PAPER

Topologically nontrivial 1T’-MoTe₂ as highly efficient hydrogen evolution electrocatalyst

Yuan He¹,², Mebrouka Boubeche³, Yecheng Zhou¹, Dong Yan¹, Lingyong Zeng¹, Xiaopeng Wang¹, Kai Yan² and Huixia Luo¹

¹ School of Materials Science and Engineering, State Key Laboratory of Optoelectronic Materials and Technologies, Key Lab of Polymer Composite & Functional Materials, Sun Yat-Sen University, No. 135, Xingang Xi Road, Guangzhou 510275, People's Republic of China
² School of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China
³ These authors contributed equally to this work.

E-mail: luohx7@mail.sysu.edu.cn

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Abstract

Rational design and synthesis of low-cost noble-metal free electrode with high efficiency for hydrogen evolution reaction (HER) is crucial for the realization of eco-friendly hydrogen economy. Here, we report and design topologically nontrivial 1T’-MoTe₂ single crystals as remarkable hydrogen evolution electrocatalyst. The catalytic 1T’-MoTe₂ was controllably synthesized via solid-state reaction and then facilely exfoliated into nanosheets by isopropanol with the aid of sonication. The overpotentials at 10 mA cm⁻² (η₁₀) can reach 73 mV with a low Tafel slope of 46.3 mV dec⁻¹, which are much lower than those reported by other preparation methods (η₁₀ > 300 mV, Tafel slope > 50 mV dec⁻¹). The electrochemical impedance spectroscopy shows fast kinetics of 1T’-MoTe₂ single crystal with low contact resistance of 0.3 Ω. Additionally, 1T’-MoTe₂ single crystal also exhibits large electrochemical active surface area of 47.0 cm², high turnover frequency of 1.02 s⁻¹ at 0.4 V and excellent durability over 10 h in 0.5 M H₂SO₄ (aq). This work reports 1T’-MoTe₂ single crystal as an excellent candidate for HER, which makes it possible to fabricate other robust Te-derived HER electrocatalysts.

1. Introduction

As the problem of the greenhouse effect from traditional fuel becomes increasingly serious, hydrogen has been drawing more and more attention in the world as an important clean energy. Currently, producing hydrogen via water electrolysis is clean from source to product [1]. During this process, a catalyst is an essential factor. Generally, the energy barrier of hydrogen evolution reaction (HER) should be reduced by catalysts [2–6].

Density functional theory (DFT) calculations have described a relationship between HER exchange current densities and free energy of hydrogen adsorption ΔG₂H, which is called the volcano plot [7]. When ΔG₂H < 0, there exists an adsorption force between catalyst and hydrogen. Otherwise, ΔG₂H > 0 means that the catalyst has difficulty adsorbing hydrogen. From the volcano plot, catalysts whose ΔG₂H closed to zero achieve higher HER exchange current density. Pt is thus regarded as the most efficient HER electrocatalyst due to its proper hydrogen binding energy. However, instability, costliness, and scarcity will hinder its actual utilizations. There exists two major routes to figure out this problem. One way is to improve Pt utilization [8]. The other way is to replace Pt by costless as well as more abundant non-noble metal containing [9, 10] or metal-free [11, 12] materials. Increasing active sites on catalysts is one of the most popular strategies to improve HER performance. In the first route, fabricate single atom Pt instead of bulk Pt can largely improve platinum utilization.
As for the second route, researchers have also developed various approaches to create more active sites for HER catalysts, such as hetero-atom doping [13], defect engineering [14, 15], nanostructure [16, 17], heterostructure [18, 19], phase-tuning [20] and atomic layer deposition [21]. Preparation of catalysts with nanostructure or atomic thickness aims to improve catalyst utilization and expose more active sites. Hetero-atom doping tends to introduce impurities to tune the electrical conductivity and interlayer spacing. Defect engineering aims to introduce more edges to increase active sites. Enhanced performance discovered in heterostructure should own to active sites sharing in the interface. Phase-tuning can intrinsically affect the electronic structures and hydrogen adsorption free energies of materials [22]. Recently, topologically nontrivial noble-metal free 1T'-MoTe₂ was reported to show both a nontrivial Berry’s phase and superconductivity with \( T_c = 0.1 \text{ K} \), whose special properties may effect catalyst [23–27]. Topological surface states of these materials will provide an alternative way to create active sites, rather than by traditionally increasing the active edge sites or vacancies. Besides, the topological charge carries will participate in HER [28]. Apart from 1T'-MoTe₂, there are other reported topological nontrivial materials for HER. For example, topological nodal line semimetal TiSi has been theoretically predicted to exhibit high HER performance [28]. Additionally, topological insulator Bi₂Se₃ can provide large electrons to promote hydrogen adsorption of monolayer ZnSe. This heterostructure shows free energy closing to 0 eV and its calculated exchange current density even surpasses that of Pt [29]. As for experimental researches, topological Weyl semimetal 1T'-WTe₂ nanoribbon shows higher HER performance than those of 2H-WS₂ and 2H-WSe₂ [30]. Topological nodal line semimetal PtSn₃ shows commercial Pt/C like HER activity due to its stable state of Pt layer, from which the adsorbed H atom can directly obtain electron [31]. Recently, our group has proposed and fabricated topological superconducting BiPd and PdTe₂ as high efficient electrocatalysts [32, 33].

