

Self-Supported Ceramic Electrode of 1T-2H MoS₂ Grown on the TiC Membrane for Hydrogen Production

Yangyang Shi, Dewen Zheng, Xi Zhang, Kai Lv, Feihong Wang, Binbin Dong, Shanyu Wang, Chunxia Yang, Jianming Li, Fengyi Yang, Lu Yuan Hao, Liangjun Yin, Xin Xu,* Yuxi Xian,* and Simeon Agathopoulos



catalytic electrodes with a customized size are urgently needed for large-scale industrial hydrogen production. Toward this challenge, self-supported TiC@MoS₂ (TCMS) ceramic membrane electrodes were fabricated by a self-template strategy. Porous TiC ceramic membranes with straight finger-like pores were first fabricated by phase inversion tape-casting and sintering. Then, a 1T-2H MoS₂ nanosheet layer grew on the porous conductive TiC skeleton. The high conductivity of the TCMS skeleton promotes charge transfer, while the porous structure, which consists of abundant finger-like and cavernous pores, favors proton transfer and bubble transfer during the electrolysis process. The optimal TCMS composition



displayed an overpotential of -127 mV at $-10 \text{ mA} \cdot \text{cm}^{-2}$, a Tafel slope of 41 mV·dec⁻¹, and an extremely high electrochemical active area of 1079.4 mF·cm⁻² as well as remarkable stability in 0.5 M H₂SO₄. A high Faradaic efficiency of 99.7% was also achieved. The superior electrocatalytic performance was ascribed to the synergistic effect of the tight bonding and the crystal matching between TiC and MoS₂, the unique dual pore structure, the abundant exposed active sites of MoS₂ nanoflakes, and the high 1T-MoS₂ content. First-principles density functional calculations showed that the 1T-MoS₂/TiC hybrid has the lowest free energy for H adsorption (0.116 eV) and the highest density of states near the Fermi level, which leads to a strong catalytic activity.

1. INTRODUCTION

Hydrogen is an excellent clean and infinitely renewable source of energy; thus, it is a viable alternative to fossil fuels, which have a known environmental impact, and their limited deposits are gradually being depleted on a global scale.^{1,2} The wide use of electrochemical water splitting to produce hydrogen must assure a sustainable hydrogen evolution reaction (HER). Accordingly, advanced electrocatalysts with high performance should be produced by easy and effective (in other words versatile, reliable, and low-cost) methods.³

Generally, noble metals, such as Pt and Pt-based materials, are the most effective HER catalysts; yet, their high cost and the scarcity of their natural occurrence hinder their scale-up deployment globally.⁴ Transition-metal compounds are potential noble metal-free alternatives, which attract great attention as electrocatalytic materials, owing to their abundant natural reserves and the superior electrocatalytic activity.⁵⁻⁸ Nonetheless, a breakthrough in the improvement of the sluggish kinetics of reactions when non-noble-metal catalysts are involved in it still poses an enormous challenge.⁹ Among other newly developed catalytic materials, the two-dimensional disulfide compounds of transition metals, such as molybdenum disulfide, are very attractive because of the low hydrogenadsorption free energy, low cost, and high chemical stability.¹⁰ According to the arrangement of S atoms, MoS₂ has two distinct crystalline phases of 2H (trigonal prismatic D_{3h}) and

1T (octahedral O_h).¹¹ It is worthy of note that the unsatisfactory catalytic performance of the thermodynamically stable bulk 2H-phase MoS_2 is a result of its poor conductivity as well as the limited number of exposed active-edge sites during the process of HER catalysis.^{12,13} Different from the 2H phase, the 1T phase is metallic and highly active to catalyze HER, but its metastable characteristics limit its application.¹⁴ Thus, it is desirable to utilize combined 1T and 2H phases of MoS_2 to achieve good HER performance with long-term stability.

Coating is a popular routine to obtain an abundance of active-edge sites of MoS_2 along with good electrical conductivity, whereby one or a few layers of MoS_2 coat the surface of conductive materials, such as transition metal-based,¹⁵ nickel foam-based,¹⁶ or carbon-based ones.¹⁷ The big challenge is to obtain MoS_2 -based materials with long-term stability and good mechanical strength in order to satisfy the requirements for HER catalytic electrodes.¹⁸ The construction of novel MoS_2 -based electrodes with high conductivity and

Received:June 8, 2021Revised:July 3, 2021Published:July 20, 2021





high HER catalytic activity through an easy preparation strategy will allow for the industrialization of hydrogen production technologies.

Ceramic membranes are widely used in daily life, such as in bone replacement,¹⁹ gas separation,²⁰ treatment of oily wastewater,²¹ energy storage,²² and so forth. When it comes to ceramic membranes, attention is focused on manipulating their structure. This is done through adjusting the particle size, sacrificial pore formers, sintering conditions, and so forth.²³ Porous structures with an appropriate pore size facilitate improved mass transfer, especially the flow of gases and liquids.²⁴ In recent years, titanium carbides (TiC) attract a lot of interest as a promising substrate for catalysts on account of its excellent electronic conductivity, corrosion resistance, and chemical and electrochemical stability.^{25–30} Zhi Wei Seh et al. reported for the first time the application of two-dimensional layered transition-metal carbides as electrocatalysts for HER.³¹ Later, Ramalingam et al. reported on TiC-based MXene $(Ti_3C_2T_x)$ as an efficient solid support to host a nitrogen- and sulfur-coordinated ruthenium single-atom catalyst.³² This work presented a good strategy for fabricating a porous TiC ceramic electrode, which can host various catalysts with good conductivity.

The present paper reports on the successful production of a self-supported HER electrode, where vertically aligned nanosheets of 1T-2H MoS_2 on the TiC porous ceramic membrane were prepared through a combined phase inversion tapecasting and sintering method, followed by an easy hydrothermal process. Through this production process, the membrane exhibits ample straight finger-like voids, which enable high loading of the catalyst and provide a sufficient number of channels for effective bubble transportation inside the electrode during HER.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

2.1. Production of Porous Conductive TiC Ceramic Membranes. A combined induced phase inversion tape-casting and sintering technique was applied to fabricate the porous conductive TiC ceramic membranes. The starting ceramic powder mixture, comprising 93 wt % commercially available TiC, 2 wt % SiC, and 5 wt % Y_2O_3 (all in fine powder form), was added to a stable polymer solution, which contained O-(2-aminopropyl)-O'-(2-methoxyethyl)-polypropylene glycol ($M_W = 600$ Da, Sigma Aldrich Co. Ltd., USA) as a dispersant, N-methyl-2-pyrrolidone (CP, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) as a solvent, and polyethersulfone (RadelA-100, Solvay Advanced Polymers) as a polymer binder.

