain slope, \( b \). Tafel slopes of 34, 40, and 60 mV/decade are obtained for commercial Pt/C catalyst, MoS\(_x\)/NCNT hybrids, and amorphous MoS\(_x\), respectively. The small Tafel slope of MoS\(_x\)/NCNT forest hybrid is advantageous for practical catalytic application, since it leads to a rapid increase of HER rate with overpotential. In general, three principal steps can be involved in a HER, as usually noted by Volmer, the Heyrovsky, and the Tafel steps. If the Volmer step associated with proton absorption is rate-determining, a slope of \( \sim 120 \) mV/decade should be obtained, while Heyrovsky and Tafel steps should give \( \sim 40 \) and \( \sim 30 \) mV/decade, respectively. Accordingly, the HER mechanism of our hybrid catalyst follows Volmer–Heyrovsky reaction where electrochemical desorption is the rate-determining step. The low Tafel slope of our hybrid catalyst is attributed to the strong electronic coupling between nanoscale thin MoS\(_x\) catalyst and NCNT surface. The fluent charge transport could also be characterized by electrochemical impedance spectroscopy (EIS), as shown in Figure 4d. MoS\(_x\)/NCNTs hybrid catalyst shows much lower charge transfer resistance than pure amorphous MoS\(_x\). Exchange current densities of various samples were also obtained by the extrapolation of Tafel plots (Supporting Information Figure S6 and Table S1). As listed in Supporting Information Table S1, MoS\(_x\)/NCNT displays the largest exchange current density of 33.11 \( \mu \)A cm\(^{-2}\).

The intrinsic per-site activity of a catalyst is an important metric to evaluate a catalyst material. We used electrochemical capacitance surface area measurements to estimate the active surface area of the catalyst film, which was further used to calculate the average activity of each site, namely, a per-site turnover frequency (TOF) (detail calculation provided in the Supporting Information). As summarized in Supporting Information Table S2, the density of electrochemically accessible site of MoS\(_x\)/NCNT forest hybrid catalyst is estimated to be \( \sim 9.8 \times 10^{16}/\text{cm}^2 \). The corresponding TOF for each active site is calculated to be as high as 3.5 s\(^{-1}\) at \( \eta = 200 \) mV versus RHE and pH = 0.

We also investigated on the HER performance of MoS\(_2\)/NCNT forest hybrid catalysts obtained after thermal annealing at 600 °C (see Supporting Information for more details, Figure S8). The HER performance has been noticeably degraded from the original amorphous MoS\(_x\) based catalyst. Crystalline MoS\(_2\) sheets stack parallel with NCNT surface such that catalytically inactive basal planes are predominantly exposed at surface instead of active edge sites.

Catalytic stability is another significant criterion for HER catalysts. The catalytic stability of our MoS\(_x\)/NCNT forest catalyst is characterized by continuous cyclic voltammetry performed between \( \sim 0.2 \) and 0.2 V vs RHE at 50 m/s scan rate (Figure 4e). Only a minor deterioration of cathodic current is observed after 1000 cycling. By contrast, MoS\(_2\)/CNT catalyst without N-doping shows serious fade of HER activity in the...
same condition (Figure 4f). In general, the durability of supported catalyst is known to strongly depend on the catalyst-support interaction. 49,50 Previous simulation and experimental results have established that strong interaction of d-orbital of transition metal with the p-orbital of N-dopants may give rise to robust bonding. 49,51-53 It is noteworthy that due to the low wettability and no specific functional groups at pristine CNT forest, MoS$_x$ was principally deposited at the top surface of CNT forest. Accordingly, the initial HER performance of MoS$_x$/CNT is much inferior to that of MoS$_x$/NCNT hybrid catalyst.

We have demonstrated facile wet chemical synthesis and remarkable HER activity of MoS$_x$/NCNT forest hybrid catalysts. N-dopants at graphitic surfaces strongly interact with anionic precursors to generate dense nanoscale amorphous MoS$_x$ layer via simple low-temperature solution process. The best HER catalytic activity with a low over-potential is obtained among molybdenum sulfide based catalysts reported thus far. The synergistic interplay between the nanometer thick amorphous MoS$_x$ layer with dense catalytic active sites and the carefully engineered NCNT forest electrodes attained such a noticeable catalytic performance. Moreover, NCNT offers excellent durability to the composite catalyst; a critical criteria for any supported catalyst. Our approach offers a general route to idealized N-doped graphitic carbon based nanohybrid catalyst structures, which can be widely useful for nonmetallic catalysts suffering from limited catalytic surface area and ineffective electron transport.

**ASSOCIATED CONTENT**

* Supporting Information

Experimental, methods, additional SEM and photo images, and additional measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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