Herein, we document layered transition-metal dichalcogenide topologically nontrivial 1T'-MoTe₂ nanosheet as an excellent HER electrocatalyst. Through the facile solid-state synthesis and simple liquid exfoliation in isopropanol, 1T'-MoTe₂ nanosheets with 5 ~ 8 nm are successfully fabricated. 1T'-MoTe₂ nanosheets delivers superior high HER activity in terms of very small overpotential of 73 mV at 10 mA cm⁻², Tafel slope of 46.3 mV dec⁻¹, very low contact resistance of 0.3 Ω, large electrochemical active surface area (ECSA) of 47 cm² with turnover frequency (TOF) of 1.02 s⁻¹ at 0.4 V. Besides, 1T'-MoTe₂ nanosheets exhibit fast kinetics with remarkable stability over 10 h in 0.5 M H₂SO₄.

### 2. Experimental section

#### 2.1. Materials

Molybdenum powder (250 mesh, 99.9%), tellurium lump (99.999 + %) and iodine (99.5%) were purchased from Alfa Aesar. Isopropanol (AR), acetone, absolute ethanol and sulfuric acid were purchased from Guangzhou Chemical Reagent Factory. Tellurium lump was firstly ground to powder before used. Other chemicals were used without any treatment. Ni foam (thickness of 1.5 mm, bulk density of 0.45 g cm⁻³, porosity 95%) was purchased from Sigma-Aldrich.

#### 2.2. Instruments

X-ray diffraction (XRD) was measured on RIGAKU D-MAX 2200 VPC from Japan. X-ray photoelectron spectroscopy (XPS) was conducted on Thermo Scientific ESCALab250 from America. Scan electronic microscope (SEM) measured on Zeiss Merlin from German. Transmission electronic microscope (TEM) was conducted on JEM-2100HR from Japan. High resolution transmission electronic microscope (HRTEM) images and selected area electron diffraction (SAED) patterns were taken on FEI Tecnai G2 F20 from America. Atomic force microscope (AFM) was conducted on Bruker Multimode 8 from German. The silicon AFM probe with resonant frequency of 300 kHz and force constant with 40 N m⁻¹ was provide by Budget Sensor, which could be applied in tapping mode and intermittent contact.

#### 2.3. Synthesis of polycrystalline and single crystal 1T'-MoTe₂

Polycrystalline 1T'-MoTe₂ was synthesized via solid-state synthesis. Briefly, molybdenum and tellurium powder were taken stoichiometric ratio, inside evacuated quartz tube at 900 °C for 3 d. After quenched in ice water, polycrystalline MoTe₂ was ground into powder. Single crystal 1T'-MoTe₂ was synthesized via chemical vapor transport. Generally, polycrystalline sample and iodine in mass ratio of 1:20 were sealed in quartz tube. The sample side was at 950 °C for 7 d and the opposite side was at 850 °C for 7 d. After cooling down to room temperature, single crystal sheets were obtained and washed by absolute ethanol.

#### 2.4. Preparation of 1T'-MoTe₂ thin sheets on Ni foam

50 mg polycrystalline or single crystal 1T'-MoTe₂ was added into 10 ml isopropanol and sonicated for 90 min. During the process, bulk MoTe₂ would be exfoliated by solvent and formed a gray supernatant. As
the catalyst carrier, Ni foam (1 cm * 2 cm) was pretreated with 3 M HCl solution under ultrasonic for 30 min, absolute ethanol, acetone, and deionized water (each for 15 min) to ensure a clean surface. Supernatant (5’100 µl) was dropped onto the clean Ni foam surface and dried naturally. Then the catalysts-contained Ni foam was maintained at 350 °C for 6 h under Ar atmosphere. Finally, the electrochemical performance of the sample was measured at 0.5 M sulfuric acid. The controlled blank Ni foam was undergoing the same process.

