Boundary activated hydrogen evolution reaction on monolayer MoS$_2$

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Recently, monolayer molybdenum disulphide (MoS$_2$) has emerged as a promising and non-precious electrocatalyst for hydrogen evolution reaction. However, its performance is largely limited by the low density and poor reactivity of active sites within its basal plane. Here, we report that domain boundaries in the basal plane of monolayer MoS$_2$ can greatly enhance its hydrogen evolution reaction performance by serving as active sites. Two types of effective domain boundaries, the 2H-2H domain boundaries and the 2H-1T phase boundaries, were investigated. Superior hydrogen evolution reaction catalytic activity, long-term stability and universality in both acidic and alkaline conditions were achieved based on a multi-hierarchy design of these two types of domain boundaries. We further demonstrate that such superior catalysts are feasible at a large scale by applying this multi-hierarchy design of domain boundaries to wafer-scale monolayer MoS$_2$ films.

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Hydrogen evolution reaction (HER) process is crucial to the production of hydrogen, the most efficient and environmental-friendly fuel. Platinum (Pt) and Pt-based materials are known as the best electrocatalysts for HER so far, but they are also very scarce and expensive. Recently, molybdenum disulfide (MoS₂) has emerged as an active, earth-abundant, and inexpensive alternative to Pt and Pt-based electrocatalysts. It is generally believed that the catalytic activity of MoS₂ originates from its edges while its basal plane is rather inert, which limits the practical application of this material for HER. In order to overcome the limited catalytic activity of the MoS₂ basal plane, various techniques have been developed, such as phase engineering, interface electronic coupling, introducing active unsaturated defects and strain. These techniques could improve the restricted factors (poor conductivity and limited active sites) for the potential of MoS₂ in HER. Recently, a pioneer strategy has been proposed by introducing S vacancies into the basal plane, where gap states around the Fermi level allow hydrogen to bind directly to exposed Mo atoms. Considering the presence of dangling bonds in vacancy defects, these vacancy defects in MoS₂ are easy to be poisoned and would lead to the surface instability from a HER point of view. To fully exploit MoS₂ materials in realistic application, searching for alternative methods is crucial.

Herein, we report a facile route toward the activation of the monolayer MoS₂ basal plane for HER by introducing domain boundaries, including both 2H–2H domain boundaries and 2H–1T-phase boundaries. We found that the domain boundaries can provide ultrahigh-density active sites, while still maintaining the surface stability. Utilizing a multi-hierarchy design of these two types of boundaries, we are able to achieve a high basal-plane electrocatalytic performance with an exchange current density of 0.57 × 10⁻⁴ A cm⁻², a Tafel slope of 73 mV dec⁻¹, and a remarkable long-term operation stability over 200 h. We also demonstrate that such catalysts are scalable, e.g., over 4-inch wafer scale, pushing a crucial technological step toward practical applications.

Results

2H–2H domain boundaries and 2H–1T-phase boundaries for HER. In this study, we investigated both single-crystalline and polycrystalline 2H-phase monolayer MoS₂ samples grown by chemical vapor deposition (CVD) for HER. The former samples (type-I) were grown on sapphire substrates with individual domain size of a few hundred micrometers (refer to ref. 25 for our previous work). The latter samples were continuous film samples grown either on sapphire substrates (type-II) with highly oriented domains of a few micrometers (refer to ref. 26 for our previous work) or on SiO₂/Si substrates (type-III) with randomly oriented domains of a few hundred nanometers (refer to ref. 27 for our previous work). Figure 1a–c show typical optical and false-color transmission electron microscope (TEM) images of these different monolayer MoS₂ samples to illustrate their domain sizes and the 2H–2H domain boundaries. Hence, we have three types of MoS₂ samples for comparable investigation of the HER performances: type-I free of 2H–2H domain boundaries, type-II with low density of 2H–2H domain boundaries, and type-III with high density of 2H–2H domain boundaries (further details in Supplementary Fig. 1). Note that the 2H–2H domain boundaries in our MoS₂ samples are not perfectly straight. These boundaries usually consist of various configurations, typically including arrays of 4–6 rings (4|6), 6–8 rings (6|8), 5–7 rings (5|7), and 4–4 rings (4|4) as shown in Supplementary Fig. 2. The high-resolution TEM and X-ray photoelectron spectroscopy (XPS) were used to confirm that all samples are of high quality with low-defect density and very clean surfaces even after transfer processes (Supplementary Fig. 3). Hence, the influence of defects in different types of samples can be excluded.

