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Vertically Oriented MoS$_2$ and WS$_2$ Nanosheets Directly Grown on Carbon Cloth as Efficient and Stable 3-Dimensional Hydrogen-Evolving Cathode

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Abstract

Development of non-noble-metal based hydrogen-evolving catalysts is essential to practical application of water-splitting devices. Improvement of both the activity and stability of such catalysts remains a key challenge. In this work, a simple solvothermal method is developed to directly grow MoS$_2$ and WS$_2$ on carbon cloth with vertically oriented nanosheet layers. With the unique layer orientation that maximally exposes active edge sites as well as a rapid release of small gas bubbles to maintain large working area, such prepared 3-dimensional electrodes exhibit high activity towards HER. In the meantime, they also exhibit prominent electrochemical durability thanks to the strong bonding between the nanosheet layers and the substrate along with the self-removal of the as-formed H$_2$ bubbles from the nano-porous electrode surface.
Hydrogen generation through water electrolysis has being extensively investigated as an attractive way to store energy from renewable sources.\textsuperscript{1, 2} The most effective electrocatalytic materials for the hydrogen evolution reaction (HER) are Pt group metals, but their high cost and scarcity limits the widespread use.\textsuperscript{3} As such, developing efficient and inexpensive HER catalysts with high stability are highly desirable but remain challenging. By far, both theoretical and experimental studies have highlighted the great promise of layered transitional-metal dichalcogenides (LTMDs), such as molybdenum disulfide (MoS\textsubscript{2}) and its derivatives, as efficient and low cost catalysts for hydrogen evolution.\textsuperscript{4-7} Tungsten disulfide (WS\textsubscript{2}) has an analogous structure to MoS\textsubscript{2} and these compounds share similar physical and chemical properties. Thus WS\textsubscript{2} has also received some attention as an electrocatalyst for HER for almost 20 years.\textsuperscript{8-11}

Since the edges of MoS\textsubscript{2} were identified as active sites for HER,\textsuperscript{12} a lot of research efforts have been focused on the growth of MoS\textsubscript{2}/WS\textsubscript{2} nanostructures that maximally expose active edge sites for large-scale application.\textsuperscript{13-16} Previously, Cui et al. first demonstrated thin film structured HER electrode with vertically aligned MoS\textsubscript{2} molecular layers grown on flat substrates.\textsuperscript{17} Later, the same approach was extended to the growth of MoSe\textsubscript{2} on rough and curved surfaces in an attempt to increase the exposed edges,\textsuperscript{18} as the number of the exposed edge sites is still limited on the flat substrates. Unfortunately, the fabrication process of the nanostructured HER electrodes is rather complicated and also difficult to control. Recently, Jiang et al. successfully demonstrated the construction of vertically aligned MoS\textsubscript{2} nanoplatelets electrode with a “superaerophobic” surface, which allows efficient removal of gas bubbles and ensures high electrochemical activity.\textsuperscript{13} Unfortunately, the use of expensive flat Ti foil as a substrate seems to limit the maximal exposure of active sites as well as its scalable application due to the high cost. Carbon cloth (CC), an easily available and cheap carbon fiber, is highly conductive and flexible. Its use as electrode support bears the intrinsic benefits of low cost, robustness and self-standing 3D structure. Although 3D electrodes composed of WS\textsubscript{2} or MoS\textsubscript{2} nanoparticles on carbon cloth have been reported, there is no report on the directly growth of vertical aligned MoS\textsubscript{2} nanoplatelets on carbon cloth which is of great significance for practical application of water-splitting devices.