2.5. Electrochemical measurement

Electrochemical performance of HER was measured on CHI 760E from Shanghai. In a standard three-electrode system, working electrode is the catalysts-contained cleaned Ni foam; counter electrode is Pt sheet; reference electrode is saturated Ag/AgCl electrode. Linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), chronoamperometry (CA) and other electrochemical measurements are conducted in an argon-saturated electrolyte of 0.5 M H₂SO₄ (aq). The potentials in this work were converted to a reversible hydrogen electrode (RHE) scale according to the Nernst equation,

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0596 \text{pH} + 0.1976. \]

ECSA was determined using cyclic voltammetry (CV) measurements. The potential range within a non-Faradaic current response was determined from CV. In this work the potential is typically range from −0.2 V ~ −0.25 V. CV measurements were conducted in quiescent solution by sweeping the potential across the non-Faradaic region from the more positive to more negative potential and back at five different scan rates; 20, 40, 80, 100, 200 mV s⁻¹. The working electrode was held at each potential vertex for 2 s before beginning the next sweep.

\[ \text{ECSA} = R_f \times S = \frac{C_{dl} \times S}{20 \mu F \text{cm}^{-2}} \]

\( R_f \) is roughness factor and \( S \) is geometric area of electrode (in this experiment, \( S = 1.0 \text{cm}^2 \)). Double-layer capacitance (\( C_{dl} \)) is estimated by CV measurements range from −0.035 V to 0.015 V (vs. RHE) at scan rates of 20, 40, 80, 100, 200 mV s⁻¹ and obtained by plotting \( \Delta J/(J_a - J_c) \) at −0.01 V (vs. RHE) against the scan rate. The slope is twice that of \( C_{dl} \). 20 µF cm⁻² is the \( C_{dl} \) of smooth metal surface.

\[ \text{TOF} = \frac{j \times S}{2 \times F \times n} \]

Current density \( j \) (mA cm⁻²) is obtained at various overpotential and \( S \) is geometric area of electrode (in this experiment, \( S = 1.0 \text{cm}^2 \)). 2 represents two electrons needed to form per mole hydrogen. \( F \) is the Faraday’s constant (96485.3 C mol⁻¹). \( n \) is the mole of catalyst loaded on Ni foam.

3. Result and discussion

Polycrystalline 1T’-MoTe₂ was synthesized via solid-state reaction [30]. And the single crystal sample was subsequently grown by chemical vapor transport (CVT) with the aid of iodine [34]. Figure 1(a) is the X-ray diffraction (XRD) pattern of the obtained polycrystalline and single crystal 1T’-MoTe₂ (PDF#71-2157). Main peaks in polycrystalline (blue line) well match the standard card (dark line), showing the highest intense crystal face (002). This most intense crystal face (002) is also the main face in single crystal (red line). And the peak shifts of face (004), (006) and (008) increase by every 13° (2 Theta). Figure 1(b) shows the centrosymmetric monoclinic lattice (the 1T’ phase, P121/m1) of MoTe₂. View from the a axis, Mo atom is in octahedral coordination in the Te-Mo-Te layers, with two triangles consisting of three Te atoms stacking in opposite way. This structure makes successive chains along the crystallographic b direction. Inset is the optical photo of the as-grown single crystal 1T’-MoTe₂, showing a thin sheet morphology with grey color. The lateral size of large single crystal sheets nearly reaches 1 cm, and that of small ones is also larger than 0.5 cm. X-ray photoelectron spectroscopy (XPS) spectra also confirms the reasonable valence of Mo (IV) (figure S1(a) (available online at https://stacks.iop.org/JPMATER/4/014001/mmedia)) and Te (-II) (figure S1(b)). Since spin-orbital coupling, the binding energy of 3dₓ/₂ and 3dᵧ/₂ peak of Mo (IV) appears in 226.57 eV and 229.78 eV, respectively. And the binding energy of 3dₓ/₂ and 3dᵧ/₂ peak of Te (-II) is in 571.77 eV and 582.16 eV, respectively. Bulk 1T’-MoTe₂ materials were subsequently exfoliated into nanosheets by isopropanol with the aid of sonication.

