Layered molybdenum disulfide has demonstrated great promise as a low-cost alternative to platinum-based catalysts for electrochemical hydrogen production from water. Research effort on this material has focused mainly on synthesizing highly nanostructured molybdenum disulfide that allows the exposure of a large fraction of active edge sites. Here we report a promising microwave-assisted strategy for the synthesis of narrow molybdenum disulfide nanosheets with edge-terminated structure and a significantly expanded interlayer spacing, which exhibit striking kinetic metrics with onset potential of $-103$ mV, Tafel slope of $49$ mV per decade and exchange current density of $9.62 \times 10^{-3}$ mA cm$^{-2}$, performing among the best of current molybdenum disulfide catalysts. Besides benefits from the edge-terminated structure, the expanded interlayer distance with modified electronic structure is also responsible for the observed catalytic improvement, which suggests a potential way to design newly advanced molybdenum disulfide catalysts through modulating the interlayer distance.
The blueprint of 'hydrogen (H₂) economy' is to store energy from renewable sources, such as sunlight or wind, into the chemical bond of H₂ via electrolysis of water, which then can be released through the reverse reaction in fuel cells on demand. However, the scalable production of H₂ from water significantly depends on the efficiency of electrocatalytic materials. Ideal electrocatalysts must be, stable and capable of reducing water rapidly at potentials close to its thermodynamic value (2H⁺ + 2e⁻ → H₂; 0 — 0.059 × pH, V versus normal H₂ electrode at 298 K)²,³. Although platinum (Pt) and its alloys can catalyse H₂ evolution reaction (HER) at potentials slightly below the thermodynamic potential for the H⁺ /H₂ couple²,⁴, the high cost and scarcity of Pt pose tremendous limitation to widespread adoption. Therefore, the critical determinant of the energy storage in electrolytic systems is to develop robust and efficient alternative catalysts that are cheap and Earth abundant.

Remarkable advances have been made recently regarding the use of chalcogenides of cobalt⁵–⁹, nickel⁸,¹⁰, molybdenum⁹,¹¹–¹⁹ and tungsten¹⁵,²⁰,²³ as promising noble metal-free catalysts for HER. Among these materials, molybdenum disulfide (MoS₂), a widely used industrial catalyst for hydrodesulfurization of petroleum⁷², has received special attention and the catalytic active sites were identified theoretically²³ and experimentally²⁴. Similar to many inorganic solids, the HER activity of MoS₂ is localized to the rare edge surfaces, whereas the (0001) basal planes are relatively inactive³⁵–²⁷. Motivated by this understanding, intense research efforts have been focused on developing highly nanostructured MoS₂ to maximize the number of exposed edge sites, including crystalline²⁶–²⁹ and amorphous materials¹²,¹⁵,³⁰,³¹ metallic 1T polymorph³², vertically aligned structures³³,³⁴ and molecular mimics³⁵. Other strategies to improve HER performance include incorporating MoS₂ with conductive materials by taking advantage of synergetic coupling effects³⁴–³⁸ or doping first-row transition metal ions (for example, Fe, Co and Ni) into MoS₂ to optimize its catalytic sites at S-edges²⁶,³⁹. Despite striking achievements, many practical challenges still remain to improve the activity and stability of MoS₂-based catalysts.

Here, we report a class of colloidal MoS₂ nanostructure with edge-terminated and interlayer-expanded (ET&IE) features that exhibits high activity and stability towards HER in acidic water. Its fast kinetic metrics (including onset potential of ~103 mV and the Tafel slope of 49 mV per decade) demonstrate superior electrocatalytic activity relative to the reported MoS₂-only catalysts. In addition to the benefit of edge-terminated structure, the expansion of interlayers can further modify electronic structures and electrical conductivity of MoS₂ edge sites, leading to improved performance. This study hints at the promise of cheap and efficient HER electrocatalysts by modulating interlayer distance in two-dimensional atomic-layered materials.

