Active hydrogen evolution through lattice distortion in metallic MoTe₂

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Abstract
Engineering surface atoms of transition metal dichalcogenides (TMDs) is a promising way to design catalysts for efficient electrochemical reactions including the hydrogen evolution reaction (HER). However, materials processing based on TMDs, such as vacancy creation or edge exposure, for active HER, has resulted in insufficient atomic-precision lattice homogeneity and a lack of clear understanding of HER over 2D materials. Here, we report a durable and effective HER at atomically defined reaction sites in 2D layered semimetallic MoTe₂ with intrinsic turnover frequency (TOF) of 0.14 s⁻¹ at 0 mV overpotential, which cannot be explained by the traditional volcano plot analysis. Unlike former electrochemical catalysts, the rate-determining step of the HER on the semimetallic MoTe₂, hydrogen adsorption, drives Peierls-type lattice distortion that, together with a surface charge density wave, unexpectedly enhances the HER. The active HER using unique 2D features of layered TMDs enables an optimal design of electrochemical catalysts and paves the way for a hydrogen economy.

1. Introduction
In designing the ideal electrochemical catalyst, the abundance of active sites, the rapid charge exchange on the surface, and the durability of the catalyst must be considered [1, 2]. In particular, a moderate binding energy or a Gibbs free energy change (ΔGθ) of atomic hydrogen adsorption close to 0 eV represents optimized catalytic activity in the case of the hydrogen evolution reaction [1–3]. Platinum (Pt) and Pt-based materials possess the above features, making them the best catalysts in electrochemistry [4]; however, there has been a continuous effort to replace the expensive Pt-based catalysts with inexpensive and earth-abundant materials such as transition metal dichalcogenides [5–7].

Active catalytic performance of the HER at MoS₂ edges that was comparable to Pt catalyst has been reported, and this has led to numerous studies of hybrid catalysts based on MoS₂ and other TMDs [8–10]. In those studies, two major limiting factors have been the limited number of active edges [1, 2, 5] and the inefficient electron transfer in MoS₂-based catalyst due to their semiconducting nature [5, 7, 11, 12]. Nanostructuring [5, 13], fabricating hybrid TMD materials [8–10], and converting the semiconducting phase partly to a metallic phase [5, 7, 14] have been extensively attempted to overcome these two bottlenecks. Unlike single-crystalline Pt, however, the new complicated TMD-based catalysts have not-controllable defect sites [15] and the absence of precise structures at the atomic scale or homogeneously over a wide area has resulted in a difficulty of clarifying exact HER mechanism in the new catalyst structures [1]. Realizing dense atomic-scale active sites on basal planes with high electric conductivity in homogeneous TMD single crystal is, therefore, required for elucidating and achieving effective HER catalysis.
Peierls distortion, spontaneous phase transition from Fermi surface nesting, occurs in group 6 TMDs such as MoTe₂ [16–19]. A critical feature of Peierls-distorted materials is the appearance of inhomogeneous surface charge distribution or charge density waves [20, 21]. In single-crystalline monoclinic (or 1T’-) MoTe₂, a spontaneous Peierls-type lattice distortion and a surface charge density wave are present with a period of ∼0.6 nm on the basal plane. Moreover, single crystalline 1T’-MoTe₂ is metallic, allowing rapid charge exchange at abundant active sites in electrochemical reactions, which lends itself to efficient HER catalysis.

We report effective HER catalysis over 1T’-MoTe₂ with intrinsic catalytic activity, per-site turnover frequency of 0.14 s⁻¹ at 0 mV overpotential, which is similar to that of Pt and cannot be explained by the traditional volcano plot. Unlike previously investigated HER catalysis, the rate-determining step of the HER on 1T’-MoTe₂, hydrogen adsorption, drives considerable electron doping and spontaneous lattice distortion. Atomic site-dependent ΔGₐₗₜ, improved by the H atom adsorption-driven lattice distortion, and surface charge density waves by the spontaneous lattice distortion in the MoTe₂ are correlated, enhancing the HER. Given that highly conductive semimetallic TMDs are arising as an ideal electrochemical catalyst, our study provides critical insights into the 2D system for hydrogen evolution.