The exfoliated nanosheets were further measured on AFM. Lateral size of single crystal (figure 2(b)) is obviously larger than that of polycrystalline sample (figure 2(a)). The inset height profiles indicate that polycrystalline sample presents a thickness of 5 ~ 6 nm, while single crystal exhibits a slightly thicker thickness of 8 nm. Polycrystalline sample shows similar length between horizontal and vertical direction, with an average lateral size of 1.2 µm. However, single crystal presents a much larger length in vertical
Figure 1. (a) XRD pattern of polycrystalline (blue line) and single crystal (red line) 1T'-MoTe$_2$ measured on RIGAKU D-MAX 2200 VPC from Japan. (b) Molecular structure of 1T'-MoTe$_2$ drawn by Vesta. Yellow ball represents Mo atom and green ball represents Te atom. Inset is optical photo of bulk single crystal 1T'-MoTe$_2$ grown by chemical vapor transport. Scale bar 1 cm.

Figure 2. AFM images of exfoliated (a) polycrystalline and (b) single crystal 1T'-MoTe$_2$ on 300 nm SiO$_2$ wafer conducted on Bruker Multimode 8 from German with tapping mode. Insets are the corresponding height profile.

direction than that in horizontal direction. The horizontal length is only 1.5 $\mu$m but the vertical length is above 5 $\mu$m or more. SEM (figure S2) images also indicate the larger aspect ratio in single crystal than that in polycrystalline, which reflect the orientation grow from polycrystalline to single crystal. The SAED pattern (figure S3(a)), taken on the $[1\bar{2}2]$ orientation, clearly shows the (20–1), (011), (−212) faces in a parallelepiped. The HRTEM (figure S3(b)) image of the MoTe$_2$ nanosheet shows clear lattice distance of 0.321 nm of (011) face. The fast Fourier transform (FFT) pattern (inset of figure S3(b)) of the white square is corresponding with its SAED pattern.

Electrochemical performance of both polycrystalline and single crystal 1T'-MoTe$_2$ were measured on CHI 760E from Shanghai. Blank Ni foam displays relatively poor activity with large overpotential. Compared with the blank Ni foam, the two catalysts present much lower overpotential and higher electrocatalyst activity. LSV curves (figure 3(a)) indicate an outstanding difference of both onset potential and overpotential between Ni foams with and without 1T'-MoTe$_2$ catalyst. For example, at 30 mA cm$^{-2}$, the overpotential of 1T'-MoTe$_2$ catalyst is around 300 mV lower than that of blank Ni foam. Besides, polycrystalline 1T'-MoTe$_2$ shows overpotential of 82 mV at 10 mA cm$^{-2}$. And single crystal 1T'-MoTe$_2$ shows an even lower overpotential of only 73 mV at the same current density. As the increase of overpotential, the current density difference between polycrystalline and single crystal becomes larger and larger. Figure 3(b) is the Tafel plots derived from LSV curves from 0 to 0.25 V by plotting overpotential against logarithm of absolute current.
density, representing how much overpotential have to provide to increase certain current density. In another word, lower slope value means less overpotential needed to increase the same current density. This also reflects faster dynamic process of HER. In this experiment, the Tafel value of blank Ni foam is higher than 200 mV dec$^{-1}$. However, when loaded with polycrystalline and single crystal 1T’-MoTe$_2$ nanosheets, the Tafel values drop down to 50.1 and 46.3 mV dec$^{-1}$, respectively. This high activity on HER is corresponding with LSV curves. Semicircle in the EIS (figure 3(c)) also confirms the dynamic control of 1T’-MoTe$_2$ during HER process. Single crystal presents a smaller semicircle than that of polycrystalline. Besides, the contact resistance of single crystal sample is 0.3 Ω, which is slightly lower than that of polycrystalline one (0.4 Ω). Inset of figure 3(c) is the whole EIS graph of blank Ni foam, indicating a rather large resistance compared with those of 1T’-MoTe$_2$. The ECSA is another important parameter for evaluating the activity of HER catalyst [24]. In this experiment, ECSA value is calculated according to the following formula [35, 36]:

$$
\text{ECSA} = \frac{R_f \times S}{20 \mu F cm^{-2}}.
$$

Parameter details are in the supporting information. Figure 3(d) shows that single crystal 1T’-MoTe$_2$ exhibit greater $C_{dl}$ value of 0.945 mF cm$^{-2}$ than that of polycrystalline counterpart (0.555 mF cm$^{-2}$), indicating that single crystal 1T’-MoTe$_2$ presents more active sites on surface. The $C_{dl}$ of blank Ni foam is only 0.495 mF cm$^{-2}$. Of course, single crystal sample also presents higher ECSA value of 47 cm$^2$ than that of polycrystalline (28 cm$^2$). The TOF, another parameter for charactering HER activity, is the number of hydrogen molecule produced by per active site per second, which can be determined by the following formula [26]:

