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In-Situ Growth of Few-Layered MoS₂ Nanosheets on Highly Porous Carbon Aerogel as Advanced Electrocatalysts for Hydrogen Evolution Reaction

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ABSTRACT: Molybdenum disulfide-based hybrids, acting as cost-effective and acid-stable electrocatalysts for hydrogen evolution reaction (HER), have been developed fast for providing a sustainable hydrogen energy in recent years. Herein, few-layered molybdenum disulfide (MoS₂) nanosheets/carbon aerogel (CA) hybrids were successfully obtained through the combination of sol-gel process, aging, freeze-drying, high temperature carbonization and solvothermal reaction. CA with highly continuous porosity and high specific surface area is used as matrix material for construction of hierarchical MoS₂/CA hybrids where few-layered MoS₂ nanosheets are uniformly covered on CA surface. In this heterostructured system, CAs not only provide three dimensional (3D) conductive pathway for fast transportation of electrons and ions, but also offer highly active regions for the growth of MoS₂, greatly preventing the aggregation of MoS₂ nanosheets. Due to the rationally designed hybrids with 3D porous nanostructures, the as-prepared MoS₂/CA hybrids with optimized MoS₂ content exhibit enhanced catalytic performance for electrocatalytic HER with a low onset potential of -0.14 V, large current density and excellent stability.

KEYWORDS: *Molybdenum disulfide, Carbon aerogels, Hydrogen evolution reaction*

INTRODUCTION

More and more scientific works have been committed to search for clean and renewable energy alternatives due to the severe stress from global environmental pollution and energy crisis derived from excessive consuming of fossil fuels.¹⁻⁴ Among various energy storage methods, water splitting reaction aroused either by light or electricity for renewable hydrogen energy has attracted tremendous attention because of its clean and potentially low cost.⁵⁻⁹ The essential step in water electrolysis is the hydrogen evolution reaction (HER), in which hydrogen is generated by electrocatalytic reduction of hydrogen ions.¹⁰⁻¹³ Platinum (Pt) and its alloys are very active catalysts for HER owing to their highly efficient energy conversion ability and low overpotential.¹⁴ However, the low natural reserves and expensive cost of Pt and Pt-based alloys hamper their commercial application in electrochemical hydrogen generation. Transition metal dichalcogenides (TMD) materials, for instance, MoS₂ and WS₂, MoSe₂, WSe₂ and VSe₂, are developed as potential alternatives of Pt-group electrocatalysts for HER due to their constrained electrons within two-dimensional (2D) layers.^{2, 15-21}

As a typical 2D TMD layered materials, MoS₂ shows graphene-like structure, in which molybdenum atoms are sandwiched between two layers of sulfur atoms. Recently, researchers have found that MoS₂ can be a promising electrocatalyst for HER.²²⁻³¹ Liu et al³² prepared 2D MoS₂ nanosheets from commercial MoS₂ powder *via* liquid exfoliation and ultrasonication. The obtained MoS₂ nanosheets exhibited extraordinary HER electrocatalytic performance, with onset potential lowered to -0.12

V. Previous works show that the defective sulfur (S) edges in MoS₂ nanosheets have excellent electrocatalytic activity, which are in favor of HER process by decreasing the overpotentials and increasing the current densities. However, the basal planes of MoS₂ are catalytically inert. Therefore, MoS₂ nanosheets with small size and few stacked layers have better electrocatalytic activity because of the existence of more exposed sulfur edge sites. Until now, there are many kinds of preparation methods for synthesis of nanosized MoS₂, such as chemical vapor deposition, electrochemical deposition, hydrothermal reaction and inverse micelle method. However, another obstacle for the practical application of MoS₂ nanosheets in HER field is their poor conductivity. Therefore, to increase the conductivity of MoS₂ nanosheets while maintaining their nanosize is the key challenge to realize the practical application of MoS₂ nanosheets in HER. In this regard, preparation of uniformly distributed and edge-rich MoS₂ nanosheets on a conductive substrate is an effective strategy to enhance their catalytic activity for HER.

Carbon materials, including graphene, carbon nanofibers (CNFs), carbon nanotubes (CNTs), activated carbon, carbon papers and so on, are ideal substrates for loading MoS₂ to advance their electrocatalytic performance due to the excellent conductivity and stability of these carbon materials.³³⁻⁴⁰ MoS₂/carbon hybrids have enormous advantages, such as great varieties, high surface-to-volume ratio, tunable molecular structures, and good stability in harsh environment. For example, Dai et al.⁴¹ first reported few-layer MoS₂ nanosheets with abundant exposed sulfur edges stacked on reduced graphene oxide (rGO) sheets by a selective solvothermal method. In the

MoS₂/rGO hybrids, rGO offers the conductive path for electron transfer between the catalyst and electrode, and provides active sites for the growth of MoS₂, which prevents the aggregation of MoS₂ and enhances the exposure of S-edges. Thus, the obtained MoS₂/rGO hybrids show excellent electrocatalytic performance, and the onset overpotential is low to -0.1 V along with a decreased Tafel slope (41 mV/decade). Du et al⁴² reported a novel synthesis of 2D MoS₂ with single layer nanosized nanoplatelets and S-edge rich by hybridization with one-dimensional (1D) CNFs. The designed hybrids exhibit a decreased overpotential of 300 mV at high current density of 80.3 mA/cm² and a low Tafel slope of 42 mV/decade. Wang et al⁴³ prepared low crystalline MoS₂ nanosheets coated CNTs which exhibited enhanced catalytic activity for HER. Among various carbon materials, carbon aerogel (CA) with 3D inter-connected network and unique properties, including highly porous structure, large surface area, and great electron transport performance, is an ideal substrate for MoS₂ loading and can be used in energy area.⁴⁴⁻⁴⁶ To our best knowledge, the nanocomposites of MoS₂ nanosheets and CAs have not been previously applied in the field of HER.

In this work, a novel and facile strategy is developed for the fabrication of 3D CA supported MoS₂ nanosheets with the combination of sol-gel process, high-temperature carbonization and solvothermal reaction. CA acting as the 3D conductive substrate can not only prevent the aggregation of MoS₂ and enhance the exposure of active S-edges, but also improve the conductivity of the MoS₂/CA hybrids, thus facilitating electron transfer during the electrocatalysis process. Morphological characterizations

show that few-layered MoS₂ nanosheets with abundant edges are vertically grown on the surface of CA substrate uniformly. Owing to the highly exposed edge sites and relatively low aggregation, the obtained MoS₂/CA hybrids exhibit excellent electrocatalytic properties, with a low onset potential of -0.14 V, large current density and excellent stability, making it a potential electrocatalyst for HER.