In order to investigate whether the 2H–2H domain boundaries could serve as active sites in HER, local probe characterizations were first performed (further details in Supplementary Note 1 and Supplementary Fig. 4). Figure 1d and e show two typical HER devices fabricated from type-I and type-III samples, respectively. Note that these devices were protected by polymethyl methacrylate (PMMA) masks with only small windows exposed on the MoS₂ samples in the center to avoid the contribution from the MoS₂ edges during the HER characterizations. The corresponding HER polarization curves and Tafel plots of both devices are shown in Fig. 1f, g, respectively. It can be clearly seen that type-III samples have better catalytic performances than type-I samples as evidenced by the drop of the overpotential from ~375 mV to ~325 mV at current density of 10 A cm⁻² and the Tafel slope from ~110 to ~95 mV dec⁻¹. Since the qualities of the two samples are very similar, except for the density of domain boundaries, we can thus draw a conclusion that the enhanced HER activity in type-III samples comes from the 2H–2H domain boundaries.

Then we explored the possibility of further introducing 2H–1T-phase boundaries as active sites in HER. In order to produce such boundaries, we performed post low-energy Ar⁺ plasma bombardments on pristine type-I and type-III samples to induce the 2H-to-1T-phase transition (refer to ref. 28 for our previous work). Note that this phase transition is quite local and the resulted samples consist of a mosaic texture of nearly half 2H- and half 1T-phases, exhibiting an average domain size of a few nanometers and high-density phase boundaries (Supplementary Fig. 5). HER performances of two typical heterophase devices similar to those described above are shown in Fig. 1f, g. For type-I sample after phase transition, a drop of the overpotential from ~370 to ~260 mV at current density of 10 A cm⁻² and the Tafel slope from ~110 to ~85 mV dec⁻¹ can be clearly seen, suggesting that 2H–1T-phase boundaries are more efficient for HER as active reaction sites than 2H–2H boundaries. Besides, the metallic 1T phase offers better charge transport capability than the 2H phase, which is consistent with previous report. Notably, the heterophase type-III sample exhibits the lowest overpotential of 200 mV and Tafel slope of 75 mV dec⁻¹. In order to confirm that no other defects in the heterophase structure contributed prominently to the enhanced HER activity, we performed atomic force microscopy (AFM) and STM characterizations. Only few S vacancies (~1.9%) having little effect on HER can be found without any other defects in the heterophase sample (details in Supplementary Figs. 6–7 and Supplementary Note 2). Particularly, we also found that these S vacancies would not introduce gap states that allow favorable hydrogen adsorption (Supplementary Fig. 7). We have also performed thermal annealing for our phase-changed samples to investigate the effect of phase boundaries. Thermal annealing was carried out in vacuum at 600 °C for 1 h. This process can recover from all 1T phases back to 2H phases in our sample (as confirmed in Supplementary Fig. 8a). Meanwhile, after annealing treatment, the HER performance degrades to the same level of pristine MoS₂, as shown in Supplementary Fig. 8b. On the basis of these results, we concluded that the phase boundaries are dominant active sites in our heterophase MoS₂ samples while those S vacancies contribute less to enhance the HER performance. Thus the composite structure containing both high-density domain and phase boundaries is the most promising candidate for HER.

Mechanism of the activation of the MoS₂ basal plane by boundaries. In order to confirm the role of 2H–1T-phase boundaries in the basal plane of MoS₂ in HER, we performed
scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) characterizations. Since STM/STS measurements require conductive substrates, MoS2 samples were epitaxially grown on graphite by CVD and treated by Ar–plasma to induce phase transitions subsequently. Figure 2a shows a typical topographic STM image of the monolayer heterophase MoS2, where bright and dark regions correspond to the 2H and 1T phases, respectively. A zoom-in image at one-phase boundary is shown in Fig. 2b with the top sulfur (S) atoms clearly resolved. The sliding of S atoms in 1T phase with respect to the 2H phase further confirmed coexistence of the two phases (details in Supplementary Fig. 9). As shown in Fig. 2c, 2H-phase domains have bandgaps as usual, e.g., ~2.5 eV; in contrast, 1T-phase domains are metallic without bandgaps.

In HER process, stable hydrogen adsorption at active sites is a crucial step. Therefore, we simulated this step via hydrogenating the heterophase sample surface by the atomic hydrogen (see Supporting Information for more details). After hydrogenation, additional depression features with atomic-size width appear exactly at the phase boundaries (Fig. 2d, e), suggesting that the atomic hydrogen prefers to adsorb at the S sites of phase boundary. Density functional theory (DFT) calculations were also carried out to confirm the STM observations. Simulated results indicate that the formation of S–H covalent bonds can lead to a significant reduction of the density of states (DOS) of S atoms around the Fermi level (Fig. 2f), which is consistent with the apparent depression observed in the STM images due to the adsorption of H atoms on the S atoms.