### Results

**Microwave-assisted synthesis of ET&IE MoS₂.** The ET&IE MoS₂ were synthesized through reduction of (NH₄)₂MoS₄ in N,N-dimethylformamide (DMF) with the assistance of microwave heating. Compared with conventional heating methods, microwave-assisted synthesis is a greener strategy with high-level thermal management and dramatically reduced reaction time and therefore new nanostructured materials are likely to be achieved⁴⁰. Reaction at 240 °C for 2 h results in a yield of ~93% of ET&IE MoS₂, demonstrating the rapid and efficient microwave chemistry. A schematic overview of the synthesis procedure is shown in Fig. 1 and the details are described in the Methods. The morphology and microstructure of MoS₂ prepared at different temperatures was studied by transmission electron microscopy (TEM) (Fig. 2a–c) and high-resolution TEM (HRTEM) (Fig. 2d–f). Reaction at low temperature (for example, 190 °C) forms reticulated network of amorphous materials (Fig. 2a), where some tiny MoS₂-layered crystals appear (Fig. 2d), indicating the formation of crystalline nuclei from the amorphous matrix. Increasing reaction temperature results in the formation and growth of crystalline nuclei into larger MoS₂ nanocrystals via consumption of the amorphous materials. For example, MoS₂ synthesized at 240 °C exhibits a sheet-like morphology with sizes of tens of nanometres (Fig. 2b). HRTEM image in Fig. 2e clearly shows the resolved S—Mo—S layers with a curved stripe-like feature (Supplementary Fig. 1) and the layer-to-layer spacing is about 9.4 Å. Further increasing temperature to 260 °C produces three-dimensional flower-like MoS₂ with better crystallinity (Fig. 2c and inset). HRTEM image of a typical MoS₂ flower reveals that it is built from interlaced crystalline MoS₂ nanosheets (Fig. 2f).

Figure 2g presents the X-ray diffraction patterns of these samples, which are significantly different from that of bulk 2H–MoS₂ (JCPDS 77-1,716; Supplementary Fig. 2). Two new peaks with diploid relationship appears at low-angle region correspond to (001) and (002) reflections with d spacings of 9.4 and 4.7 Å, respectively. In comparison to the d spacing of 6.15 Å for pristine 2H–MoS₂, the expanded interlayers of our samples is likely due to the intercalation of oxidized DMF species into two S—Mo—S layers (Supplementary Fig. 3). The asymmetric nature of the reflection at 2θ ≈ 32.7° revealed the presence of stacking faults⁴¹ among MoS₂ layers as a result of a—b plane gliding caused by intercalated DMF species. A recent work also reported a large interlayer spacing of 9.5 Å in hydrothermally prepared MoS₂, which however was ascribed to oxygen incorporation⁴². Unlike the product formed at 260 °C, the barely recognizable diffraction peaks of other two samples indicate the low crystallinity, which is consistent with their selected-area electron diffraction (SAED) patterns. Particularly, the greatly broad first peak for 240 °C sample was the result of its curly and crossed edge-terminated structure (Fig. 2e). The calculated X-ray diffraction pattern using an interlayer spacing of 9.4 Å along the c axis was found to agree well with experimentally collected patterns (Fig. 2g).

Energy-dispersive X-ray spectra showed that the as-synthesized samples are mainly composed of Mo and S (Supplementary Fig. 4). Raman spectra in Fig. 2h exhibited two distinct peaks at 379.2 cm⁻¹ and 402.7 cm⁻¹, which correspond to the in-plane Mo—S phonon mode (E₁g) and the out-of-plane Mo—S mode (A₁g) of typical MoS₂-layered structure, respectively³³,³⁷. The relative intensities of A₁g/E₁g provide texture information on the surface of deposited MoS₂ films and the largest ratio of 2.02 for 240 °C
sample suggests that it favours the vibration of $A_{1g}$ mode and thus the best edge-terminated structure$^{33,37}$, which is consistent with the TEM observations (Fig. 2a–f). The phase and morphology evolutions of ET&IE MoS$_2$ were also studied by time-dependent reactions at 240 °C and the results are presented in Supplementary Figs 5 and 6.