The slurry, with a solid content of 50%, was poured into a ball-mill pot with alumina balls. A homogeneous and stable suspension was prepared after planetary ball-milling for 48 h at room temperature. Then, the suspension was transferred to a vacuum degassing box for degassing. The degassed suspension was cast on a glass plate at room temperature and in ambient humidity through a doctor-blade method with a gap of 1 mm. Then, soaking in a water bath for 12 h and in turn drying at room temperature for 12 h took place.

Rectangular ceramic membranes of $3 \times 1 \times 0.1$ cm³ were cut from the green body and placed on alumina plates. The TiC ceramic membranes were sintered at 1600 °C under a nitrogen atmosphere. The heat treatment involved the following stages: (i) heating with a rate of 5 K/min up to 1000 °C, (ii) slower heating with 3 K/min up to 1600 °C and a dwell for 4 h, and (iii) slow cooling inside the furnace to room temperature. The resultant shrunk ceramic membranes had a size of 2.7 \times 0.9 \times 0.09 cm³.

2.2. Production of TiC@MoS₂ Self-Supported Electrodes. The TiC@MoS₂ (TCMS) self-supported electrodes were produced through an easy one-step hydrothermal reaction as follows: 3.75 mmol of sodium molybdate dihydrate (Na₂MoO₄:2H₂O) and 30 mmol of thiourea (CS (NH₂)₂) were dissolved in a mixture of 20 mL of deionized water and 10 mL of propanoic acid. The solution was stirred for 20 min to get a homogeneous solution. Then, the solution, along with one piece of the prepared TiC membrane, was transferred into a 50 mL Teflon-lined stainless-steel autoclave, which was sealed and then heated in an electric oven at 180 °C for 8 h. After heating, the autoclave was left to cool to room temperature naturally.

The obtained ceramic membrane was rinsed with deionized water and ethanol, and this was repeated for three consecutive times. Finally, it was dried at 70 °C under vacuum for 12 h. The average loading of 1T-2H MoS₂ on TiC ceramics was 187.7 \pm 0.2 mg·cm⁻², calculated by the increase in the weight of 10 pieces of TiC after the hydrothermal process. Moreover, various molar Mo/S ratios (adjusted by the amounts of Na₂MoO₄·2H₂O and CS (NH₂)₂, respectively), more specifically, 1: 1, 1: 4, 1: 6, 1: 8, and 1: 10, were used in order to investigate the influence of this ratio on the growth of 1T-2H MoS₂ on the surface of the TiC ceramics and on the properties and the performance of the resultant electrodes. The produced TCMS electrodes are designated as TCMS 1, TCMS 2, TCMS 3, TCMS 4, and TCMS 5, respectively.

2.3. Material Characterization. The microstructure analysis was performed using a scanning electron microscope (HITACHI SU8220 series, Japan) and a transmission electron microscope (JEM-2100F, Japan) equipped with an energy-dispersive spectroscopy (EDS) device for elemental analysis. Raman spectra were obtained with a 532 nm laser. X-ray diffraction (XRD) analysis was also carried out (Philips PW 1700, using Cu K_{a1} radiation with an accelerating voltage of 40 kV and a current of 40 mA at a scanning rate of 2 deg./min). X-ray photoelectron spectroscopy (XPS) was conducted on an Escalab 250 (Thermo-VG Scientific, America) within a scanning range of binding energy from 0 to 1350 eV in steps of 1 eV.

The Brunauer–Emmett–Teller (BET) surface area and the pore size distribution of the membranes were measured by Tristar II 3020 M equipment (Micrometrics, America). Measurements of the electrical conductivity of the TiC ceramic membranes were performed at room temperature using a four-point probe method.

2.4. Electrochemical Measurements. Electrochemical measurements were performed on an electrochemical workstation (CHI 660D) using a standard three-electrode system in N_2 -saturated 0.5 M H_2SO_4 aqueous solution. The pre-made pure TiC ceramic membranes and the TCMS ceramic membranes were directly used as working electrodes. A graphite rod and Ag/AgCl (in 3 M KCl solution) served as the counter electrode and the reference electrode, respectively. The test voltages were normalized with respect to the reversible hydrogen electrode (RHE) using the following formula:

 $E_{\text{with respect to RHE}} = E_{\text{with respect to Ag/AgCl}} \text{ (measured value)}$ $+ 0.059 \cdot \text{pH} + 0.1989$

Linear sweep voltammetry (LSV) measurements were performed in the range of 0 to -0.6 V (with respect to the RHE) at a rate of 1 mV· s^{-1} after i-R correction. Tafel slopes were derived from their corresponding LSV data by fitting into the equation $\eta = a + b \cdot \log j$. Cyclic voltammetry (CV) tests were conducted in the range of 0.22 to 0.3 V (with respect to the RHE) with scanning rates from 1 to 5 mV· s⁻¹. The Nyquist plots were obtained with frequencies ranging from 100,000 to 0.01 Hz at an overpotential of -315 mV (with respect to RHE). The impedance data were fitted to a simplified Randles circuit in order to extract the series of the charge transfer resistance. Measurements for determining the Faradaic efficiency (FE) were also performed. More specifically, a three-electrode device, which contained a H-type gas-tight electrolytic cell with a Nafion membrane, was used in order to determine the FE (Figure S1). A synthesized TCMS 4 electrode, a graphite rod, and an Ag/AgCl electrode were used as working, counter, and reference electrodes, respectively. A constant current of 0.02 A for 0.05 h was applied on the TCMS cathode to evaluate the FE, and the FE of H_2 was calculated by the following equation:³

where *n* is the mol of the generated $H_{2^{j}}F$ is the Faraday constant, *I* is the passed current (A), and *t* is the time (s). The generated H_{2} gas in the headspace of the cell was analyzed (i.e., measured) by a Techcomp GC-7900 gas chromatograph.

2.5. Density Functional Theory Calculations. First-principles density functional theory (DFT) calculations were performed to calculate the free energy of H adsorption ($\Delta G_{\rm H}$) on various surfaces. More specifically, the Cambridge Serial Total Energy Package (CASTEP) code was used within the generalized-gradient approximation in the Perdew-Burke-Ernzerhof implementation. In all calculations, ultrasoft pseudopotential and Koelling-Hamon relativistic treatment were used. The other conditions were all in the default settings of "fine" quality, while a plane-wave basis set with a cutoff of 310 eV was used. All the lattice constants and atomic coordinates were optimized until the maximum force of all atoms was less than 0.03 eV/Å. Γ -centered K-points with 5 \times 5 \times 1 and 5 \times 5 \times 2 mesh were used for sampling the Brillouin zone of the single layer and the double layer structure, respectively. To avoid interaction between images, a vacuum space of 15 Å was included. All the structures were downloaded from Springer Materials. More details related to calculations performed in the section of the DFT calculations are presented in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Structural Features. In order to shed light on the features of the structure and the texture of the produced TCMS self-supported electrodes, the experimental procedure of this synthesis process (schematically represented in Figure 1a) should be kept in mind. In brief, the green TiC ceramic membranes were obtained by phase inversion tape-casting; then, they were cut into customized small pieces and sintered at high temperature. Finally, the 1T-2H MoS₂ layer was grown on the TiC grains through the hydrothermal method.