2. Results and discussion

We synthesized 2H- and 1T’-MoTe₂ single crystals, as previously reported, by the flux method [17]. The two atomic structures (2H and 1T’) of MoTe₂ are schematically described in figures 1(a) and (b). Whereas 2H-MoTe₂ has flat terrace composed of Te atoms on top, 1T’-MoTe₂ exhibits a distortion of Mo and Te atoms [17]. Similarly to its counterpart in group 6 TMDs, MoS₂, the two polymorphs have different electronic properties: the 2H phase is semiconducting, and the bulk 1T’ phase is semimetallic. The room-temperature resistivity of our bulk 1T’-MoTe₂ was measured to be 3.6 × 10⁻⁶ Ω·m (conductivity of ~2.8 × 10⁴ S m⁻¹) by an independent two-probe electric measurement using a formula, ρ = RA/l where R is the resistance, A is the cross sectional area and l is the channel length; the low resistivity realizes a rapid charge transfer in the HER that is advantageous over the inefficient charge transfer exhibited by semiconducting 2H group 6 TMDs [5, 7]. Defect-free single-crystalline characteristics of the MoTe₂ were verified by Raman spectroscopy, x-ray diffraction (XRD), low energy electron diffraction (LEED) data (figures 1(c)–(e), supplementary figure S1) and high-angle annular dark field scanning transmission electron microscope (HAADF STEM) images (figure 2, see also supplementary figure S2). The high quality single crystals allow us to rigorously investigate the HER process using scanning tunneling microscopy (STM) and first-principles calculations with an accurate lattice model of the entire surface.

2.1. Electrochemical measurements of 2H- and 1T’-MoTe₂

The HER performances of single-crystalline 2H-MoTe₂, 1T’-MoTe₂ and Pt are shown in figure 3. The Pt sample, with a thickness of 200 nm, was prepared on 300 nm SiO₂ wafer by sputtering deposition. As expected from previous studies on semiconducting 2H-TMDs [6, 7, 24], an inefficient HER performance was observed with 2H-MoTe₂ (blue curve) in figures 3(a) and (b). The inefficient HER performance of 2H-MoTe₂ is directly reflected in electrochemical impedance spectroscopy (EIS) in figure 3(c). The red curves in figures 3(a) and (b) show the intrinsic HER performance of single-crystalline 1T’-MoTe₂ while figure 3(d) exhibits the HER stability of 1T’-MoTe₂ compared to our reference Pt sample.

Measurements of two primary activities, ‘total electrode’ and ‘intrinsic’ activities [2] were conducted with the three catalysts (2H-MoTe₂, 1T’-MoTe₂, Pt), and the results are summarized in table 1. Practical parameters for the comparison of ‘total electrode’ activity such as reversible hydrogen electrode (RHE) potential for a current density of 10 mA cm⁻², Tafel slope, and exchange current density were obtained by a series of measurements. The exchange current density was derived from the Tafel curves (figure 3(b)) using linear extrapolation to the overpotential of 0 mV.

2.2. First-principles calculations

Investigating the intrinsic activity, per-site TOF, requires separate experiments to determine the total number of active sites per unit area [1, 2]. For this purpose, we combined first-principles calculations and STM studies [25, 26]. Because the active site density of Pt catalysts is known to be $S \sim 1.50 \times 10^{15}$ sites cm⁻², we deduced the TOF of the reference Pt (0.94 s⁻¹, table 1) by using the exchange current density from our HER measurement and the formula describing the catalytic current density, $j = S \cdot \mathrm{TOF} \cdot \frac{n \cdot F}{A \cdot N_A}$ where j is the exchange current density, n is the number of electrons transferred per molecule (2 for HER), F is the Faraday constant (96.458 C mol⁻¹ electrons), A is the superficial electrode area, and $N_A$ is Avogadro’s number (6.022 × 10²³ mol⁻¹) (ref. 2). In the case of our 2H-MoTe₂, the estimation of active site density was not possible because the amount of edge sites, where the catalytic performance is greatly enhanced, could not be deduced. Even with a certain amount of edge sites, the basal plane of 2H-MoTe₂ shows a poor HER as the exchange current density of 2H-MoTe₂ indicates in table 1.