**Electrocatalytic HER activity.** The electrocatalytic properties of ET&IE MoS$_2$ for evolving H$_2$ were evaluated in Ar-saturated 0.5 M H$_2$SO$_4$ electrolyte and compared with state-of-the-art Pt/C catalyst. The ohmic potential drop (iR) losses from the solution resistance were corrected. The electrodes were kept rotating at 1,600 r.p.m throughout the measurements in order to remove in situ produced H$_2$ bubbles. Figure 3a compares the current densities achieved within a cathodic potential window for the glassy carbon electrodes modified with different catalysts. The featureless polarization curve for bare glassy carbon guarantees a minimal background. Scanning cathodically reveals that the onset potential of H$_2$ evolution occurs at approximately $0.10$ V versus reversible hydrogen electrode (RHE) for the MoS$_2$ synthesized at 240 °C, beyond which a sharp increase in catalytic reduction current emerges (Fig. 3a). The optimum catalyst loading was determined to be 0.28 mg cm$^{-2}$ (Supplementary Fig. 7). In contrast, MoS$_2$ prepared at 190 °C and 260 °C mediate hydrogen evolution at larger overpotential ($\eta$) of 0.15 and 0.12 V, respectively, while bulk MoS$_2$ offers negligible H$_2$-evolving activity. The superior activity of the MoS$_2$ synthesized at 240 °C is believed to originate from both its edge-terminated and interlayer-expanded structure. The dependence of the logarithmic current density on $\eta$ (log $j$–$\eta$) was plotted to probe the HER kinetics. Figure 3b shows that a sharp increase in current density appeared once the onset potential was reached. The linear relationship of log $j$ and $\eta$ delivers useful kinetic metrics of above catalysts, namely the Tafel slope. The Tafel slope of 49 mV per decade was measured for the MoS$_2$ synthesized at 240 °C, which is smaller than those of other catalysts except for the state-of-the-art Pt/C catalyst (Fig. 3b). This Tafel slope is comparable to or smaller than that of other MoS$_2$-only HER catalysts (Supplementary Table 1) and even many MoS$_2$-based hybrid catalysts (Supplementary Table 2) reported in literature, indicating the efficient kinetics of H$_2$ evolution catalysed by the MoS$_2$ synthesized at 240 °C. The $\eta$
required for starting HER on various MoS2-only catalysts was compared in Fig. 3c, where ET&IE MoS2 shows a 20–100 mV decrease in \( \eta \) relative to that of documented MoS2. The fast HER kinetics also enabled this ET&IE MoS2 catalyst to reach a high current density of 10 mA cm\(^{-2} \) at \( \eta \) as low as 0.149 V, outperforming most of the MoS\(_2\)-based HER catalysts (Fig. 3d, Supplementary Tables 1 and 2). Exchange current density (\( j_0 \)), the most inherent measure of HER activity, was carefully determined to evaluate the quality of ET&IE MoS\(_2\) (Supplementary Fig. 8). The \( j_0 \) of 9.62 \times 10\(^{-3} \) mA cm\(^{-2} \) for 240 °C sample surpasses the values of 7.59 \times 10\(^{-4} \) mA cm\(^{-2} \) for 190 °C sample and 2.46 \times 10\(^{-3} \) mA cm\(^{-2} \) for 260 °C sample, as well as the \( j_0 \) values reported for MoS\(_2\)-only HER catalysts (Supplementary Table 1).

Moreover, the turnover frequency of H\(_2\) molecules evolved per second (s\(^{-1} \)) for ET&IE MoS\(_2\) was determined to be 1.14 s\(^{-1} \) at \( \eta \) of 200 mV, comparing favourably with the reported MoS\(_2\)-only and even some MoS\(_2\)-based hybrid catalysts (Supplementary Table 3 and Supplementary Note 1). These results highlight the exceptional H\(_2\)-evolving efficiency of this new ET&IE MoS\(_2\).

We also applied electrochemical impedance spectroscopy (EIS) technique to provide further insight into the electrode kinetics under HER process (that is, adding a \( \eta \) of 0.2 V). The Nyquist plots (Fig. 3e and inset) show that ET&IE MoS\(_2\) synthesized at 240 °C has the smallest charge transfer resistance (\( R_{ct} \)) of only 3.13 Ω, indicating the ultrafast Faradaic process and thus a superior HER kinetics. We attribute this measured small \( R_{ct} \) to its
synergetic ET&IE structure. The edge-terminated feature can ensure an isotropic electron transport from glassy carbon substrate to MoS2 edges and significantly decrease the resistance for traversed layers. In addition, the expanded interlayer distance can bring beneficial structural and electronic modulations (which will be discussed below), enabling each MoS2 layer to resemble more closely to a monolayer structure and a better overall conductivity of our ET&IE MoS2. The double-layer capacitance (Cdl), which is proportional to the effective electrochemically active surface area\(^{27,32}\), was further measured to probe the advantage of the ET&IE structure (Fig. 3f). The observed large Cdl of 15.3 mF cm\(^{-2}\) for 240 °C sample indicated its high exposure of active edge sites, comparing favourably with other studied catalysts (Fig. 3f, Supplementary Fig. 9) and thus the improved HER activity. HER performance of the MoS2 nanostructures synthesized at 240 °C for different reaction times was compared and the results are presented in Supplementary Figs 10 and 11.