The microstructure of the cross section of the green TiC ceramic membrane is shown in Figure 1b. A typical asymmetric structure is observed, which consists of a finger-like void region on the upper surface and a sponge-like region on the bottom surface. Small changes in the asymmetric structure occurred after sintering at 1600 °C (Figure 1c). Finger-like voids with a diameter of about 10–40 μ m are perpendicular to the surface and cover ~90% of the entire cross-sectional area of the membrane, while the sponge-like region occupies ~10%.

The top view of the surface of the finger-like voids (Figure 1d) reveals many large open pores. In the microstructure of the walls of the finger-like voids (Figure 1e), small pores with a diameter of several micrometers are observed. This microstructure is similar to that in the sponge-like region. The high porosity and the hierarchical pore structure favor the penetration of the electrolyte toward the internal space, provide a large area for the growth of the MoS₂ catalyst, and facilitate the escape of the produced gas from the inside layer to the environment. The conductivity was verified by a four-point probe method. Indeed, a small resistance of 0.23 m Ω sq⁻¹ was measured, which is ascribed to the good crystallization of TiC grains and the tight bonding of TiC grains with one another (Figure 1e).

The microstructure of the cross section for the TCMS 4 produced after the hydrothermal process is illustrated in Figure 2a,b. The microstructure of the TCMS 1, 2, 3, and 5 is depicted in Figure S2. It is observed that nano-MoS₂ sheets were homogeneously grown directly on the TiC grains. With the increase of the amount of thiourea, the density of the





Figure 1. (a) Schematic representation of the synthesis of the TiC@ MoS_2 self-supported electrodes and the microstructure of the TiC ceramic membrane (b) before and (c) after calcinations, (d) top view of the sintered membrane at the point marked with I in 1c, and (e) observation at high magnification in the region marked with II in 1c.



Figure 2. Microstructure (observed by SEM) of TCMS 4 at (a) low and (b) high magnification (b is the magnification of the marked area in a), HRTEM images of TCMS 4 (c) of the interface between MoS_2 nanosheet and TiC grain, and of a MoS_2 nanosheet at (d) low and (e) high magnification, (f) structural configuration of 2H and 1T MoS_2 at the c-axis view, and (g–l) EDS elemental mapping of TCMS 4.

nanosheets increases, and the petal-shaped MoS_2 nanosheets are evolved into hydrangea-shaped MoS_2 nanosheets. The edges of the MoS_2 nanosheets provide highly catalytic-active sites for HER, as will be discussed later.

A characteristic high-resolution transmission electron microscopy (HRTEM) image of the TiC-MoS₂ interface for the TCMS 4 is shown in Figure 2c. This image suggests a tight



Figure 3. (a) Raman and (b) XPS spectrum of TCMS 4 and analysis of the XPS spectra at (c) Mo 3d and (d) the S 2p peak regions. 289×202 mm.

bonding between the 1T-2H MoS₂ nanosheets and the TiC grains, which favors electron transfer between the catalyst of MoS_2 and the TiC skeleton. The crystalline space of 0.25 nm is indexed to the (111) plane of TiC. The layer distance of 0.64 nm is slightly larger than the 0.62 nm of the MoS_2 crystal, suggesting an expansion of the interlayer due to the strong interactions between TiC and $MoS_2^{.34}$ MoS_2 belongs to the layered transition-metal dichalcogenides, which is a type of 2D materials composed of S-Mo-S layers, where Mo is the transition metal and S is a chalcogen, with the stoichiometry of MoS_2 . The structure is held by strong intralayer covalent bonds and weak interlayer distance.^{35,36} This lattice expansion should result in more available basal sites and, therefore, it should improve the catalytic activity.³⁷

The HRTEM image of a $1T-2H MoS_2$ nanosheet, presented in Figure 2d, suggests that the nanosheet is a polycrystal. In the magnified image of one crystal plane shown in Figure 2e, two distinct kinds of lattice exist in a plane, which can be identified as the 1T phase and the 2H phase of MoS₂, whose structural configurations are illustrated in Figure 2f.^{38,39} 1 T-MoS₂ (Figure 2e) displays a hexagonal lattice structure, where the purple dots indicate the Mo atoms, and each Mo atom is at an equal distance from the six surrounding Mo atoms. 2H-MoS₂ (Figure 2e) exhibits a honeycomb lattice structure, where the purple dots represent the Mo atoms. Each hexagonal ring comprises three Mo atoms and three S atoms, and each Mo atom is at an equal distance from the three surrounding Mo atoms. The 1T phase reduces the charge transfer resistance and provides additional catalytic-active sites for HER.⁴⁰ According to the EDS elemental mapping for the elements of Ti, C, Mo, S, and O (Figure 2g–l), MoS_2 was uniformly distributed. In the layered MoS_2 nanosheets, the bond length between the Mo and S atoms (calculated as 2.42 Å) is shorter than the distance between the S atoms (calculated as 3.13 Å),⁴¹ while the S–Mo–S bond angle is the same as that for the structure with the covalent bond. Note that the bond between adjacent S atoms is weak. Consequently, cleavage surfaces with low surface energy occur easily, resulting in high hydrophilicity.⁴²

The Raman spectra confirm the coexistence of 1T and 2H MoS_2 (Figure 3a). More specifically, the two main Raman bands at 378 and 403 cm⁻¹ are attributed to in-plane E_{2g}^1 mode and out-of-plane A_{1g} modes, respectively, which are characteristic signals of 2H-MoS2. The A1g modes are associated with out-of-plane vibration of the sulfur atoms in the opposite direction, while the E_{2g}^1 mode is linked to the inplane displacement owing to the shear force applied between Mo and S atoms. Meanwhile, the peak at 450 cm⁻¹ is ascribed to the longitudinal acoustic phonon mode of $2H-MoS_2$, and the E_{1g} band at 283 cm⁻¹ is related to the octahedral coordination of Mo in 1T MoS₂.⁴³ The three signals at 148, 221, and 335 cm⁻¹ correspond to J_{12} , J_{22} , and J_{33} , respectively, and they are related to the phonon modes of 1T-MoS₂. These results support the coexistence of 1T and 2H phases in the TCMS electrode. It is noteworthy that the high edge-exposed degree of the 1T MoS₂ phase is beneficial for the HER process.44

In the X-ray diffractograms of the TiC membrane and TCMS 4 (presented in Figure S3), only the diffraction patterns of TiC (JCPDS 32-1383) can be detected. There is no