EXPERIMENTAL SECTION

Materials. Pyromellitic dianhydride (PMDA), *N,N*-dimethylacetamide (DMAc), triethylamine (TEA, 99%), 4,4'-oxidianiline (ODA), 30% H₂O₂, 98% H₂SO₄, KMnO₄, 37% HCl, *N,N*-dimethylformamide (DMF), ammonium molybdate and thiourea were obtained from Sinopharm Chemical Reagent Co., Ltd. All the above reagents were used as received without any treatments. Natural graphite powder (325 mesh) was supplied by Alfa-Aesar (Ward Hill, MA) and used without further treatments. All other chemicals were obtained from Aladdin Chemical Reagent, Co., Ltd. and used as received.

Preparation of MoS₂/CA hybrids. Polyimide (PI) based CAs (derived from graphene crosslinked PI aerogels) were synthesized according to our methods reported previously.⁴⁷ The preparation of MoS₂/CA hybrids is shown in Scheme 1. First of all, the bulk CAs were smashed into powder by continuously ball-milling at 500 rpm for 4 h. MoS₂/CA hybrids with various MoS₂ amount were synthesized *via* a one-step solvothermal method according to Xie's method.²⁸ In brief, proper contents of ammonium molybdate and thiourea with a molar ratio of 1:2 were added to 60 mL

water and followed by adding a certain amount of CAs. Then the mixture was well mixed by magnetically stirring for 2 h at room temperature. The obtained dispersion were transferred to a 100 mL Teflon stainless-steel autoclave and reacted at the temperature of 200 °C for 12 h. The precipitates were obtained through centrifugation at 12000 rpm for 10 min, and then washed with DI water and anhydrous ethanol for several times and finally dried under vacuum at 80 °C for 6 h. Afterwards, the samples were calcined at 300 °C for 2 h with a heat rate of 2 °C min⁻¹ under N₂ atmosphere. Finally, the MoS₂/CA hybrids with the initial CA/Mo weight ratio of 1:2, 1:4 and 1:8 were obtained and denoted as MoS₂/CA-2, MoS₂/CA-4 and MoS₂/CA-8, respectively. For comparison, pure CA and pure MoS₂ were prepared under the same conditions.

Characterization. The microstructures of the obtained samples were characterized by field emission scanning electron microscopy (FESEM) (Ultra 55, Zeiss) at 5 kV acceleration voltage. The chemical composition was characterized by the energy dispersive X-ray spectroscopy (EDX). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) observations were by conducted JEOL JEM 2100 TEM under 200 kV acceleration voltage. X-ray diffraction (XRD) patterns were performed on an X'Pert Pro X-ray diffractometer with Cu K α radiation (λ = 0.1542 nm) under a current of 40 mA and a voltage of 40 kV with 2 θ ranges from 5° to 80°. X-ray photoelectron spectroscopy (XPS) analyses were performed with a VG ESCALAB 220I-XL device and all XPS spectra were corrected using C1s line at 284.5 eV. In addition, the curve fitting and background

subtraction were accomplished using XPS PEAK41 software. In order to calculate the mass content of MoS₂ nanosheets in the hybrids, thermogravimetric analysis (TGA) was used under air flow from 100 to 700 °C at a heating rate of 20 °C/min.

Electrochemical measurements. Prior to all the experiments of hydrogen evolution performance, glassy carbon electrodes (GCE) of 3 mm in diameter were preprocessed according to the previous report.²¹ Typically, the working electrode was prepared as follows. 2 mg of MoS₂/CA hybrid was dispersed in 1 mL of a mixed solvent (DMF and deionized water by a volume ratio of 1:1) containing 20 μL 5wt% nafion. Then, the mixture was sonicated at least 15 min in order to obtain the homogeneous suspension. Finally, 10 μL of the homogeneous mixture was dropped onto GCE to form MoS₂/CA hybrid modified GCE. The required loadings of the electrocatalyst were adjusted by repeatedly adding 5 μL of the obtained MoS₂/CA hybrid slurry.

All electrochemical catalytic research were carried out by a CHI 660D electrochemical workstation (Chenhua Instruments Co, Shanghai, China) at room temperature. The hydrogen evolution performance tests were performed in the electrolyte solution of 0.5 M H₂SO₄. For a standard typical three-electrode cells, the different electrocatalysts modified GCE was applied as the working electrode, with saturated calomel electrode (SCE) as the reference electrode and Pt wire as counter electrode, respectively. In our electrochemical tests, all the potentials were calibrated to RHE according to the equation of $E_{\text{RHE}} = E_{\text{SCE}} + (0.241 + 0.059 \text{ pH}) \text{ V}$. The electrocatalytic performance of MoS₂/CA hybrid towards HER was performed by

liner sweep voltammetry (LSV) in nitrogen purged electrolyte solution, and the scan rate was 2 mV/s. Electrochemical impedance spectroscopy (EIS) measurement was conducted in 0.5 M H₂SO₄ by applying an AC voltage in the frequency range between 100 kHz and 10 mHz with 5 mV amplitude.

RESULTS AND DISCUSSION

Morphology and structures of MoS₂/CA hybrids. The typical structure of CA and CA particles after ball-milling is shown in Figure 1. As shown in Figure 1A, the obtained CA possesses high porosity, and the pore sizes range from dozens of nanometers to hundreds of nanometers. These porous structures can offer a 3D conductive substrate, which is beneficial for ions and electrons transport. Irregular structures with many sharp edges and sizes of hundreds of nanometers are observed for CA particles (Figure 1B). The irregular structure of CA particles favors the growth of MoS₂ nanosheets due to that they can not only prevent the agglomeration of MoS₂ nanosheets, but also increase the exposure of the active MoS₂ edges, thus highly improving the catalytic performance for HER. Specific surface area and porous structure of the obtained CA is characterized by nitrogen physisorption isotherms (Figure 1C and Figure 1D). The specific surface area of CA is 978 m²/g and the isotherm curve belongs to type IV with a hysteresis loop, indicating that the CA possesses large quantity of mesopores. The pore size distribution (in the range of 0 to 140 nm) measured by the Barrett-Joiner-Halenda method presents a relatively narrow distribution, which was centered at 15 nm. Therefore, the obtained CA with large

surface area and high porosity is considered as a promising template for further construction of MoS₂/CA hybrids with hierarchical nanostructures.