**Material stability of ET&IE MoS2.** The long-term stability of ET&IE MoS2 and associated ability to continuously catalyse the generation of H\(_2\) was examined using chronoamperometry (j ∼ t). This quasi-electrolysis process was conducted at a constant η of 200 mV in 0.5 M H\(_2\)SO\(_4\) (Fig. 4a). Remarkably, the H\(_2\) evolution can proceed at a sustained current density of −28 mA cm\(^{-2}\) even over 65 h of continuous operation, suggesting the ultrahigh stability of the ET&IE MoS2 catalyst. The striking stability was further proved by a long-term cyclic voltammetry cycling test operating in the same electrolyte. Figure 4b shows that, after 3,000 cyclic voltammetry cycles, only negligible decay was observed in high current density region, where the massive H\(_2\) bubbles generated at the electrode surface raise the mass transport resistance for the HER. Moreover, this new MoS2 demonstrates good chemical stability with no obvious degradation of HER activity after storing it under lab environment for 3 months (Supplementary Fig. 12). Digital photos (Fig. 4c) taken from the ET&IE MoS2-coated fluorine-doped tin oxide (FTO) show vigorous effervescence maintained with no decay even after 5 h of continuous operation while clean FTO is inert (Supplementary Fig. 13). The substantial long-term stability and chemical stability of ET&IE MoS2 suggest the great promise of using this catalyst to fabricate cost-effective and efficient H\(_2\) evolution electrode in viable water electrolysis systems.

**HER enhancement mechanism.** An understanding of intrinsic reasons for the remarkable HER property of ET&IE MoS2 will be helpful for future HER catalyst design. It is agreed that for a highly active HER catalyst the Gibbs free energy of adsorbed hydrogen (ΔG\(_{\text{H2}}\)) is close to thermoneutral (that is, ΔG\(_{\text{H2}}\) ≈ 0\(^{1,23,26}\)). Deviating from this value will make the hydrogen either form a strong bond or not bind efficiently to the catalyst, leading to inefficient hydrogen release and proton–electron transfer and therefore decreased catalytic activity. Recent density functional theory (DFT) calculations revealed that MoS2 has a ΔG\(_{\text{H2}}\) of 0.08 eV at the Mo edges and should be a good HER catalyst\(^{23}\). This prediction was later experimentally verified by the finding that MoS2 edge sites are highly HER active while its basal planes are inert\(^{24}\). Here, our microwave-synthesized MoS2 preferentially has a high ratio of catalytically active edge sites relative to basal sites due to its highly curved sheet-like structure (Fig. 2b,e and Supplementary Fig. 1), which provides one reason for its striking HER activity.

The superior \(j_0\) (9.62 × 10\(^{-3}\) mA cm\(^{-2}\)) of the ET&IE MoS2 relative to that of documented MoS2 (Supplementary Table 1) prompted us to further consider another underlying enhancement mechanism in this material. Previous reports demonstrated that the electronic structure of MoS2 can be modified to optimize

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**Figure 4** | HER stability of ET&IE MoS2. (a) Chronoamperometric responses (j ∼ t) recorded from synthesized ET&IE MoS2 at a constant overpotential of 200 mV (no iR compensation). (b) Polarization curves recorded from ET&IE MoS2 with a sweep rate of 5 mV s\(^{-1}\) before and after 3,000 potential cycles between −0.3 and 0.3 V versus RHE at a sweep rate of 200 mV s\(^{-1}\) (with iR compensation). (c) Digital photos show the H\(_2\) bubbles on ET&IE MoS2-modified FTO before and after 5 h of operation (MoS2 loading: ∼22.1 µg cm\(^{-2}\)). All the measurements were performed in Ar-saturated 0.5 M H\(_2\)SO\(_4\) (pH ∼ 0).
ΔG_H2 decrease of 0.01 eV on S edges, Supplementary Fig. 14). This electronic effect will strengthen the H adsorption and offer an increased H coverage on the edge sites48. Our calculations also show that the hydrogen adsorption energy (ΔE_H2) on Mo edges decreases by about 0.05 eV (a decrease of 0.01 eV on S edges, Supplementary Fig. 15 and Supplementary Note 2) for ET&IE MoS2 as compared to that for non-expanded MoS2 (Fig. 5c). For pristine 2H–MoS2, previous calculations revealed that it has a ΔE_H2 of +0.08 eV at the Mo edges with only 25% H coverage under operating conditions and a strengthened H adsorption on the edge sites is needed to improve its activity23,24. The reduced ΔE_H2 (∼0.05 eV) of the ET&IE MoS2 enables an optimized bond strength of the adsorbed H on the Mo edges and thereby a faster proton adsorption kinetics24, agreeing well with the DOS results. The advantages of edge-terminated nanostructure that exposes an abundance of active edge sites, as well as the enlarged interlayer distance with modified edge electronic structures, together lead to the high HER performance of this single MoS2 catalyst (Fig. 5d).