Figure 4. (a) Linear sweep voltammetry (LSV) curves (scan rate $1 \text{ mV} \cdot \text{s}^{-1}$) of TiC, TCMS 1/2/3/4/5, and commercial Pt/C electrodes in HER in 0.5 M H₂SO₄, (b) Tafel plots derived from the LSV curves for HER, (c) linear fitting of the capacity current density at various scan rates for TiC and TCMS electrodes, (d) Nyquist plots for TiC and TCMS electrodes at an overpotential of -315 mV (with respect to the RHE), (e) chronoamperometry profile of TCMS 4 at the overpotential of -150 mV for 24 h, and (f) LSV curves of the fresh (as prepared) TCMS 4 electrode and after 5000 cycles of CV testing.

evidence of the MoS_2 crystal, which can be attributed to its low amount and the severe lattice distortion (Figure S3). The addition of SiC aimed at removing the low amount of TiO₂ existing on the surface of TiC and the Y₂O₃ sintering additive, according to the following chemical equations:⁴⁵

$$TiO_2 + 3 SiC \rightarrow TiC + 3 Si(g) + 2 CO(g)$$

$$Si(g) + Y_2O_3 \rightarrow SiO(g) + 2 YO(g)$$

$$SiC + 2Y_2O_3 \rightarrow SiO(g) + CO(g) + 4YO(g)$$

The remaining Si should exist in the form of the amorphous phase, which cannot be detected by XRD analysis.

The chemical features of the elements were investigated through XPS. The peaks in the XPS spectrum (Figure 3b) show that TCMS 4 is composed of the elements of Ti, C, Mo, S, O, N, and Si, where N is attributed to the sintering atmosphere. There are six deconvoluted Mo 3d peaks in the high-resolution XPS spectrum (Figure 3c and Figure S4a–d). The peaks at 233.1 and 236.2 eV are related to Mo⁶⁺ from the oxidation in air (MoO₃). The surface oxidation is inevitable and cannot be neglected for nonoxide crystals.⁴⁶ The surface oxidation was further studied through XPS analyses on fresh (as-prepared) TCMS 4 and TCMS 4 that was aged in a drying cabinet for various periods of time. As shown in Figure S5, the MoO₃ content increases with the increase of aging time and remains stable after 5 days, suggesting that the surface

oxidation has reached a stable state after 5 days. The influence of aging on the catalytic performance is discussed later.

The four peaks at 232.2, 228.9, 233.0, and 229.7 eV correspond to $Mo^{4+} 3d_{3/2}$ and $3d_{5/2}$ of 1T phases and $Mo^{4+} 3d_{3/2}$ and $3d_{5/2}$ of 2H phases, respectively. The peaks of the 1T phase exhibit an obvious negative shift of approximately 0.8 eV, in comparison with the corresponding peaks of the 2H phase. Based on the ratio of the areas of the peaks in Figure 3c and Figure S4, the 1T content in TCMS 1/2/3/4/5 is 47.2, 47.8, 58.0, 66.5, and 55.61%, respectively, that is, the highest content in 1T, which efficiently promotes the charge transfer during the HER process, 47-51 was achieved in TCMS 4. The calculation of the abovementioned contents is presented in the Supporting Information.

In the S 2p region of TCMS 1/2/3/4/5 (Figure 3d and Figure S6a-d), additional peaks of the 1T phase at 162.9 and 161.9 eV are observed, besides the known doublet peaks of S²⁻ 2p_{1/2} and 2p_{3/2} of the 2H phase, which occur at 164.4 and 163.4 eV, respectively. This further confirms the coexistence of 1T and 2H phases.

The features of the texture of TCMS 4 were determined by the BET method. From the results of the adsorption and desorption curves and the pore size distribution (Figure S7), the specific surface area was calculated as 17.5 m² g⁻¹, the specific volume as 0.0928 cm³g⁻¹, and the mean pore size as 21.2 nm. Furthermore, a type II isotherm with a hysteresis loop was observed, which is characteristic of the nanostructure.⁵²



Figure 5. Theoretical models used in DFT calculations for the various adsorption sites of H on these model surfaces for (a) TiC, (b) $1T-MoS_2$, (c) $2H-MoS_2$, (d) $2H-MoS_2/TiC$, and (e) $1T-MoS_2/TiC$ and (f) corresponding Gibbs free energy for HER. The green, yellow, gray, white, and red spheres refer to Mo, S, Ti, C, and H, respectively.

The combination of the interconnected finger-like structure with the nanostructure of MoS_2 greatly facilitates the accessibility to the abundant catalytic sites of the hydrangea-shaped orbicular MoS_2 , as well as the release of the bubbles, the infiltration of the electrolyte, and the charge transfer needed for efficient HER.¹⁰

3.2. Electrocatalytic Performance. The electrocatalytic performance of TCMS was evaluated by electrochemical measurements performed in acidic conditions $(0.5 \text{ M H}_2\text{SO}_4)$ using a conventional three-electrode setup. The as-prepared TCMS was used directly as a working electrode for HER, and its electrocatalytic activity was evaluated by LSV measurements with the aid of a commercial purchased Pt/C (20%) wire and a TiC electrode for comparison purposes.

According to Figure 4a, Pt/C is an excellent catalyst with an ultrasmall overpotential, whereas the HER performance of the pure TiC substrate is very poor. All the TCMS samples displayed good electrocatalytic performance, ascribed to the good compatibility of the hybrid 1T-2H MoS₂ with the conductive TiC skeleton. A higher Mo/S ratio results in a lower density for the aligned MoS₂ nanosheets on the surface of the TiC skeleton. This means that fewer active edges of MoS₂ are obtained. However, if the Mo/S ratio is too low, then excess MoS₂ clusters will reunite together and cover the exposed active edges.

TCMS 4 demonstrates outstanding activity toward the HER, and small overpotentials of -127 and -160 mV were observed in order to reach current densities of -10 and -50 mA·cm⁻², respectively. As far as the original conductive skeleton of the TiC membrane is concerned, current densities of -10 and -50 mA·cm⁻² were not achieved until overpotentials of -266 and -330 mV, respectively, were observed. It was found that TCMS 4 greatly surpasses its powdery counterpart (1T-2H MoS₂).⁴⁸ To achieve a current density of -10 mA·cm⁻², a powdery 1T-2H MoS₂ catalyst loaded on a glassy carbon electrode requires an overpotential of -220 mV, which is almost 100 mV bigger than that for TCMS 4.

The surface oxidation significantly influences the HER performance. As shown in Figure S8, fresh TCMS 4 exhibits an overpotential of -81 mV at $-10 \text{ mA} \cdot \text{cm}^{-2}$. After aging for 3, 5, and 10 days, the overpotential decreases to -93, -127, and

-127 mV, respectively. Although the fresh TCMS 4 exhibits the best performance, it decays quickly and becomes finally worse than the sample which was aged for 5 days. This is in good agreement with the oxygen content, suggesting that the formation of the MoO₃ surface layer might decrease HER performance, but can stabilize the electrode. Accordingly, in order to achieve a stable HER performance, all the electrodes were aged for a period of time before performing the test.