CAs with different loading amounts of MoS₂ nanosheets were prepared with the same procedure by adjusting the weight ratio of CA/Mo from 1:2, 1:4 to 1:8. After in-situ solvothermal reaction of CA powder in molybdenum salt solution, few-layered MoS₂ nanosheets are evenly grown onto 3D conductive CA substrate (Figure 2A-2C). By increasing the loading amount of molybdenum salt, more and more thin MoS₂ nanosheets begin to form and densely grow on the CA particles. It is worth mentioning that MoS₂ nanosheets are evenly and perpendicularly grown on the porous CA substrate when the weight ratio of molybdenum salt precursor to CA is 4:1. However, with increasing the weight ratio of molybdenum salt precursor to CA to 8:1, MoS₂ nanosheets began to accumulate and stack together on CA substrate due to the limited growth space (Figure 2C). The EDX mapping analysis of MoS₂/CA-4 hybrid (Figure 2D) proves the coexistence and homogeneous dispersion of C, Mo, S elements, further confirming that MoS₂ nanosheets are evenly anchored on the surface of CA particles. In contrast, as shown in Figure 3, pure MoS₂ prepared without adding CA particles consists of large micro-sized sheets, which are disorderly stacked together and aggregated into nanospheres. In addition, specific surface area and porous structure of the obtained pure MoS₂ and MoS₂/CA-4 hybrid is characterized by nitrogen physisorption isotherms, as shown in Figure S1. The specific surface area of MoS₂/CA-4 hybrid is 107 m²/g, which is much larger than that of pure MoS₂ (13 m²/g). The main reason is due to that the special structure of CA with high surface

area ($978 \text{ m}^2/\text{g}$) is able to offer more active sites for the growth of MoS_2 nanosheets, which is beneficial for preventing the aggregation of MoS_2 nanosheets. The pore size distribution of pure MoS_2 and $\text{MoS}_2/\text{CA-4}$ hybrid calculated by the Barrett-Joiner-Halenda method presents a relatively narrow distribution, which is centered at 4 nm. The high surface area and porous structure of $\text{MoS}_2/\text{CA-4}$ hybrid is beneficial for electrolyte permeation and efficient ion diffusion, thus facilitating the HER electrocatalytic performance.

Morphology of $\text{MoS}_2/\text{CA-4}$ hybrid is further confirmed by TEM observations (Figure 4). The irregular CA particles are clearly observed and few layered MoS_2 nanosheets are evenly coated on CA substrate, which is in good accordance with SEM observations (Figure 2). From HRTEM image in Figure 4B, five to eight layers of MoS_2 nanosheets can be clearly observed, and the interlayer spacing of MoS_2 nanosheets is about 0.65 nm, which is in accordance with the (002) lattice of hexagonal MoS_2 .

The XRD patterns of pure CA, pure MoS_2 and $\text{MoS}_2/\text{CA-4}$ hybrid are shown in Figure 5. As for CA sample, the broad diffraction peak centered at $2\theta = 26^\circ$ and the weak diffraction peak at $2\theta = 44^\circ$ can be assigned to the (002) and (100) planes, respectively, revealing the low crystalline degree of CA. For pure MoS_2 and $\text{MoS}_2/\text{CA-4}$ hybrid, the diffraction peaks present similar to each other, indicating that no additional crystallization behavior is introduced into the $\text{MoS}_2/\text{CA-4}$ hybrid. In addition, all the diffraction peaks of pure MoS_2 and $\text{MoS}_2/\text{CA-4}$ hybrid can be indexed to the hexagonal MoS_2 phase, which are in good accordance with the

literature values (JCPDS: 00-037-1492). As shown in Figure 5, MoS₂/CA-4 hybrid shows sharp peaks at $2\theta = 14.2^\circ$, 33.8° and 59.3° , which can be indexed to (002), (100) and (110) planes of MoS₂, respectively. To be emphasized, the diffraction peak of (002) shifted from $2\theta = 16.7^\circ$ to 14.2° compared to the standard hexagonal 2H-MoS₂ structure, indicating an expanded interlayer. In addition, the (103) and (201) peak at $2\theta = 39.8^\circ$ and 69.8° can be weakly detected. Therefore, the XRD results suggest that MoS₂ has been successfully grown on the surface of CA.

Figure 6 shows the XPS spectra of the MoS₂/CA-4 hybrid. As shown in Figure 6A, the survey scan indicates that C, Mo, S, and O elements are co-existed in MoS₂/CA-4 hybrid. The peak of C 1s spectrum is centered at 284.5 eV, which corresponds to sp² C (Figure 6B). High resolution Mo 3d spectrum (Figure 6C) shows characteristic peaks centered at 232.3 and 229.2 eV corresponding to Mo 3d_{3/2} and Mo 3d_{5/2} orbitals, suggesting that Mo in the MoS₂/CA-4 hybrid is in Mo (IV) state. In addition, the binding energies of S 2p_{1/2} and S 2p_{3/2} orbitals centered at 163.1 eV and 162.0 eV, indicating the existence of divalent sulfide ions (S²⁻) (Figure 6D). The loading amounts of MoS₂ in the MoS₂/CA hybrids are calculated from the TGA curves (Figure 7), which is 21.6%, 38.4%, and 68.1% for MoS₂/CA-2, MoS₂/CA-4 and MoS₂/CA-8 hybrids, respectively.