Herein, we demonstrate a simple way to fabricate vertically oriented MoS\textsubscript{2} and WS\textsubscript{2} nanosheet thin films grown on CC as efficient 3D electrodes for HER (detail available in the Supporting Information). Thanks to the nanostructured films composed of vertically aligned layers, resulting in large number of exposed active edges and timely repelling of as-formed H\textsubscript{2} bubbles, the well-designed 3D electrodes showed much higher electrochemical activities than flat MoS\textsubscript{2} and WS\textsubscript{2} nanosheet on CC.
Figure 1a&b show the low-magnification scanning electron microscopy (SEM) images of MoS\(_2\)/CC (a) and WS\(_2\)/CC (b), indicating the entire surface of the CC was uniformly covered with a layer of MoS\(_2\)/WS\(_2\) nanosheet film. These films possessed a porous structure with only ~100 nm in depth (Figure S1, as indicated by the black arrows). The high-magnification SEM images (insets of Figure 1a&b) further reveal that such MoS\(_2\)/WS\(_2\) nanosheets are vertically aligned on the CC surface, possessing a lateral size of around 200-300 nm. The corresponding energy dispersive X-ray (EDX) spectra (see Figure S2) suggest that the atomic ratio between Mo/W and S is close to 2:1. CC is a porous 3D electrode consisting of carbon fiber of 8 \(\mu\)m in diameter (see Figure S3). The highly textured surface of the carbon fiber facilitates the nucleation and growth of a sulfide layer with strong mechanical interaction. It is noted that, after annealing at 350 °C for 2 h, the 2D nanosheet morphology is intact and the 3D porous architectures are well retained (Figure S4a&b). Figure1c&d are representative transmission electron microscopy (TEM) images of the MoS\(_2\) and WS\(_2\) nanosheet films, respectively, showing good agreement with SEM observation (Figure 1a&b). The light contrast in various areas of the TEM image indicates the thin two-dimensional (2D) nature. Moreover, the high-resolution (HR) TEM image (inset of Figure 1c) of the curled edge shows those MoS\(_2\) nanosheets are composed of 7-10 layers (4-6 nm) with an interlayer spacing of 0.67 nm, while the WS\(_2\) nanosheets show a thickness of ~ 10 nm with an interlayer distance of 0.62 nm (inset of Figure 1d), verifying the ultrathin nature of these vertically oriented MoS\(_2\)/WS\(_2\) nanosheets. Figure 1e&f show the SEM images and the corresponding EDX elemental mapping images of the as-prepared MoS\(_2\)/CC and WS\(_2\)/CC electrodes, respectively, revealing that both Mo/W and S elements are uniformly distributed on the whole nanofiber.

To further characterize the chemical nature and bonding state of MoS\(_2\)/WS\(_2\) on CC surfaces, X-ray photoelectron spectroscopy (XPS) was employed. As shown in Figure 2a, two characteristic peaks arising from Mo 3d\(_{5/2}\) and Mo 3d\(_{3/2}\) orbitals are located at 229.1 eV and 232.2 eV, suggesting the dominance of Mo (IV) in the freshly prepared MoS\(_2\)/CC product. Besides, small shoulder signals for Mo (VI) oxidation state are observed. In contrast, the Mo 3d spectrum of the annealed sample shows only a single doublet. Furthermore, the S 2p\(_{3/2,1/2}\) doublet peaks for the freshly prepared MoS\(_2\) exhibit broader peaks at ~163 eV and 162 eV when compared with those of the annealed sample, indicating the existence of other binding signals, such as bridging S\(_2^2\) or apical S\(^2\), which could result from the unsaturated S atoms and are known as active sites for HER\(^{19,20}\). Thus better HER performance can be expected from the freshly-prepared S-rich MoS\(_2\) sample.

Figure 2b shows the high-resolution XPS spectra of the W 4f and S 2p regions of the WS\(_2\)/CC products. For the WS\(_2\)/CC composite after annealing, black dotted lines have been added to bisect the W 4f\(_{7/2}\), W 4f\(_{5/2}\) and
W 5p\(_{3/2}\) peaks appeared at about 33.1 eV, 35.2 eV and 38.7 eV, suggesting an oxidation state of W (IV), and the corresponding single doublet peaks for S 2p\(_{1/2}\) and 2p\(_{3/2}\) appeared at 162.4 eV and 163.6 eV, indicating the S\(^{2-}\). These peaks in the annealed WS\(_2\)/CC are identical to those of highly crystalline WS\(_2\).\(^{21}\) For the freshly-obtained WS\(_2\)/CC, the doublet peaks of W 4f and S 2p were broader than those of the annealed WS\(_2\)/CC. Besides, a small negative shift about 0.5 eV was observed, which could be attributed to the adsorption of oxygen,\(^{22}\) while the small shoulder observed at ~36 eV illustrates the existence of W (VI) at oxygen-rich environment as in WO\(_3\).\(^{23, 24}\) This indicates that the freshly-prepared WS\(_2\)/CC is more susceptible to oxidation.\(^{25}\) It has been reported that WS\(_2\) sample appear to be more susceptible to oxidation than MoS\(_2\).\(^{8}\)

For MoS\(_2\) materials, the basal edges have been identified as the active sites for HER, but unfortunately, the overall conductivity of such materials is limited due to the poor electron transport among the domains and it thus reduces the total HER activity. In this work, the vertically oriented MoS\(_2\)/WS\(_2\) nanosheet film grown on CC (a rough and curved surface) is expected to not only maximize the exposed active sites and overcome the limited electron/proton transport, but also accelerate the timely repelling of the as-formed bubbles by reducing the gas bubble adhesion due to the highly ‘super-aerophobic’ surface.\(^{12}\)