$$
\text{TOF} = \frac{j \times S}{2 \times F \times n}.
$$

Parameter details are in the supplementary material. As can be seen from figure S4, the TOF values of single crystal 1T’-MoTe$_2$ are always higher than those of polycrystalline at different overpotential. As the increase of overpotential, this difference becomes greater and greater. For example, at 0.1 V, the TOF of single crystal is 0.12 s$^{-1}$ and that of polycrystalline is 0.11 s$^{-1}$. But at 0.4 V, the TOF of single crystal increases to 1.02 s$^{-1}$ while that of polycrystalline is only 0.87 s$^{-1}$. Except for higher activity, single crystal 1T’-MoTe$_2$ nanosheets are more stable during CA measurement (figure S5). After 10 h, overpotential at 10 mA cm$^{-2}$ of polycrystalline increases to 109 mV, which is 27 mV larger than its initial state (82 mV). And the two LSV curves are not corresponding well with each other. Instead, overpotential is without obvious increase for single crystal sample (still 73 mV at 10 mA cm$^{-2}$), whose LSV curves show well repeatability.

Insets of figure S5 are the corresponding CA curves. Single crystal 1T’-MoTe$_2$ nanosheets also show more stable and linear-like curve. Figure 4 is the statistic graph of overpotential and Tafel slope of 1T’-MoTe$_2$ prepared in this work and other reported methods. As can be seen, no matter overpotential or Tafel slope of 1T’-MoTe$_2$ in this work are the lowest in comparison with other preparation methods. As for exfoliation, N-methyl-2-pyrrolidone (NMP) [37] and n-butyl lithium (BuLi) [38] exfoliated 1T’-MoTe$_2$ nanosheets show very high overpotential of 309 and 380 mV, respectively, which is three times higher than those in this work by isopropanol exfoliation. As the authors pointed out, MoTe$_2$ would be oxidized by BuLi exfoliation to some extent [38]. Additionally, single crystal grown by flux method presents rather high overpotential of 356 mV and Tafel slope of 127 mV dec$^{-1}$ [39]. These are also several times higher than those in this work by CVT method. That is because thin 1T’-MoTe$_2$ single crystal grown by CVT has large ECSA value that abundant active sites are exposed. Low resistance also triggers fast kinetics during HER process. Both these contribute to the high performance of 1T’-MoTe$_2$ toward HER in this work.

4. Conclusions

In conclusion, layered transition-metal dichalcogenide 1T’-MoTe$_2$ was controllably synthesized via facile solid-state reaction and subsequently exfoliated into nanosheets by isopropanol with the aid of sonication. Both the polycrystalline and single crystal 1T’-MoTe$_2$ nanosheets show high catalytic activity toward HER that overpotential at 10 mA cm$^{-2}$ is 82 and 73 mV, with Tafel value of 50.1 and 46.3 mV dec$^{-1}$, respectively. Moreover, low contact resistances are also achieved as 0.4 Ω for polycrystalline and 0.3 Ω for single crystal sample. Single crystal catalyst exhibits higher ECSA (47 cm$^2$) and TOF value (1.02 s$^{-1}$) than those polycrystalline catalyst (28 cm$^2$, 0.87 s$^{-1}$). Both 1T’-MoTe$_2$ nanosheet catalysts show good durability over 10 h. These excellent experimental results indicate 1T’-MoTe$_2$ nanosheets are efficient electrocatalysts on HER. This work provides good guideline to fabricate a large family of Te-derived HER catalysts.
Figure 3. Electrochemical performance of blank Ni foam, polycrystalline and single crystal 1T’-MoTe$_2$ measured on CHI 760E from Shanghai in a standard three-electrode system with the catalysts-contained cleaned Ni foam of working electrode, saturated Ag/AgCl electrode of reference electrode and Pt sheet of counter electrode in an argon-saturated electrolyte of 0.5 M H$_2$SO$_4$ (aq). (a) LSV curves recorded at 0.02 V s$^{-1}$. (b) Tafel plots for the catalysts derived from (a). (c) Electrochemical impedance spectroscopy for polycrystalline and single crystal 1T’-MoTe$_2$. Inset is that of blank Ni foam. (d) The difference in current density at $-0.01$ V (vs. RHE) plotted against scan rate.

Figure 4. Statistic graph of overpotential and Tafel slope among 1T’-MoTe$_2$ prepared in this work and other reported methods. NMP = N-methyl-2-pyrrolidone, BuLi = n-butyl lithium. NMP exfoliation [37], flux method [39], BuLi exfoliation [38], electro-deposition [40].

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ORCID iDs

Kai Yan  https://orcid.org/0000-0001-9001-6337
Huixia Luo  https://orcid.org/0000-0003-2703-5660

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