Electrochemical performance of MoS₂/CA hybrids. Generally speaking, an optimal HER catalyst is a material that could give the highest current at the lowest overpotential, as well as a low HER onset potential (*i.e.*, the potential at which HER

activity begins) comparable to that of Pt catalyst. The electrocatalytic performance of the MoS₂/CA hybrids for HER were carried out in the electrolyte solution of 0.5 M H₂SO₄ using a standard typical three-electrode cells. Typically, the hybrids with an optimized electrocatalyst loading weight of 20 µg were deposited on GCE. The polarization curves for all the hybrids were optimized, and commercial Pt/C catalysts, pure CA and pure MoS₂ were also measured as reference (Figure 8). As shown in Figure 8A, either CA or pure MoS₂ exhibit no or poor HER electrocatalytic performance due to the large onset overpotential and low current densities. All the three MoS₂/CA hybrids with different Mo/CA ratios do have good electrocatalytic activity, while MoS₂/CA-4 hybrid exhibits the optimized electrocatalytic performance, with onset potential at approximately -0.14 V (vs RHE), and high current densities of 1.72 and 9.68 mA/cm² at overpotentials of 150 and 200 mV, respectively. The improved electrocatalytic HER activity for MoS₂/CA hybrids suggests the synergistic effect between 3D conductive CAs and electroactive MoS₂ nanosheets. As mentioned above, highly porous CA provides 3D conductive templates, which are conducive to reduce the diffusion path for ions and electrons. Besides, the distinctive structures of CA particles are able to offer many active sites for the homogeneous growth of MoS₂ nanosheets and thus prevent the self-aggregation of MoS₂ nanosheets. Furthermore, the irregular shape of CA particles can provide many sharp edges, maximizing the exposure of accessible active catalytic sites of MoS₂ nanosheets. For MoS₂/CA-2 hybrid, only sparse MoS₂ nanosheets are interspersed on the surface of CA particles, leading to less electroactive sites for hydrogen evolution. In contrast, as for

MoS₂/CA-8 hybrid, excess loading of MoS₂ nanosheets could result in the aggregation of MoS₂ nanosheets, limiting the exposure of MoS₂ edges and electroactive sites. Therefore, with uniform distribution of MoS₂ nanosheets and 3D conductive network of CA template, MoS₂/CA-4 hybrids shows synergistically improved catalytic performance for HER.

A Tafel slope is closely related to reaction path and adsorption type during the HER process. Therefore, it is always used to evaluate the catalytic effectiveness of catalysts. Usually, the Tafel curve derived from the polarization curves is obtained based on fitting of the straight line part and the Tafel slope is the slope of the fitting line. For the Tafel curve, the overpotentials (η) and the relevant current densities (j) are obtained from the LSV curves. The linear portions of the Tafel curve agree with the Tafel equation ($\eta = b \log(j) + a$, where η is the overpotential, j is the current density and b is the Tafel slope) at different overpotential ranges. The Tafel curves for pure MoS₂, MoS₂/CA-4 hybrid and Pt, obtained from the LSV curves are shown in Figure 8B. As calculated from Figure 8B, the Tafel slopes are ~86, ~59 and ~31 mV/decade for pure MoS₂, MoS₂/CA-4 hybrid and Pt, respectively. Compared to pure MoS₂, the improved HER performance of MoS₂/CA-4 hybrid suggests a smaller activation energy for HER, which can be attributed to the effective hybridization of 3D electrical conductive CA and the homogenous, nanosized and S-edge rich MoS₂ nanosheets. According to the typical electrocatalytic mechanism in acidic aqueous for HER, the rate determining step of the obtained pure MoS₂ belongs to the Volmer-reaction due to the intrinsic poor conductivity and low activity arose from its micro-size and

disordered stacking. The evidently reduced slope for MoS₂/CA-4 hybrid indicates that the hydrogen evolution takes place via the rapid Volmer reaction followed by a rate-determining Heyrovsky step.

Figure 9 shows the HER catalytic performance of different loadings of MoS₂/CA-4 hybrid on GCE. As shown in Figure 9A and Figure 9B, the optimal loading of MoS₂/CA-4 hybrid is 20 µg with current densities of 1.72 and 9.68 mA/cm² at overpotentials of 150 and 200 mV, respectively. For 30 µg and 40 µg loadings, the current densities at different overpotentials are lower than that of 20 µg loading, which may be explained by that excess loading of catalyst will increase the internal resistance and decrease the effective active sites.

In order to assess the electrode kinetics and electrical conductivity of the different electrocatalysts, EIS of pure CA, pure MoS₂ and MoS₂/CA hybrids were measured from 0.01 to 100 000 Hz. As can be seen from Figure 10, the Nyquist plots of the catalysts modified electrodes consist of an inconspicuous arc in the high frequency region and a straight line with a certain slope in the low frequency region. According to the previous reports, the more vertical the line is, the faster ion diffuse at low frequency. It is clear that pure CA has more vertical curve due to its good conductivity, which conduces to fast ions and electrons transport.⁴⁷ Besides, all the three MoS₂/CA hybrids have more vertical curves than pure MoS₂, indicating that MoS₂/CA hybrids offer faster HER kinetics due to the 3D conductive CA template. For the high frequency area, the solution resistance (R_s) of pure CA, MoS₂/CA-2, MoS₂/CA-4, MoS₂/CA-8 hybrid and pure MoS₂ are about 8.1, 8.9, 10.8, 11.4 and 13.0

Ω , respectively. The reduced R_s value for MoS₂/CA hybrids compared with that of pure MoS₂ indicates the improved electrical conductivity result from the effective hybridization of MoS₂ with porous CA, which can efficiently shorten the transport path of ions and charges due to its 3D porous structure. With the weight ratio of molybdenum salt precursor to CA increased, it is clear that the values of R_s become larger and the constant inclining angle of the straight line is smaller, indicating increased internal resistance with the excess loading of MoS₂. In addition, AC impedance spectroscopy of MoS₂/CA-4 hybrid in 0.5 M H₂SO₄ from 10⁻² to 10⁵ Hz under different overpotentials was investigated. As shown in Figure S2, there is almost no difference among the AC impedance spectroscopy of MoS₂/CA-4 hybrid under different overpotentials and this phenomenon shows that the conductivity of MoS₂/CA-4 hybrid is stable under the potential range of hydrogen evolution.

To evaluate the long-term stability of MoS₂/CA-4 hybrid, potential sweeps were carried out continuously for 2000 cycles from -0.4 to +0.2 V vs. RHE. As seen from Figure 11, the LSV curves of MoS₂/CA-4 hybrid retains similar before and after continuous 2000 cycles, indicating it has good durability. To further investigate the stability of MoS₂/CA hybrids in HER, the current-time plots (IT curves) at different potentials (to achieve 10 mA/cm²) were examined. As shown in Figure S3, all the catalytic current densities slightly fluctuated up and down due to the bubble formation in the process. Besides, with increasing the weight ratio of molybdenum salt precursor to CA, the current density reduced faster while MoS₂/CA hybrid needs higher voltage to ensure the current density due to the decrease of conductivity with less CA

particles.