To verify our hypothesis, the HER performance of the 3D MoS\(_2\)/CC and WS\(_2\)/CC electrodes were demonstrated in 0.5 M H\(_2\)SO\(_4\) solution using a three-electrode setup, where the electrode was tested in a static state without rotation to mimic real industrial operation. Electrochemical impedance spectroscopy (EIS) reveals similar system resistance (Rs, 2.5 ± 0.3Ω) for all the tested electrodes (Figure S5). To exclude the influence of the series resistance from the system (Rs, such as wiring, solution and substrate), all of the data have been \(iR\)-corrected by subtracting the ohmic resistance loss form the overpotential. As control samples, flat MoS\(_2\)/CC and WS\(_2\)/CC film were also prepared and characterized by SEM (Figure S6) and XPS (Figure S7). As shown in Figure 3b, the cathodic polarization curve recorded for the nanostructured MoS\(_2\)/CC exhibited a low onset potential of ~0.1 V, which is much smaller than that of the flat MoS\(_2\)/CC and annealed MoS\(_2\)/CC and even lower than that of the reported Ti foil supported MoS\(_2\) nanostructure.\(^{13}\) As expected, our nanostructured MoS\(_2\)/CC electrode displays a highest current density among all the tested electrodes, 86 mA cm\(^{-2}\) at overpotential around -0.25 V. This is equivalent to ~450 mA mg\(^{-1}\) after normalized by the loading weight, which is almost two times larger than the value of the Ti foil supported MoS\(_2\) nanostructure.\(^{13}\) Since the cathodic current density is proportional to the amount of evolved hydrogen, the large current density here indicates prominent hydrogen evolution behavior of the vertically gowned
MoS$_2$/CC electrode. This may arise from the unique designed electrode structure which brings in more active sites along with the optimized conductivity and reduced gas bubble adhesion.

Interestingly, in the case of the WS$_2$/CC electrodes (Figure 3c), the annealed nanostructured WS$_2$/CC showed a highest current density (~15 mA cm$^{-2}$) among the tested WS$_2$ samples at the overpotential of 0.25 V. Although the annealed WS$_2$/CC electrode show lower activity than the nanostructured MoS$_2$/CC with 0.15 V larger overpotential to achieve cathodic current density of 86 mA cm$^{-2}$, it is still noteworthy because after normalized by the loading weight, this value (~15 mA cm$^{-2}$ at 0.25 V) is about 7 times larger than that of carbon cloth supported WS$_2$ nanoparticles$^{23}$ and even slightly higher than that of WS$_2$/rGO.$^{26}$ This is likely due to the vertically oriented feature of our WS$_2$/CC electrode. It is noted that the annealed WS$_2$/CC electrode display much higher activity than the as-prepared WS$_2$/CC, this may be attributed to the removal of inactive impurities such as WO$_3$,$^{23}$ as verified by the XPS analysis.

The Tafel plots of these catalysts are shown in Figure 3d and are used to determine Tafel slopes and exchange current densities by fitting the Tafel plots to the equation of $\eta = b \log(j) + \log(j_0)$, where $\eta$ is the overpotential, $j$ the current density, $j_0$ the exchange current density, and $b$ the Tafel slope.$^{27}$ The fitted Tafel plot for the nanostructured MoS$_2$/CC gives a $b$ value of 50 mV/dec, which is much lower than that of the annealed MoS$_2$/CC and even slightly smaller than the recently reported value for pure MoS$_2$ nanoplates (53 mV/dec)$^{28}$ It is likely due to the oriented growth of MoS$_2$ nanosheets on CC which results in the improvement conductivity of the MoS$_2$ materials and the increase number of the exposed active sites. Then the exchange current density is determined to be $9.2 \times 10^{-3}$ mA cm$^{-2}$ for the nanostructured MoS$_2$/CC sample, almost one order of magnitude higher than the Ti foil supported MoS$_2$ nanostructure ($3.87 \times 10^{-4}$ mA cm$^{-2}$)$^{13}$ and carbon fiber paper supported MoSe$_2$ ($3.80 \times 10^{-4}$ mA cm$^{-2}$).$^{18}$ Although the Tafel slope for annealed WS$_2$/CC is smaller than the freshly-prepared nanostructured WS$_2$/CC, this is still much higher than the MoS$_2$ and consistent with previous results.$^{23,26}$ Moreover, these values compare favorably to most of the reported values for non-precious HER catalysts in acidic aqueous electrolytes (see Table S1 in the Supporting Information).