The estimation of active site density was conducted on a basal plane of 1T’-MoTe₂ by combining ab initio calculations and STM studies of the single crystal. Our first-principles calculations revealed a site-dependent Gibbs free energy, ΔGₐₗₜ, of the hydrogen adsorption (figure 4). A low Te atom site (‘α’ site in figure 4(a)) shows the best ΔGₐₗₜ, −0.77 eV, among five possible atomic sites (α ~ ε site in figure 4(a). Other atomic sites show ΔGₐₗₜ much higher than 0.77 eV (figures 4(b) and (c)).
the hydrogen adsorption would mainly occur at the \textit{‘}\textit{α}’ site. Considering the large Tafel slope (~100 mV) and $\Delta G_{\text{H}}$ (~0.7 eV) in the performance of HER over 1T$'$-MoTe$_2$, the bottleneck of the hydrogen evolution is the hydrogen atom adsorption on the surface [1, 2]. This provides a picture of hydrogen evolution dominantly at \textit{‘}\textit{α}’ sites in 1T$'$-MoTe$_2$ as described in figure 4(e). We note that our defect-free single-crystalline surface enables a quantitative study combining experiments and \textit{ab initio} calculations on the reactivity at the precise atomic position (\textit{‘}\textit{α}’ sites) in 2D semimetallic substrates in figure 4.

Another possible scenario is the HER on Te vacancy, which shows a $\Delta G_{\text{H}}$ similar to Pt (blue line in figure 4(c)). However, our 1T$'$-MoTe$_2$ possesses few Te vacancies as verified by STEM (figure 2), transport studies showing high magnetoresistance with a Shubnikov–de Hass oscillation [17], surface-sensitive LEED and STM analysis (figures 1(d) and 4(d) and supplementary figure S1). If the HER takes place at Te vacancies with such a low active site (Te vacancy) density, the TOF at the site (Te vacancy) would be an unreasonable value. Moreover, our 2H-MoTe$_2$ grown by the sample flux method shows poor HER by its few Te vacancies. Based on these reasons, we estimate the active site density on the 1T$'$-MoTe$_2$ by considering only \textit{‘}\textit{α}’ site density without Te defect sites, $S = 4.54 \times 10^{14}$ sites cm$^{-2}$. Using the formula of the catalytic performance, the TOF of 1T$'$-MoTe$_2$ is deduced as 0.14 s$^{-1}$ at 0 mV overpotential, which means that the amount of H$_2$ gas produced per second by one active site of 1T$'$-MoTe$_2$ is similar to that of Pt catalysts (table 1).

2.3. STM experiments

Our 1T$'$-MoTe$_2$ has a surface charge density wave in its distorted octahedral structure originating from lattice instability of octahedral MoTe$_2$ in nature [17]. While the spatially inhomogeneous electron density is a general characteristic of 2D semimetallic TMDs, the role of such localized electron density in basal planes for HER has not been considered yet. Atomic-scale microscopy exploring local electronic properties, especially near the lowest $\Delta G_{\text{H}}$ sites, was conducted by STM in our study as shown in figure 4(d). Low sample bias ($V = 0.02$ V) image at $T = 4$ K (figure 4(d) left) exhibits atomic resolution topography, with a slightly mixed feature with local electron density, similar to the theoretically obtained lattice model in figure 1(b). On the other hand, relatively high sample bias ($V = 0.5$ V) image (figure 4(d) right) shows a series of stripes whose height does not match the atomic lattice height; the contrast at high voltage bias exhibits mainly local electron density rather than surface topography.

Our calculations confirmed that the local density of states at low Te sites (\textit{‘}\textit{α}’ site) is higher than that of high Te sites (\textit{‘}\textit{ε}’ site) (see supplementary figure S4), which explains the bright strips at high sample bias. This clearly indicates that the bright region in figure 4(d) (right) coincide with the best $\Delta G_{\text{H}}$ position (\textit{‘}\textit{α}’ site) in figure 4(a).
Figure 4(e) schematically describes the correlation of the higher local density of states (surface charge density wave) at dark orange Te atoms on the top surface and the best $\Delta G_{\text{H}}$ location for efficient hydrogen evolution.