HER is a multistep electrochemical process occurring on the cathode that produces hydrogen. The general reaction mechanism in acid is summarized by the following reactions:

(a) Volmer step:

$$H^+ + TCMS + e^- \rightarrow TCMSH_{ads}$$

(b) Heyrovsky step:

$$TCMSH_{ade} + H^+ + e^- \rightarrow TCMS + H_2$$

(c) Tafel step:

$$2TCMSH_{ads} \rightarrow 2TCMS + H_2$$

where TCMSH_{ads} represents the state that a hydrogen atom is chemically adsorbed on an active site of the catalyst (TCMS). More specifically, the first step, called the Volmer step, corresponds to the adsorption of H by coupling one proton from the acid electrolyte with one electron from TCMS. In the second step, the adsorbed H atom is combined with another proton accompanied by an electron to form a hydrogen molecule, and this is called the Heyrovsky step, or with another adjacent adsorbed H atom, and this is called Tafel step, whereby a hydrogen molecule is formed as well.⁴

The value of the Tafel slope allows for the determination of the rate-controlling step.⁵³ Tafel slopes (Figure 4b) were determined as 38, 117, 48, 43, 42, 41, and 43 mV·dec⁻¹ for Pt/C, TiC, and TCMS 1/2/3/4/5, respectively. Generally, a small Tafel slope corresponds to a greater catalytic current density at a lower overpotential, which leads to faster chemical reaction kinetics. All TCMS electrodes exhibit a low Tafel slope close to that of Pt/C, suggesting fast reaction kinetics. TCMS 4 demonstrates the smallest Tafel slope, which is attributed to its

higher 1T content (the highest of the others). It is also suggested that the HER on TCMS takes place through the Volmer–Heyrovsky process.

In order to cast light on the origin of the superior activity of TCMS electrodes, the electrochemical double-layer capacity $(C_{\rm dl})$ that reflects the electrochemically active surface area was measured. The results of the tests, carried out by scanning the voltage ranging from 0.483 to 0.512 V (with respect to RHE) at a rate of 1-5 mV·s⁻¹, are shown in Figure 4c and Figure S9a–f. TCMS 4 has an extremely high electrochemical activity area of 1079.4 mF·cm⁻². The markedly high density of the catalytic active sites is attributed to the high density of the MoS₂ nanosheets and to the high 1T content.

The results from the electrochemical impedance spectroscopy manifest that the Nyquist plot of TCMS 4 (13.4 Ω) has the smallest semicircle among all the investigated electrodes (Figure 4d). This features its low charge transfer impedance, which is consistent with the higher intrinsic conductivity of 1T-MoS₂, ascribed to the higher proportion of 1T-2H.

The stability of the electrodes during HER was also investigated. According to Figure 4e, long-term controlled potential electrolysis of HER at -150 mV overpotential, carried out with iR compensation, showed that TCMS 4 delivers almost constant current density under a stationary overpotential. In addition, the LSV curve (Figure 4f), recorded after 5000 cycles of CV testing, is a good match to that of the fresh sample. A small decrease of only 4% was recorded after 24 h. Figure S10 presents a scanning electron microscopy image of MoS₂ layer on TCMS 4 after 5000 cycles of CV testing, and Figure S11a—f shows the results of transmission electron microscopy-EDS analysis of TCMS 4. It is clearly seen that the original morphology and the homogeneous elemental distribution were perfectly maintained. These results indicate the excellent electrochemical stability of TCMS 4.

It is well known that a low value of $|\Delta G_{\rm H}|$ reflects a high catalytic activity.⁵⁴ Hence, in order to throw light on the excellent HER performance of the TCMS, the free energy of H adsorption $(\Delta G_{\rm H})$ on various surfaces was evaluated by firstprinciples DFT calculations. The models for hydrogen adsorption on TiC, 2H-MoS₂, 1T-MoS₂, 2H-MoS₂/TiC, and 1 T-MoS₂/TiC are depicted in Figure 5a-e, respectively. 1T-MoS₂ has an extremely low $|\Delta G_{\rm H}|$ value of 0.281 eV; yet, its synthesis is difficult, which restricts its large-scale production. According to Figure 5f, hydrogen can easily be adsorbed on the S site of 2H-MoS₂/TiC or of 1T-MoS₂/TiC. The value of $|\Delta G_{\rm H}|$ is 0.116 eV for the combination of 1T-MoS₂ with TiC and 0.525 eV for that of 2H-MoS2 with TiC, which are significantly lower than those of TiC (0.849 eV) and 2H-MoS₂ (1.153 eV) (Figure 5f). Consequently, 1T-MoS₂/TiC is revealed to be the TCMS with the most active centers needed for HER.

In light of the abovementioned good results, we explored the advanced practical use of TCMS electrodes for hydrogen generation using an acidic electrolyte (0.5 M H_2SO_4). A high FE of 99.7% was achieved (Figure 6). Moreover, the experimentally determined amount of hydrogen was a good match with the theoretically calculated values (Figure 6).

The synergistic effect of the tight bonding between TiC and MoS_2 on the superior electrocatalytic activity was further studied with the aid of first-principles DFT calculations, as shown in Figure 7. Both 1T-MoS₂ with TiC and 2H-MoS₂ with TiC have higher densities of states near the Fermi level, compared with 1T and 2H MoS₂ alone. This suggests that the



pubs.acs.org/cm

Figure 6. Amount of hydrogen, experimentally determined, is a good match with the theoretically calculated values as a function of time for TCMS 4.



Figure 7. Density of states (DOS) calculated for $1T-MoS_2/TiC$, $2H-MoS_2/TiC$, $1T-MoS_2$, $2H-MoS_2$, and TiC.

TCMS catalytic electrode has fast charge transfer and good catalytic performance.

A comparison between the results of HER performance of TCMS 4 produced in the present study and other MoS₂containing catalysts synthesized on various substrates reported in literature is comprehensively presented in Table S1. As previously mentioned, the substrates which were employed to support powder catalysts are generally poorly conductive and catalytically inert, providing low current density. The use of binders may block the active sites and suppress rapid electron transfer. TCMS 4 exhibits superior electrocatalytic activity and good long-term stability, attributed to the synergistic effect of the tight bonding and the crystal matching between TiC and MoS₂, to the unique dual pore structure, the abundant exposed active sites in MoS₂ nanosheets, and the high 1T-MoS₂ content. Compared to other electrodes, the TCMS electrodes produced in the present study also possess high mechanical strength due to the intrinsic mechanical properties of TiC and resistance to erosion in acidic conditions. Additionally, they were produced by an easy and reliable synthesis method, which (i.e., the synthesis method), therefore, reveals high potential for fabrication of these electrodes on a large scale in order to promote the industrial production of hydrogen.