CONCLUSIONS

In summary, a highly active electrocatalyst of MoS₂/CA hybrid was fabricated where MoS₂ nanosheets were grown uniformly on 3D mesoporous CA template by a simple solvothermal reaction. CA has abundant mesopores, a high surface area, and a highly conductive skeleton which provide a specific microenvironment and conductive pathways to accelerate the transportation of electrons and ions during the HER process. Besides, CA acting as conductive substrate can effectively prevents the aggregation of MoS₂ nanosheets, and thus the well-dispersed and edge-rich MoS₂ nanosheets grown on CA template guarantee the full exposure of active edge sites. Therefore, the obtained MoS₂/CA-4 hybrid possesses excellent catalyst performance for HER with a low onset potential of -0.14 V, large current densities (1.72 mA/cm² at η = 150 mV; 9.68 mA/cm² at η = 200 mV, relatively), and a small Tafel slope of 59 mV/decade. Besides, the MoS₂/CA-4 hybrid shows long-term durability after 2000 cycles. Therefore, the highly electrocatalytically active CA supported nanosized MoS₂ is a promising candidate for low cost electrocatalysts in hydrogen evolution field.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

N₂ adsorption-desorption analysis, AC impedance spectroscopy of MoS₂/CA-4 hybrid under different overpotentials, current-time responses of MoS₂/CA hybrids, and LSV polarization curves for MoS₂/CA-4 hybrid at different scan rates (PDF).

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Notes

The authors declare no competing financial interest.

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Figure captions

Scheme 1. Schematic for the preparation of MoS₂/CA hybrids.

Figure 1. FESEM images of CAs (A) and CA particles (B). N₂ adsorption/desorption isotherm at 77 K (C) and pore size distribution (D) of CAs.

Figure 2. FESEM images of MoS₂/CA-2 (A), MoS₂/CA-4 (B) and MoS₂/CA-8 hybrids (C). The bottom row shows the EDX mapping of MoS₂/CA-4 hybrid (D).

Figure 3. FESEM images of pure MoS₂ at low (A) and high (B) magnifications.

Figure 4. TEM (A) and HRTEM (B) images of MoS₂/CA-4 hybrid.

Figure 5. XRD patterns of pure CA, pure MoS₂ nanosheets and MoS₂/CA-4 hybrid.

Figure 6. XPS survey spectrum (A), C 1s spectrum (B), Mo 3d spectrum (C) and S 2p spectrum (D) of MoS₂/CA-4 hybrid.

Figure 7. TGA curves of pure CA, pure MoS₂, and MoS₂/CA hybrids.

Figure 8. LSV polarization curves for GCE modified with different materials in N₂ purged 0.5 M H₂SO₄ solution (A). Scan rate: 2 mV/s. Tafel plots for pure MoS₂ nanosheets, Pt and MoS₂/CA-4 modified GCE (B).

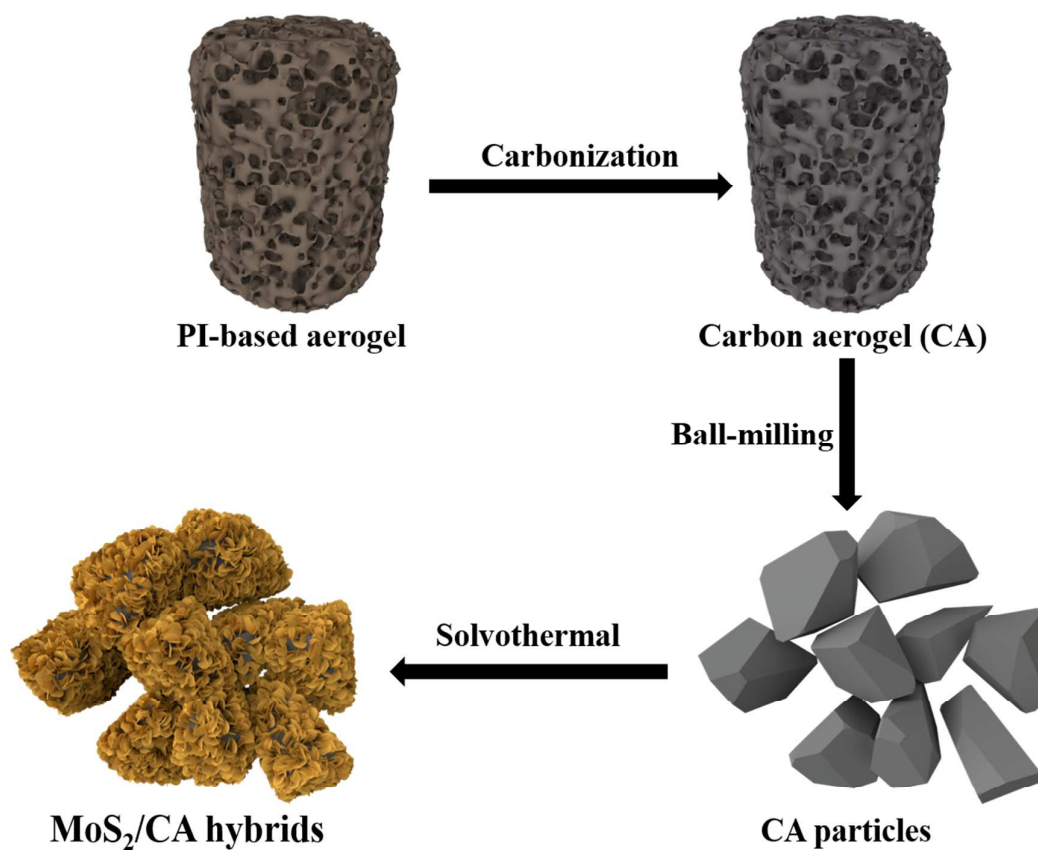
Figure 9. LSV polarization curves for MoS₂/CA-4 modified GCE with different loadings in N₂ purged 0.5 M H₂SO₄ solution (A). Scan rate: 2 mV/s. Current densities for MoS₂/CA-4 modified GCE with various loadings at overpotentials of 150 and 200 mV (B).

Figure 10. AC impedance spectroscopy of CAs, pure MoS₂ nanosheets and MoS₂/CA hybrids in 0.5 M H₂SO₄ from 10⁻² to 10⁵ Hz with an AC amplitude of 5 mV.

Figure 11. Polarization curves of MoS₂/CA-4 hybrid in 0.5 M H₂SO₄ initially and

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after 2000 cycles between -0.4 and +0.2 V at 100 mV/s.