Next, we performed further DFT calculations on the 2H–2H grain boundaries and the 2H–1T-phase boundaries to investigate their catalytic activities (see Supporting Information for computational details). Figure 3a, b show the structural model of

Fig. 1 Activity of 2H–2H domain boundaries and 2H–1T-phase boundaries for HER. a Optical image of the type-I MoS2 with individual domain size of few hundreds microns transferred onto a TEM grid. b HRTEM images of as-grown type-II MoS2 film with highly orientated domains of few microns for the domain sizes. c False-color dark-field TEM image of type-III MoS2 with high-density 2H–2H domain boundaries. d, e Optical microscope image of a individual MoS2 single-crystal domain without 2H–2H domain boundaries (d) and polycrystalline ML–MoS2 with domain boundaries (e). Dashed regions indicate the HER window opened on the basal plane. f Polarization curves of the pristine type-I MoS2 (without any domain boundaries), pristine type-III MoS2 (with 2H–2H domain boundaries), heterophase type-I MoS2 (with 2H–1T-phase domain boundaries), and heterophase type-III MoS2 (with both 2H–2H and 2H–1T domain boundaries), respectively. g Tafel plots of the corresponding curves in f
2H–1T-phase boundaries and four typical kinds of 2H–2H boundary configurations (4|8, 6|8, 4|4, 5|7) \(^{24}\). Figure 3c shows the calculated Gibbs free energy of the adsorbed atomic hydrogen (\(\Delta G_{\text{H}}\)). Note that \(\Delta G_{\text{H}}\) is a widely accepted indicator for the catalytic activity and the optimal value is \(\Delta G_{\text{H}} = 0\) eV, where hydrogen is bounded neither too strongly nor too weakly \(^{31}\). For comparison, we also performed calculations on Pt (111) surface, basal plane of 2H–MoS\(_2\) and 1T–MoS\(_2\) with the same sized supercells as for the phase boundaries, yielding \(\Delta G_{\text{H1T}} = -0.18\) eV, 1.87 eV, and \(-6.97\) eV, respectively (Fig. 3b). These numbers are consistent with previous calculations \(^{10,12–36}\). Due to the high instability of the pristine 1T phase, the initial binding of hydrogen on a pure 1T-phase basal plane is quite strong, which results in heavy relaxation of the adsorption area. This releases most of the 1T energy, making the structure rather inert for the further adsorption of hydrogen atoms \(^{14,37,38}\). Moreover, for the 1T phase confined within 2H phase by interfaces, the strong relaxations at the interfaces have the similar effect as the initial H adsorption, which prevents the confined 1T phase to adsorb more H atoms favorably (further details in Supplementary Fig. 10). This can explain the absence of H adsorption at the nanometer-size 1T phase as shown in the STEM image (Fig. 2d, e). The Gibbs free energy of all the H adsorption sites in 2H–2H boundaries can indeed break the inertia of the basal plane and enhance the interaction between the H atom and the adsorption sites. Impressively, the 2H–1T-phase boundaries exhibit \(\Delta G_{\text{H1T}} = -0.13\) eV (Fig. 3b), very close to that of the Pt (111) surface and Mo-edge of 2H–MoS\(_2\). Thus, phase boundaries in the basal plane of monolayer MoS\(_2\) could serve as effective sites to tune hydrogen reaction barriers and optimize the overall kinetics of H\(_2\) evolution \(^{39,40}\).

**Multi-hierarchy monolayer MoS\(_2\) catalysts for HER.** Based on the above experimental and theoretical results, we can conclude that both domain boundaries and phase boundaries can serve as active sites in HER. More boundaries, in principle, should offer better HER performance. We thus investigated the effect of boundary density in a systematic way. MoS\(_2\) electrodes for electrocatalytic HER testing were fabricated from pristine type-II and type-III samples (with low density of 2H–2H domain boundaries), pristine type-III samples (with high density of 2H–2H domain boundaries), and a series of heterophase type-III samples with varying density of 2H–1T-phase boundaries. As mentioned above, the heterophase MoS\(_2\) can be produced by Ar–plasma bombardments; while the percentage of 1T-phase in 2H-phase matrix, thus the density of phase boundaries, can be actually tuned by the treatment durations. The illustrated multi-hierarchy...
adsorbed H on 2H-phase of MoS2, 1T-phase of MoS2, Pt(111) surface, and HER context of HER potential at 10 mA/cm² decreased linearly with increasing the resistive loss and accelerate electron transport from the MoS2 layers, as an internal electron transport channels, can decrease the currents, but have long-term stability and universality in both acidic and alkaline conditions. Moreover, the ML–MoS2 electrocatalysts with composite boundary can also be easily scaled up. As a proof-of-concept demonstration, a 4-inch wafer-scale catalysts, exhibited in Fig.4f, was prepared for HER. The wafer-scale catalysts sample still exhibit good HER properties (see Supplementary Fig. 18 and Supplementary Movie 1 for more details).