4. CONCLUSIONS

A self-supported HER electrode, which consists of vertically aligned nanosheets of 1T-2H MoS₂ on the TiC porous-ceramic membrane, was successfully produced through a combined phase inversion tape-casting and sintering method, followed by an easy hydrothermal routine. The hydrangea-shaped MoS₂ provides numerous active sites, and the porous conductive skeleton allows for sufficient accessibility to active sites and efficient charge transfer. DFT calculations showed that the combination of 1T-2H MoS₂ with TiC leads to small hydrogen adsorption energy, in other words, to a remarkable activity of HER. An outstanding performance, with a small overpotential of $-127 \text{ mV} (-10 \text{ mA} \cdot \text{cm}^{-2})$, a favorable Tafel slope of 41 mV·dec⁻¹, and an excellent electrochemical stability, was recorded, which is better than that reported in other studies on similar MoS₂-based catalysts in literature. A high FE of 99.7% was also determined. The results suggest that this synthesis protocol can be further extended to produce various catalytic electrodes with various electrocatalytic properties. It can also be extremely useful in the industry of hydrogen production as well as in other catalytic processes.

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.1c01965.

Additional details for calculations, setup demonstration, scanning electron microscopy images, XRD patterns, XPS spectra, BET measurements, linear sweep voltammetry curves, cyclic voltammogram curves, EDS elementary mapping, and comparative tables (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Xin Xu CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China; orcid.org/0000-0001-6547-255X; Phone: +86-551-63600824; Email: xuxin@ ustc.edu.cn; Fax: +86-18655117978
- Yuxi Xian CAS Key Laboratory of Mechanical Behaviors and Design of Materials, Department of Modern Mechanics, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China; Email: yxxian@ustc.edu.cn

Authors

- Yangyang Shi CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China
- **Dewen Zheng** New Energy Research Center, Research Institute of Petroleum Exploration & Development (RIPED), PetroChina, Beijing 100083, P. R. China
- Xi Zhang New Energy Research Center, Research Institute of Petroleum Exploration & Development (RIPED), PetroChina, Beijing 100083, P. R. China

Kai Lv – CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Feihong Wang – CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

- Binbin Dong CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China
- Shanyu Wang New Energy Research Center, Research Institute of Petroleum Exploration & Development (RIPED), PetroChina, Beijing 100083, P. R. China

Chunxia Yang – New Energy Research Center, Research Institute of Petroleum Exploration & Development (RIPED), PetroChina, Beijing 100083, P. R. China

Jianming Li – New Energy Research Center, Research Institute of Petroleum Exploration & Development (RIPED), PetroChina, Beijing 100083, P. R. China

Fengyi Yang – ĆAŠ Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Lu Yuan Hao – CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Liangjun Yin – School of Energy Science and Engineering, University of Electronic Science and Technology of China, Chengdu 611731, P. R. China; orcid.org/0000-0003-0297-5488

Simeon Agathopoulos – Department of Materials Science and Engineering, University of Ioannina, Ioannina GR-451 10, Greece

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.chemmater.1c01965

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the National Natural Science Foundation of China (U1732115 and 21533007) and China National Petroleum Corporation (KD200121).

REFERENCES

(1) Winsche, W. E.; Hoffman, K. C.; Salzano, F. J. Hydrogen: Its Future Role in the Nation's Energy Economy. *Science* **1973**, *180*, 1325–1332.

(2) Turner, J. A. Sustainable hydrogen production. *Science* 2004, 305, 972–974.

(3) Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I. B.; Nørskov, J. K.; Jaramillo, T. F. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* **2017**, *355*, No. eaad4998.

(4) Li, Y.; Sun, Y.; Qin, Y.; Zhang, W.; Wang, L.; Luo, M.; Yang, H.; Guo, S. Recent Advances on Water-Splitting Electrocatalysis Mediated by Noble-Metal-Based Nanostructured Materials. *Adv. Energy Mater.* **2020**, *10*, No. 1903120.

(5) Shan, J.; Ling, T.; Davey, K.; Zheng, Y.; Qiao, S. Z. Transition-Metal-Doped RuIr Bifunctional Nanocrystals for Overall Water Splitting in Acidic Environments. *Adv. Mater.* 2019, *31*, No. 1900510.
(6) Lin, L.; Sherrell, P.; Liu, Y.; Lei, W.; Zhang, S.; Zhang, H.; Wallace, G. G.; Chen, J. Engineered 2D Transition Metal Dichalcogenides—A Vision of Viable Hydrogen Evolution Reaction Catalysis. *Adv. Energy Mater.* 2020, *10*, No. 1903870.

(7) Fu, Q.; Han, J.; Wang, X.; Xu, P.; Yao, T.; Zhong, J.; Zhong, W.; Liu, S.; Gao, T.; Zhang, Z.; Xu, L.; Song, B. 2D Transition Metal Dichalcogenides: Design, Modulation, and Challenges in Electrocatalysis. *Adv. Mater.* **2021**, *33*, No. 1907818.

(8) Guo, Y.; Park, T.; Yi, J. W.; Henzie, J.; Kim, J.; Wang, Z.; Jiang, B.; Bando, Y.; Sugahara, Y.; Tang, J.; Yamauchi, Y. Nanoarchitectonics for Transition-Metal-Sulfide-Based Electrocatalysts for Water Splitting. *Adv. Mater.* **2019**, *31*, No. 1807134.

(9) Wang, J.; Xu, F.; Jin, H.; Chen, Y.; Wang, Y. Non-Noble Metalbased Carbon Composites in Hydrogen Evolution Reaction: Fundamentals to Applications. *Adv. Mater.* **201**7, *29*, No. 165838.

(10) Ko, D. J.; Jin, X. Z.; Seong, K. D.; Yan, B. Y.; Chai, H.; Kim, J. M.; Hwang, M.; Choi, J.; Zhang, W.; Piao, Y. Z. Few-layered MoS_2 vertically aligned on 3D interconnected porous carbon nanosheets for hydrogen evolution. *Appl. Catal. B.* **2019**, *248*, 357–365.

(11) Chang, K.; Hai, X.; Pang, H.; Zhang, H.; Shi, L.; Liu, G.; Liu, H.; Zhao, G.; Li, M.; Ye, J. Targeted Synthesis of 2H- and 1T-Phase MoS₂ Monolayers for Catalytic Hydrogen Evolution. *Adv. Mater.* **2016**, *28*, 10033–10041.

(12) Wang, H.; Xiao, X.; Liu, S.; Chiang, C. L.; Kuai, X.; Peng, C. K.; Lin, Y. C.; Meng, X.; Zhao, J.; Choi, J.; Lin, Y. G.; Lee, J. M.; Gao, L. Structural and Electronic Optimization of MoS₂ Edges for Hydrogen Evolution. J. Am. Chem. Soc. **2019**, 141, 18578–18584.