Scheme 1

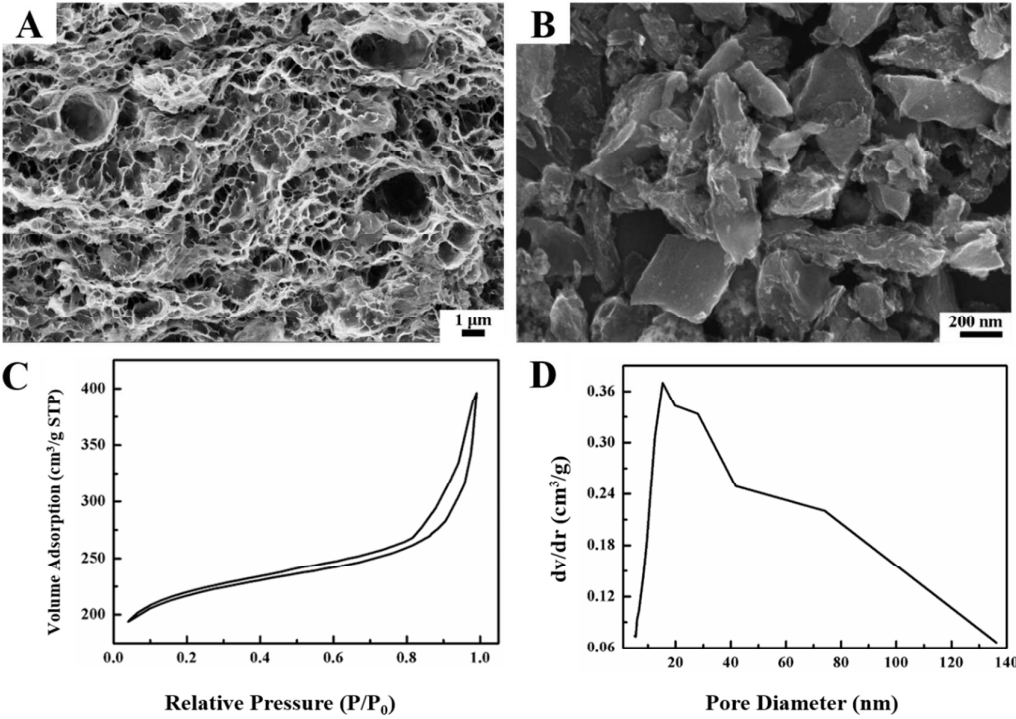


Figure 1

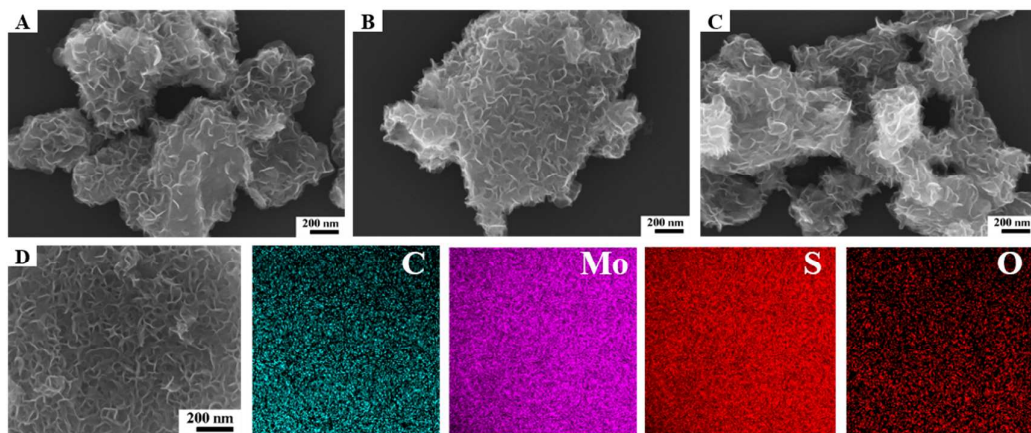


Figure 2

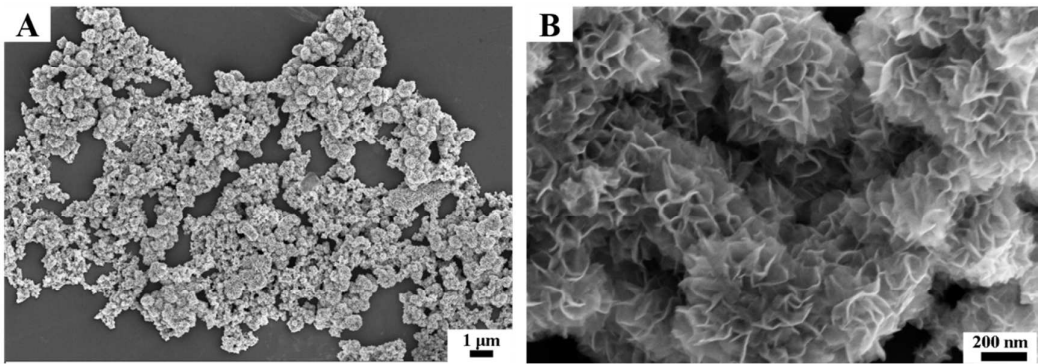


Figure 3

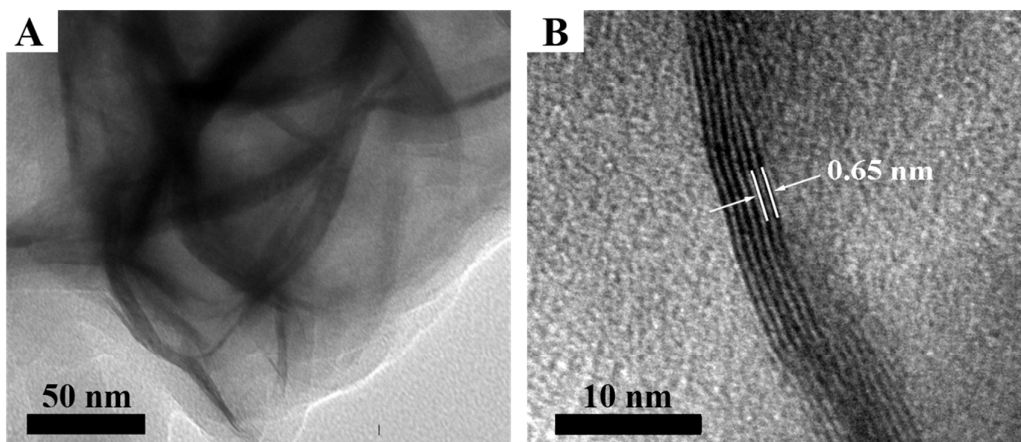


Figure 4

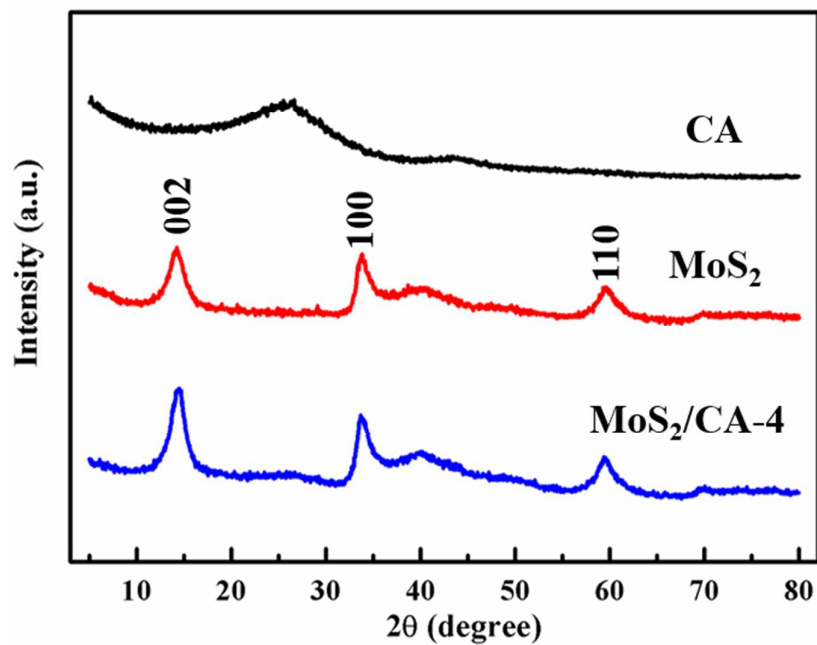


Figure 5

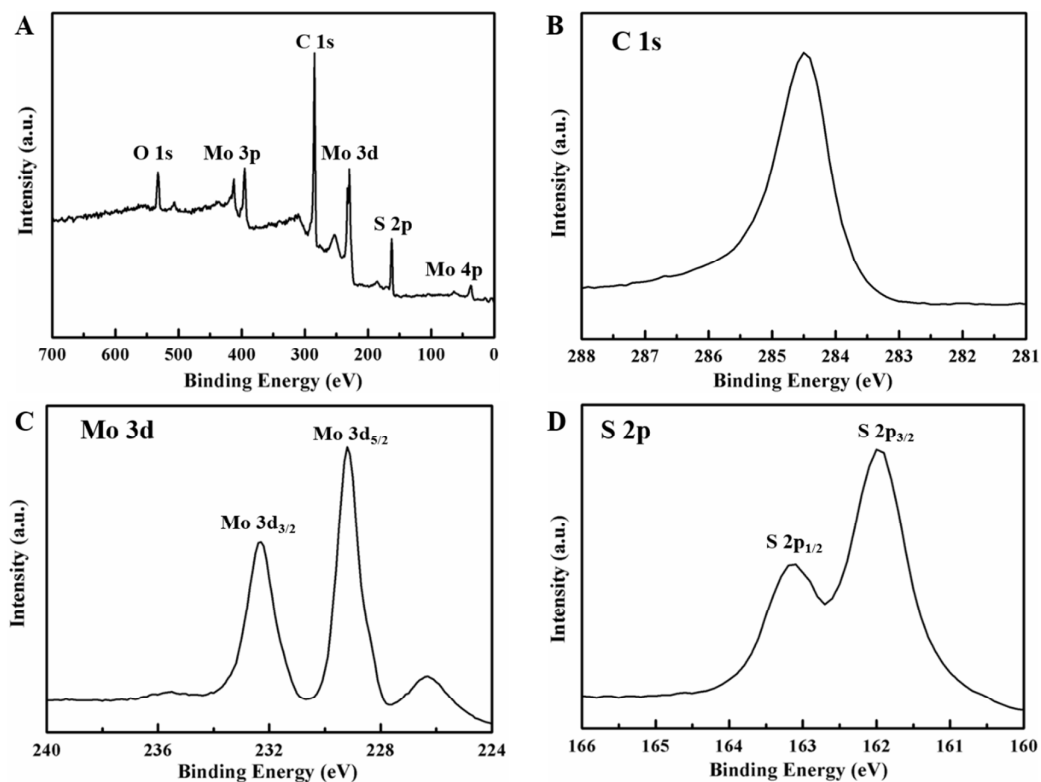


Figure 6

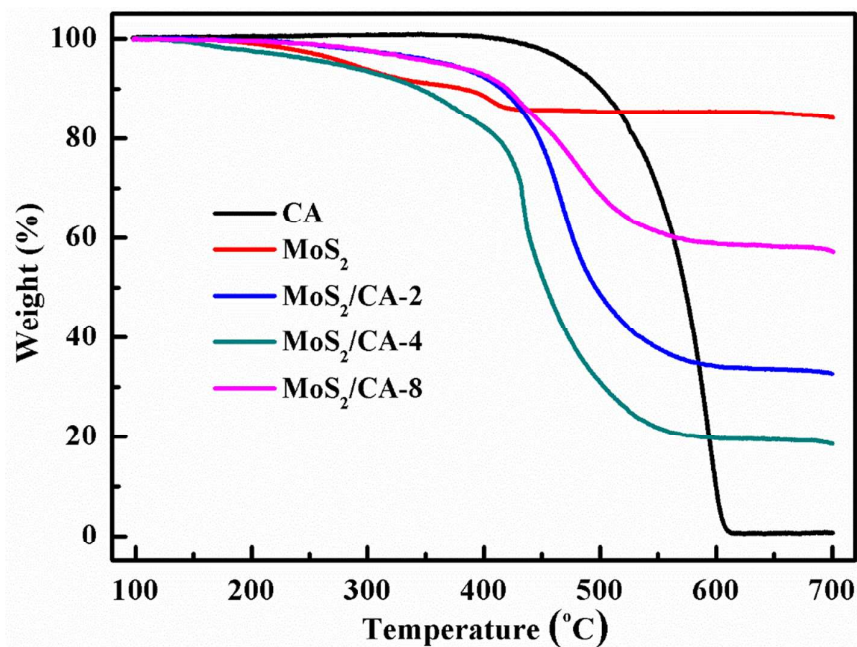