Discussion
In summary, we demonstrate a new nanostructured MoS2 catalyst with edge-terminated and interlayer-expanded features that was synthesized through a microwave heating strategy. The measured HER activity and stability of this MoS2 structure exceed almost all the documented counterpart MoS2 and enable the promise for exploring it as a realistic H2 evolution electrode. Beside the edge-terminated structure that allows more active edge sites, the expanded interlayer distance can further optimize its electronic structure and therefore permits the performance gains. Our results here raise a new catalyst design concept regarding to layered materials through modulating their interlayer coupling.

Methods
Material synthesis. All chemicals were used as received without further purification. In a typical synthesis, 10 mg (NH4)2MoS4 (99.97%, Sigma-Aldrich) was added to 6 ml DMF (anhydrous, 99.8%, Sigma-Aldrich) followed by stirring for
15 min under ambient condition. The resulting solution was transferred into a 10 ml microwave reaction vessel, which was then heated to 240°C at the fast ramp of 180°C/s. The mixture was maintained for 2 h in a microwave (CEM corporation) operated under the sealed vessel mode. The reaction solution was cooled to room temperature with pressurized nitrogen flow and the resulting black product was collected via centrifugation (8,000 r.p.m. for 5 min). The precipitate was washed with distilled water and absolute ethanol for at least four times to remove ions and possible remnants, followed by drying at 60°C in an oven for 4 h. For the time-dependent experiment, the temperature was set at 240°C while reactions stopped at different times; for the temperature-dependent experiment, the reaction time was 2 h while the reaction temperatures were altered intentionally, all the corresponding products were collected for further studies.

**Characterization.** The as-synthesized samples were examined by X-ray powder diffraction was carried out on a Bruker D2 Phaser X-ray diffractometer with Cu Ka radiation (λ = 1.5406 Å) at 30 kV and a current of 10 mA. The morphology of the as-synthesized samples was determined by using a JOEL 1010FS) TEM. The HRTEM observation and SAED were taken on the same machine with an FEI Tecnai G2 F20 (USA) microscope. All samples were prepared by dropping the ethanol suspension containing uniformly dispersed nanocrystals onto the carbon-coated copper grids and dried at room temperature naturally. Raman spectra were performed using a Renishaw Microscope (excited with a 514 nm excitation laser. The Fourier transform infrared (FTIR) spectra were measured on a Thermo Fisher/Nicolet 6700 FTIR spectrometer at room temperature.

**Electrocatalytic study.** Electrocatalytic measurements were performed at room temperature using a rotating disk working electrode made of glassy carbon (PINE, 5 mm diameter, 0.196 cm²) controlled by a CH Instruments 700C potentiostat. The glassy carbon electrode was polished to a mirror finish and thoroughly cleaned before use. Pt coil and double junction Ag/AgCl (PINE, 4 M KCl) were used as counter and reference electrodes, respectively. All the potentials reported in this work were normalized against that of the RHE.

The preparation method of the working electrodes containing investigated catalysts can be found as follows. In short, 5 mg of catalyst powder was dispersed in 1 ml of 3:1 vol/vol deionized water/isopropanol mixed solvent, which was ultrasonicated for about 30 min to generate a homogeneous ink (no sedimentation occurred). The ink was added onto the r-SCA X-ray diffraction analysis system placed on the JOEL 1010FS) microscope. All samples were prepared by dropping the ethanol suspension containing uniformly dispersed nanocrystals onto the carbon-coated copper grids and dried at room temperature naturally. Raman spectra were performed using a Raman microscope (excited with a 514 nm excitation laser. The Fourier transform infrared (FTIR) spectra were measured on a Thermo Fisher/Nicolet 6700 FTIR spectrometer at room temperature.

**DFT calculations.** The hydrogen adsorption energy (ΔEh) calculations on strip models of non-expanded MoS2 and ET&IE MoS2 were performed by periodic DFT using the plane wave code Vienna Ab-initio Simulation Package (VASP). The change in hydrogen adsorption energies is reported as ΔEh. Structural models are represented using the visualization tool Visualization for Electronic and Structural Analysis (VESTA). Details of the calculation and relevant references are provided in the Supplementary Note 3.

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Author contributions
Y.S. and M.-R.G. conceived the idea. M.-R.G. planned and performed the experiments, collected and analysed the data. M.K.Y.C. performed the DFT calculations and analysed the computational data. M.-R.G., M.K.Y.C. and Y.S. co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

Additional information
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