(13) Wan, Y.; Zhang, Z.; Xu, X.; Zhang, Z.; Li, P.; Fang, X.; Zhang, K.; Yuan, K.; Liu, K.; Ran, G.; Li, Y.; Ye, Y.; Dai, L. Engineering active edge sites of fractal-shaped single-layer MoS₂ catalysts for high-efficiency hydrogen evolution. *Nano Energy* **2018**, *51*, 786–792.

(14) Ekspong, J.; Sandström, R.; Rajukumar, L. P.; Terrones, M.; Wågberg, T.; Gracia-Espino, E. Stable Sulfur-Intercalated $1T' MoS_2$ on Graphitic Nanoribbons as Hydrogen Evolution Electrocatalyst. *Adv. Funct. Mater.* **2018**, *28*, No. 1802744.

(15) Xiong, Q.; Wang, Y.; Liu, P. F.; Zheng, L. R.; Wang, G.; Yang, H. G.; Wong, P. K.; Zhang, H.; Zhao, H. Cobalt Covalent Doping in MoS₂ to Induce Bifunctionality of Overall Water Splitting. *Adv. Mater.* **2018**, *30*, No. 1801450.

(16) Song, S.; Wang, Y.; Li, W.; Tian, P.; Zhou, S.; Gao, H.; Tian, X.; Zang, J. Amorphous MoS₂ coated Ni₃S₂ nanosheets as bifunctional electrocatalysts for high-efficiency overall water splitting. *Electrochim. Acta* **2020**, 332, No. 135454.

(17) Han, X.; Tong, X.; Liu, X.; Chen, A.; Wen, X.; Yang, N.; Guo, X. Y. Hydrogen Evolution Reaction on Hybrid Catalysts of Vertical MoS₂ Nanosheets and Hydrogenated Graphene. *ACS Catal.* **2018**, *8*, 1828–1836.

(18) Yang, W.; Chen, S. Recent progress in electrode fabrication for electrocatalytic hydrogen evolution reaction: A mini review. *Chem. Eng. J.* **2020**, *393*, No. 124726.

(19) de Aza, P. N.; Guitián, F.; de Aza, S. Bioeutectic: a new ceramic material for human bone replacement. *Biomaterials* **1997**, *18*, 1285–1291.

(20) Wang, J.-W.; Li, N.-X.; Li, Z.-R.; Wang, J.-R.; Xu, X.; Chen, C.-S. Preparation and gas separation properties of Zeolitic imidazolate frameworks-8 (ZIF-8) membranes supported on silicon nitride ceramic hollow fibers. *Ceram. Int.* **2016**, *42*, 8949–8954.

(21) Yu, L.; Kanezashi, M.; Nagasawa, H.; Tsuru, T. Phase inversion/sintering-induced porous ceramic microsheet membranes for high-quality separation of oily wastewater. *J. Membr. Sci.* 2020, 595, No. 117477.

(22) Chang, Y.; Sun, X.; Ma, M.; Mu, C.; Li, P.; Li, L.; Li, M.; Nie, A.; Xiang, J.; Zhao, Z.; He, J.; Wen, F.; Liu, Z.; Tian, Y. Application of hard ceramic materials B_4C in energy storage: Design $B_4C@C$ coreshell nanoparticles as electrodes for flexible all-solid-state microsupercapacitors with ultrahigh cyclability. *Nano Energy* **2020**, *75*, No. 104947.

(23) Nishihora, R. K.; Rachadel, P. L.; Quadri, M. G. N.; Hotza, D. Manufacturing Porous Ceramic Materials by Tape Casting – A Review. *J. Eur. Ceram. Soc.* **2018**, *38*, 988–1001.

(24) Fulazzaky, M. A.; Khamidun, M. H.; Omar, R. Understanding of mass transfer resistance for the adsorption of solute onto porous material from the modified mass transfer factor models. *Chem. Eng. J.* **2013**, *228*, 1023–1029.

(25) Qiu, Z.; Huang, H.; Du, J.; Tao, X.; Xia, Y.; Feng, T.; Gan, Y.; Zhang, W. Biotemplated synthesis of bark-structured TiC nanowires as Pt catalyst supports with enhanced electrocatalytic activity and durability for methanol oxidation. *J. Mater. Chem. A* **2014**, *2*, 8003–8008.

(26) Song, S.; Li, W.; Deng, Y. P.; Ruan, Y.; Zhang, Y.; Qin, X.; Chen, Z. TiC supported amorphous MnO_x as highly efficient bifunctional electrocatalyst for corrosion resistant oxygen electrode of Zn-air batteries. *Nano Energy* **2020**, *67*, No. 104208.

(27) Xu, J.; Yang, N.; Heuser, S.; Yu, S.; Schulte, A.; Schönherr, H.; Jiang, X. Achieving Ultrahigh Energy Densities of Supercapacitors with Porous Titanium Carbide/Boron-Doped Diamond Composite Electrodes. *Adv. Energy Mater.* **2019**, *9*, No. 1803623.

(28) Yang, D.; Zhou, Y.; Yan, X.; Wang, H.; Zhou, X. Highly conductive wear resistant $Cu/Ti_3SiC_2(TiC/SiC)$ co-continuous composites via vacuum infiltration process. J. Adv. Ceram. 2020, 9, 83–93.

(29) Lorenz, M.; Travitzky, N.; Rambo, C. R. Effect of processing parameters on in situ screen printing-assisted synthesis and electrical properties of Ti₃SiC₂-based structures. *J. Adv. Ceram.* **2021**, *10*, 129–138.

(30) Fang, Y.; Liu, X.; Feng, Y.; Zhu, J.; Jiang, W. Microstructure and mechanical properties of $Ti_3(Al,Ga)C_2/Al_2O_3$ composites prepared by in situ reactive hot pressing. *J. Adv. Ceram.* **2020**, *9*, 782–790.

(31) Seh, Z. W.; Fredrickson, K. D.; Anasori, B.; Kibsgaard, J.; Strickler, A. L.; Lukatskaya, M. R.; Gogotsi, Y.; Jaramillo, T. F.; Vojvodic, A. Two-Dimensional Molybdenum Carbide (MXene) as an Efficient Electrocatalyst for Hydrogen Evolution. *ACS Energy Lett.* **2016**, *1*, 589–594.

(32) Ramalingam, V.; Varadhan, P.; Fu, H. C.; Kim, H.; Zhang, D.; Chen, S.; Song, L.; Ma, D.; Wang, Y.; Alshareef, H. N.; He, J. H. Heteroatom-Mediated Interactions between Ruthenium Single Atoms and an MXene Support for Efficient Hydrogen Evolution. *Adv. Mater.* **2019**, *31*, No. 1903841.

(33) Yang, Q.; Zhang, C.; Dong, B.; Cui, Y.; Wang, F.; Cai, J.; Jin, P.; Feng, L. Synergistic modulation of nanostructure and active sites: Ternary Ru&Fe-WOx electrocatalyst for boosting concurrent generations of hydrogen and formate over 500 mA cm⁻². *Appl. Catal. B: Environ.* **2021**, *296*, No. 120359.