2.4. Peierls-type lattice distortion

It has been verified that the lattice and electronic structures of TMD materials are easily affected by electric doping and mechanical strain [17, 27]. However, the structural change of 2D TMDs during hydrogen evolution and its influence on the performance of HER have not been explored and remain unknown. This consideration is particularly important when we use the full basal plane for HER because possible modifications of atomic and electronic structures at certain atomic sites by instant hydrogen adsorption can largely affect the reaction at numerous neighbor sites.

Our first-principles calculations reveal that hydrogen adsorption on the semimetallic MoTe$_2$ for HER produces a considerable electron doping effect that drives Peierls-type lattice distortion. The atomic model of 1T$'$-MoTe$_2$ with fully covered H atoms on low Te sites is shown in figure 5(a) (for the electronic and phonon band structures of this model, see supplementary figure S9–12). The $\Delta G_{\text{H}}$ with the pristine 1T$'$-MoTe$_2$ structure shown in figure 5(a) was calculated to be $\sim 0.93$ eV that indicates a poor HER.
like semiconducting TMDs. However, the instability by the electron doping (driven by the hydrogen adsorption) and resulting Fermi surface nesting, which can be verified by negative phonon energy dispersion (see supplementary figure S10), modifies the pristine lattice structure (figure 5 (a)) to a more distorted one (figure 5(b)). The spontaneous lattice distortion by hydrogen adsorption activates the HER and improves the $\Delta G_H$ by 0.16 eV, thus the full coverage HER over the distorted 1T$'$-MoTe$_2$ (figure 5(b)) shows $\Delta G_H \approx 0.77$ eV. We note that the improved HER performance by lattice distortion is a common feature among semimetallic group 6 TMDs because of the lattice instability in the layered materials [17].

The more distorted 1T$'$-MoTe$_2$ or 1T$''$-MoTe$_2$ structure is qualitatively supported by a comparative study of x-ray photoemission spectroscopy (XPS) before and after the HER (figure 5(c)). Wider peaks of binding energies with slight energy shifts indicate the small distortion of the original single crystal, improving the $\Delta G_{H}$. We believe that a part of the basal plane (if not the whole plane) can undergo the structural phase transition from the pristine 1T$'$ structure to the distorted 1T$''$ structure because the incommensurate charge density wave transition temperature of TMDs is higher than the room temperature [28].

### 2.5. HER with surface charge waves and lattice distortion

Given few Te vacancies in our sample, the calculated Gibbs free energy, $\Delta G_H \approx 0.77$ eV, at the ‘α’ site of 1T$'$-MoTe$_2$ (figure 4(a)) still seems to be unfavorable to the efficient HER whose exchange current density reaches $2.1 \times 10^{-2}$ mA cm$^{-2}$ at 0 mV overpotential (table 1). For example, gold and silver (111) surface with $\Delta G_H \approx 0.4$ eV exhibits a much lower exchange current density ($\sim 10^{-4}$ mA cm$^{-2}$) [2]. Our results on MoTe$_2$ may thus imply the limit of the conventional rate-determining Volmer step and ‘volcano plot’ analysis to describe diverse catalytic aspects of 2D TMDs for HER.

In former HER studies and conventional the volcano plot analysis, limited density of atomic reaction sites (sparse active sites), surface charge density wave and hydrogen adsorption-driven lattice distortion have not been considered. We interpret the three fac-

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**Table 1.** Comparison of catalytic activities. Total electrode and intrinsic activities of 2H-MoTe$_2$, 1T$'$-MoTe$_2$, and Pt. The TOF values of 2H-MoTe$_2$ catalyst is not available.

| Catalyst     | Potential for 10 mA cm$^{-2}$ (V versus RHE) | Tafel slope (mV per decade) | Exchange current density (mA cm$^{-2}$) | TOF ($s^{-1}$) |
|--------------|-----------------------------------------------|-----------------------------|----------------------------------------|--------------|
| 2H-MoTe$_2$ | −0.650                                        | 184                         | $7.0 \times 10^{-4}$                   | N/A          |
| 1T$'$-MoTe$_2$ | −0.356                                       | 127                         | $2.1 \times 10^{-2}$                   | N/A          |
| Pt           | −0.046                                        | 36                          | $4.5 \times 10^{-1}$                   | 0.94         |