In conclusion, we have both experimentally and theoretically verified that 2H–2H and 2H–1T domain boundaries in basal plane of ML–MoS2 could act as new highly active and tunable catalytic sites for HER. Based on the observed phenomena, we then achieved multi-hierarchy ML–MoS2 electrocatalysts containing both types of domain boundaries for HER. These electrocatalysts not only show remarkable electrocatalytic performances with a small overpotential of ~0.1 V and large cathodic currents, but have long-term stability and universality in both acidic and alkaline conditions. Moreover, the ML–MoS2 electrocatalysts with composite boundary can be easily scaled up. Our results provide a comprehensive understanding of the HER mechanism for the MoS2 basal plane, as well as a facile route to design high-performance electrocatalysts.

Methods

Growth of the monolayer 2H-MoS2 using CVD method. A three zone furnace was used for CVD growth of MoS2. SiO2 (300 nm)/P++Si and highly oriented pyrolytic graphite (HOPG) served as substrates. Sulfur (S) (Alfa Aesar 99.99%) and molybdenum trioxide (MoO3) (Alfa Aesar 99.999%) were used as precursors and loaded in zone I and II, respectively. The distance between the two sources was 22 cm. The substrates were put in the third zone. The temperatures of MoO3, S, and substrates were 560, 120, and 780 °C, respectively. Each temperature zone was kept stable for 20 min before the growth. During the growth, argon was used as carrying gas at a flow rate of 130 sccm, and the vacuum pressure was kept at 0.67 Torr.

Formation of heterophase MoS2. Phase transition of MoS2 was also performed in the home-made, remote plasma system reported in our previous work29. An
inductively coupled plasma was generated by dispersing a 20 W RF power at the entrance of a 4-inch quartz-tube furnace. The pressure in the tube furnace was fixed at 0.69 Torr for phase transition by flowing argon at 100 sccm and vacuum pumping. The process was carried out for 10, 20, 30, 40 s at room temperature, respectively.

**Characterization details.** The as-grown layer monolayer MoS2 samples were characterized by optical microscopy, AFM (Bruker Icon microscope, tapping mode), Raman spectroscopy (532 nm laser, Horiba Jobin Yvon LabRAM HR-Evolution Raman), X-ray photoelectron spectroscopy (Kratos Analytical Axis Ultra).

**Electrochemical characterizations.** All of the electrochemical measurements were performed in a typical three-electrode system on electrochemical workstation (Autolab PGSTAT 302 N). A Pt foil or a glassy carbon electrode (for long time test) were used as counter electrodes, and saturated Ag/AgCl electrode serve as the reference electrode. The linear sweep voltammetry (LSV) with the scan rate of 5 mV s−1 was carried out. All the applied potentials were converted to reversible hydrogen electrode (RHE) potentials scaled using the equation $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.204$ V + 0.0591 VPH, after IR correction. The stability tests for the heterogeneous MoS2 was performed using chronoamperometry at a constant applied overpotential.

**Computational details.** First-principles calculations based on DFT were carried out by using the Vienna Ab initio Simulation Package (VASP)7,10. The interactions between valence electrons and ions were treated with the projector-augmented wave (PAW) method8. The exchange-correlation interactions were described by generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional9. The electron wave functions were expanded in a plane-wave basis set with cutoff energy of 520 eV. The convergence criterion for residual force on each atom during structure relaxation was set to 0.02 eV/Å, and the geometries were relaxed to minimize the total energy of the system until a precision of 10−6 eV was reached.

**Data availability** All data are available from the authors upon reasonable request. All source data underlying Figs. 1a, f, 2c, 3c, 4b-e and Supplementary Figs. 1g, h, 3d, e, 5a-c, 7c, 8a, 12a, d, 13a-c, 16, 17 and 18d are provided as a Source Data file.

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