Stability is another important criterion used to evaluate a catalyst. A long-term cyclic voltammetry test was performed to assess the electrochemical stability of the nanostructured MoS$_2$/CC electrode in an acidic environment. As shown in Figure 4a, working under such condition, the nanostructured MoS$_2$/CC electrode and the annealed WS$_2$/CC electrode performed still steadily, suggested by the smooth curve recorded after 2000 cycles along with negligible current degradation. Furthermore, continuous chronoamperometric curve was also presented in Figure 4b, where a stable current density of ~22 mA cm$^{-2}$ (at a overpotential of 0.2 V)
and ~17 mA cm\(^{-2}\) (at a overpotential of 0.25 V) over an operating period of 24 h were observed for the nanostructured MoS\(_2\)/CC and annealed WS\(_2\)/CC, respectively, further revealing the high stability of these nanostructured electrodes. Although, for a practical electrode device, the stability performance will need to be maintained much longer time, the performance of as-prepared electrodes in this work show great potential for scalable application. Notably, our MoS\(_2\)/CC and WS\(_2\)/CC electrodes are robust enough to withstand an ultrasonication even for 30 min (Figure S8), indicating the strong binding between the CC and the nanostructured MoS\(_2\) /WS\(_2\) sheets, which ensures the excellent stability of those nanostructured electrodes. Notably, it is observed that the small H\(_2\) bubbles formed on the 3D electrode can be timely released during the working process, which in turn ensures sufficient number of active sites, resulting in a stable electrocatalytic performance (details can be seen in SI-2). This is fully consistent with the previous observation.\(^{13}\)

As discussed above, such high catalytic performance of the nanostructured MoS\(_2\)/WS\(_2\) electrodes could be due to following reasons: (1) The intimate contact of MoS\(_2\) and WS\(_2\) nanosheets with CC enables good mechanical binding and electrical connection, facilitating the flow of electrons from CC to MoS\(_2\) or WS\(_2\) nanosheet arrays during HER. This is of great significance for the semi-conductive catalysts such as MoS\(_2\) and WS\(_2\). (2) The 3D configurations of the vertically oriented MoS\(_2\)/CC and WS\(_2\)/CC electrodes not only facilitate the self-removal of as-formed H\(_2\) bubbles form the nano-porous electrode surfaces, but also ensure enough and open spaces which allows easy diffusion of electrolyte into all the active sites and thus more efficient use of the entire electrode. (3) The ultrathin MoS\(_2\)/WS\(_2\) vertical nanosheets could be a better structure compared to the multilayer nanoparticles because electrons only need to be transferred from the support to the platelets, instead of passing through different layers. (4) The vertically oriented S-rich MoS\(_2\) nanosheet arrays and the annealed WS\(_2\) nanosheets with low oxidized species expose more active sites for HER than those of flat ones.

In summary, we developed a simple solvothermal method to fabricate MoS\(_2\) and WS\(_2\) grown on CC electrodes with vertically oriented nanosheet layers. With the unique layer orientation that maximally exposes the active edge sites as well as a rapid release of small gas bubbles to provide constant working electrode area, the nanostructured MoS\(_2\)/CC electrode exhibits excellent HER activity, while the WS\(_2\)/CC catalyst is also investigated here as a novel active HER architecture for potential use as HER catalyst. Both materials exhibit prominent electrochemical durability thanks to the strong bonding between the nanosheet layers and the substrate along with the self-removal of the as-formed H\(_2\) bubbles from the nano-porous electrode surface. Moreover, these vertically oriented layered catalysts can be readily applied in diverse
water electrolysis devices as easily-available, high-performance and stable HER catalysts.

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Electronic supplementary information (ESI) available: Experimental section and figures. See DOI:
References


Figures and Captions

Figure 1. (a, b) Low and high-magnification (insets) SEM images of nanostructured MoS$_2$/CC electrode (a) and WS$_2$/CC electrode (b). (c, d) TEM and high-resolution (HR) TEM (insets) images of nanostructured MoS$_2$/CC electrode (c) and WS$_2$/CC electrode (d). (e, f) The corresponding SEM image and EDX elemental mapping of Mo, S and C for the nanostructured MoS$_2$/CC electrode (c) and W, S and C for WS$_2$/CC electrode (d).
Figure 2. XPS spectra of Mo 3d and S 2p in the MoS$_2$/CC sample (a) and W 4f and S 2p in the WS$_2$/CC sample (b), as-synthesized and after thermally annealed at 350 °C.
Figure 3. (a) Schematic illustration of nanostructured MoS$_2$/CC and WS$_2$/CC electrodes. The active Mo/W edge for HER is marked in the magnified crystal structure image. Blue sphere: Mo/W; yellow sphere: S. Polarization curves (after $iR$-correction) of MoS$_2$/CC (b) and WS$_2$/CC catalysts (c). (d) The corresponding Tafel plots of the samples.
Figure 4. Stability testing of the nanostructured MoS$_2$/CC electrode and annealed WS$_2$/CC electrode.  (a) Polarization curves of the electrodes before and after 2000 CV scans between +0.1 and −0.5 V vs. RHE. (b) Chronoamperometric curve for both electrodes under static overpotential of 200 mV and 250 mV for 24 h, respectively.
Vertically oriented MoS$_2$ and WS$_2$ nanosheet thin films grown on CC have been designed as efficient 3D electrodes for hydrogen evolution reaction.