(34) Feng, Y.; Zhang, T.; Zhang, J.; Fan, H.; He, C.; Song, J. 3D 1T- MoS_2 /CoS₂ Heterostructure via Interface Engineering for Ultrafast Hydrogen Evolution Reaction. *Small* **2020**, *16*, No. e2002850.

(35) Park, S.; Kim, C.; Park, S. O.; Oh, N. K.; Kim, U.; Lee, J.; Seo, J.; Yang, Y.; Lim, H. Y.; Kwak, S. K.; Kim, G.; Park, H. Phase Engineering of Transition Metal Dichalcogenides with Unprecedentedly High Phase Purity, Stability, and Scalability via Molten-Metal-Assisted Intercalation. *Adv. Mater.* **2020**, *32*, No. 2001889.

(36) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L. J.; Loh, K. P.; Zhang, H. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nat. Chem.* **2013**, *5*, 263–275.

(37) Xue, Y.; Zhang, Q.; Wang, W.; Cao, H.; Yang, Q.; Fu, L. Opening Two-Dimensional Materials for Energy Conversion and Storage: A Concept. *Adv. Energy Mater.* **2017**, *7*, No. 1602648.

(38) Kim, H.-U.; Kim, M.; Seok, H.; Park, K.-Y.; Moon, J.-Y.; Park, J.; An, B.-S.; Jung, H. J.; Dravid, V. P.; Whang, D.; Lee, J.-H.; Kim, T. Realization of Wafer-Scale 1T-MoS₂ Film for Efficient Hydrogen Evolution Reaction. *ChemSusChem* **2021**, *14*, 1344–1350.

(39) Zhang, K.; Jin, B.; Gao, Y.; Zhang, S.; Shin, H.; Zeng, H.; Park, J. H. Aligned Heterointerface-Induced 1T-MoS₂ Monolayer with Near-Ideal Gibbs Free for Stable Hydrogen Evolution Reaction. *Small* **2019**, *15*, No. 1804903.

(40) Wang, S.; Zhang, D.; Li, B.; Zhang, C.; du, Z.; Yin, H.; Bi, X.; Yang, S. Ultrastable In-Plane 1T-2H MoS₂ Heterostructures for Enhanced Hydrogen Evolution Reaction. *Adv. Energy Mater.* **2018**, *8*, No. 1801345.

(41) Pan, H.; Zhang, Y.-W. Tuning the Electronic and Magnetic Properties of MoS₂ Nanoribbons by Strain Engineering. *J. Phys.Chem. C.* **2012**, *116*, 11752–11757.

(42) Lei, L.; Huang, D.; Zeng, G.; Cheng, M.; Jiang, D.; Zhou, C.; Chen, S.; Wang, W. A fantastic two-dimensional MoS_2 material based on the inert basal planes activation: Electronic structure, synthesis strategies, catalytic active sites, catalytic and electronics properties. *Coord. Chem. Rev.* **2019**, 399, No. 213020.

(43) Chou, S. S.; Sai, N.; Lu, P.; Coker, E. N.; Liu, S.; Artyushkova, K.; Luk, T. S.; Kaehr, B.; Brinker, C. J. Understanding catalysis in a multiphasic two-dimensional transition metal dichalcogenide. *Nat. Commun.* **2015**, *6*, 8311.

(44) Kong, D.; Wang, H.; Cha, J. J.; Pasta, M.; Koski, K. J.; Yao, J.; Cui, Y. Synthesis of MoS_2 and $MoSe_2$ films with vertically aligned layers. *Nano Lett.* **2013**, *13*, 1341–1347.

(45) Khodaei, M.; Yaghobizadeh, O.; Ehsani, N.; Baharvandi, H. R. The effect of TiO_2 additive on the electrical resistivity and mechanical properties of pressureless sintered SiC ceramics with Al_2O_3 - Y_2O_3 . *Int. J. Refract. Hard Met.* **2018**, *76*, 141–148.

(46) Xu, Q.; Liu, Y.; Jiang, H.; Hu, Y.; Liu, H.; Li, C. Unsaturated Sulfur Edge Engineering of Strongly Coupled MoS₂ Nanosheet– Carbon Macroporous Hybrid Catalyst for Enhanced Hydrogen Generation. *Adv. Energy Mater.* **2019**, *9*, No. 1802553.

(47) Nam, G. H.; He, Q.; Wang, X.; Yu, Y.; Chen, J.; Zhang, K.; Yang, Z.; Hu, D.; Lai, Z.; Li, B.; Xiong, Q.; Zhang, Q.; Gu, L.; Zhang, H. In-Plane Anisotropic Properties of 1T'-MoS₂ Layers. *Adv. Mater.* **2019**, 31, No. 1807764.

(48) Liu, Z.; Gao, Z.; Liu, Y.; Xia, M.; Wang, R.; Li, N. Heterogeneous Nanostructure Based on 1T-Phase MoS₂ for Enhanced Electrocatalytic Hydrogen Evolution. *ACS Appl. Mater. Interfaces* **201***7*, *9*, 25291–25297.

(49) Lei, Z.; Zhan, J.; Tang, L.; Zhang, Y.; Wang, Y. Recent Development of Metallic (1T) Phase of Molybdenum Disulfide for Energy Conversion and Storage. *Adv. Energy Mater.* **2018**, *8*, No. 1703482.

(50) Liu, Z.; Zhao, L.; Liu, Y.; Gao, Z.; Yuan, S.; Li, X.; Li, N.; Miao, S. Vertical nanosheet array of 1T phase MoS₂ for efficient and stable hydrogen evolution. *Appl. Catal. B.* **2019**, *246*, 296–302.

(51) Zhang, W.; Liao, X.; Pan, X.; Yan, M.; Li, Y.; Tian, X.; Zhao, Y.; Xu, L.; Mai, L. Superior Hydrogen Evolution Reaction Performance in 2H-MoS₂ to that of 1T Phase. *Small* **2019**, *15*, No. 1900964.

(52) Su, J.; Yang, Y.; Xia, G.; Chen, J.; Jiang, P.; Chen, Q. Ruthenium-cobalt nanoalloys encapsulated in nitrogen-doped graphene as active electrocatalysts for producing hydrogen in alkaline media. *Nat. Commun.* **2017**, *8*, 16028.

(53) Jiao, Y.; Zheng, Y.; Jaroniec, M.; Qiao, S. Z. Design of electrocatalysts for oxygen- and hydrogen-involving energy conversion reactions. *Chem. Soc. Rev.* **2015**, *44*, 2060–2086.

(54) Sahoo, S. K.; Ye, Y.; Lee, S.; Park, J.; Lee, H.; Lee, J.; Han, J. W. Rational Design of TiC-Supported Single-Atom Electrocatalysts for Hydrogen Evolution and Selective Oxygen Reduction Reactions. *ACS Energy Lett.* **2019**, *4*, 126–132.