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**Figure 3.** HER measurements. (a) Polarization curves of 2H-MoTe$_2$ (blue), 1T$'$-MoTe$_2$ (red), and Pt (black). (b) Tafel plots obtained from the polarization curves (a). (c) Electrochemical impedance spectra (Nyquist plots) for HER with 2H-MoTe$_2$ (blue) and 1T$'$-MoTe$_2$ (red) at an overpotential of −0.6 V versus RHE. An equivalent circuit with solution resistance($R_S$), double layer capacitance($C_{DL}$) and charge transfer resistance ($R_{CT}$) is described as an inset. (d) The stability comparison between reference Pt (black) and 1T$'$-MoTe$_2$ (red).
tors, which are common in semimetallic group 6 TMDs, as the origin of the unexpectedly active HER on 1T’-MoTe2 with its $\Delta G_H$ of ~0.77 eV (or 0.93 eV before the spontaneous lattice distortion); those novel factors were investigated at the atomic-scale with a pristine semimetallic TMD, 1T’-MoTe2, combining electrochemical analyses, DFT calculations and STM studies. We note that 1T- and 1T’-MoS2 have been studied using the volcano plot analysis, but the presence of surface charge density waves could not be rigorously highlighted due to inhomogeneous phase distribution and not-controllable Te vacancies in MoS2.

3. Conclusion

Unlike typical metallic and semiconducting substrates that have dense active sites without surface charge density waves, the correlation between sparse active sites (where the best $\Delta G_H$ is found) and surface charge density waves (where the electron flow for HER can be enhanced) was revealed in our study. Our findings indicate that, beyond the volcano plot analysis, local density of states or atomic lattice geometry (e.g. distortion) should be additionally considered in HER on 2D materials. Therefore, our study on unexpected HER in a pristine MoTe2 underscores the surface and solid-state physics concerning atomic hydrogen adsorption as a new strategy to design an ideal electrochemical catalyst.

4. Methods

4.1. Synthesis of 1T’- and 2H-MoTe2

We synthesized 2H- and 1T’-MoTe2 single crystals, as previously reported, by the flux method [17]. Mo and Te powders were mixed with NaCl (sodium chloride) in a tube which was sealed in glass under a pressure of $10^{-5}$ torr. The insertion of NaCl in the tube prevents Te vacancy formation during the growth process. The glass tube was
heated to a temperature of 1100 °C and maintained for 12 h. A rapid cooling from the high temperature produces 1T′-MoTe2, while a slow cooling makes 2H-MoTe2.

4.2. Sample preparation for HER measurement
2H- and 1T′-MoTe2 single crystals were attached to Au (100 nm)/SiO2 (300 nm)/Si substrate. Excluding a certain window area of the single crystals, we used nail polish to screen other exposed areas, to fix the sample and to define the exact reaction window area of the target single crystal. A typical exposed area of the single crystal for the HER measurement was approximately 1.0 × 10−7 m2, as measured by optical microscopy. Separate reference experiments revealed that silver paste and the Au area exhibit poor HER activity (almost negligible compared to our HER signal), which reveals the reliability of our experimental system.

4.3. Electrochemical measurement
HER was conducted using a three-electrode cell with a 200 ml 0.5 M sulfuric acid (H2SO4) electrolyte solution at room temperature. Silver–silver chloride electrode (Ag/AgCl) and platinum wire (both from Neo Science in Seoul, Korea) were used as reference and counter electrodes, respectively. Potential sweeps were performed with a scan rate of 1 mV s−1 using a Potentiostat (VMP3, Bio Logic). During the HER measurement, electrolyte was stirred by magnetic bar at 1000 rpm. At least 20 cycles of voltage sweep were performed before all HER measurements to avoid initial artifact signals.

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Author contributions
All authors participated in scientific discussion. J S, B J, Y H L and H Y conducted HER measurements and interpreted the results. J-H L and Y-W S calculated Gibbs free energies and electronic structures of systems including hydrogen atoms, platinum and MoTe2. Y-M K and S H O. obtained the STEM images of 1T′-MoTe2. S C and S W K grew the MoTe2, conducted XRD and XPS analysis of the MoTe2. M. K. and D K conducted LEED measurements. H W K conducted low temperature STM. H Y is the principle investigator.

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Competing financial interests
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