Figure 7

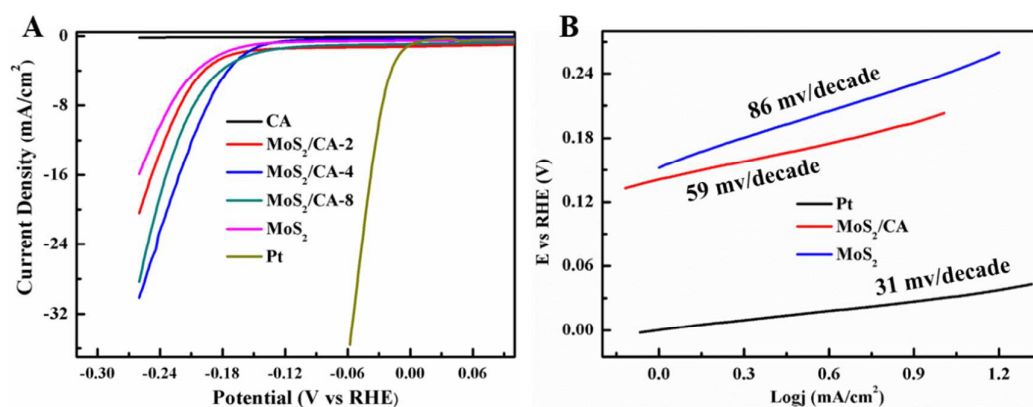


Figure 8

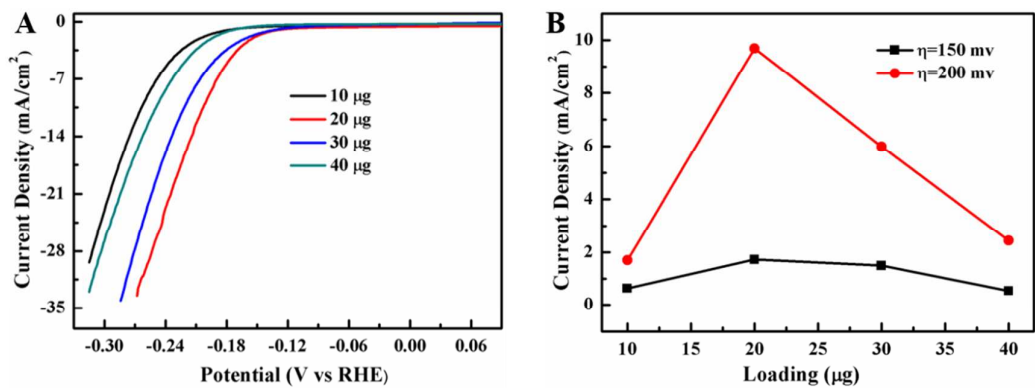


Figure 9

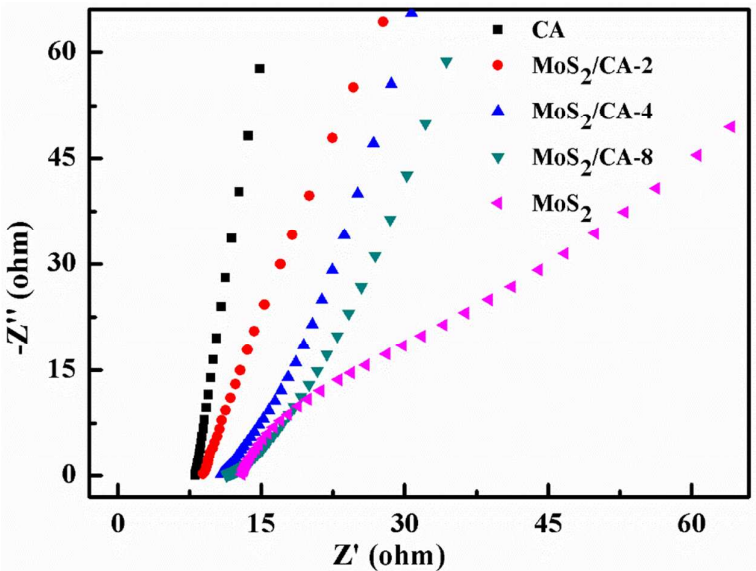


Figure 10

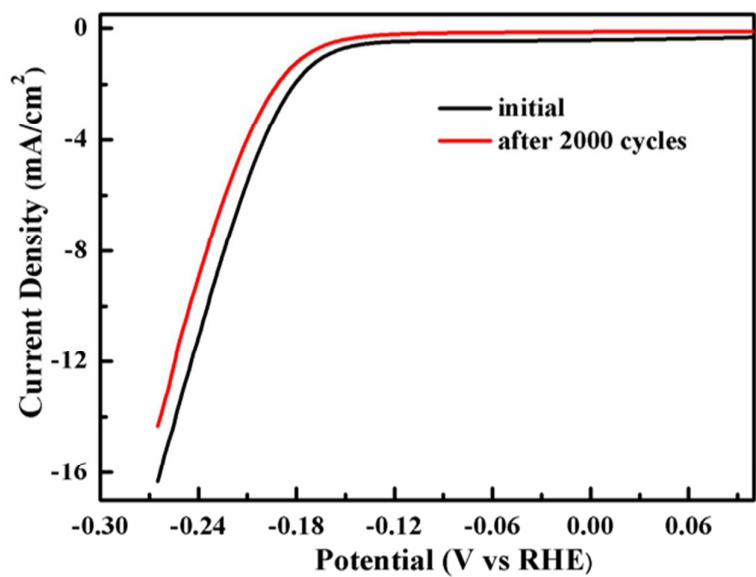


Figure 11

Graphic for the Table of Contents (TOC):

In-Situ Growth of Few-Layered MoS₂ Nanosheets on Highly Porous Carbon Aerogel as Advanced Electrocatalysts for Hydrogen Evolution Reaction

Youfang Zhang,[†] Lizeng Zuo,[†] Yunpeng Huang,[†] Longsheng Zhang,[†] Feili Lai,[†] Wei Fan,^{*,‡} and Tianxi Liu^{*,†,‡}

Carbon aerogels (CAs) supported nanosized MoS₂ nanosheets were demonstrated as highly active and stable electrocatalysts for hydrogen evolution reaction.



MoS₂/CA hybrids

