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Layered transition metal ditellurides in electrocatalytic applications – contrasting properties

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ABSTRACT

The layered compounds and especially transition metal dichalcogenides are at the forefront of current research on electrocatalytic materials. Despite the fact that electrocatalytical properties of molybdenum and tungsten disulfides are well known their tellurium analogues are significantly less explored. Here we show an effective method for MoTe₂ and WTe₂ chemical exfoliation based on alkali metal intercalation and subsequent reaction with water. The as synthesized and exfoliated tellurides were characterized in detail and investigated for potential application in electrocatalysis. The inherent electrochemical activity related to both cation and anion was observed. This is dominantly related to the oxidation tendency of tellurium. The MoTe₂ and WTe₂ shows highly increased HER activity with little dependence on

electrochemical treatment whereas WTe₂ shows slightly worse improvement and strong dependence on the electrochemical treatment. In particular, the exfoliated MoTe₂ exhibits improved electrocatalytic activity for hydrogen evolution reaction and possesses a huge application potential.

KEYWORDS

tellurides; transition metals; hydrogen evolution; exfoliation; nanostructures

INTRODUCTION

With the demand of renewable energy sources, more and more attention is being funneled into the research of efficient hydrogen evolution reaction (HER) catalysts. It is highly desirable to replace high-cost platinum with cheaper and more available alternatives. A large number of candidates have been recently proposed and widely explored. These include porous metallic nanocatalysts, doped graphene, metal oxides, metal phosphides and transition metal dichalcogenides.¹⁻¹¹ Over the past years, enormous amount of attention has been paid to the last mentioned: transition metal dichalcogenides (TMDs).^{12, 13}

TMDs are composed of stacked layers with general formula of MX_2 (M= transition metal, X= S, Se, Te). Strong covalent bonds within layers and weak Van der Waals forces between layers make this group of materials excellent candidates for exfoliation.¹⁴⁻¹⁶ Several methods have been developed for the preparation of atomically thin layers. These include chemical vapor deposition (CVD), mechanical exfoliation and also probably the most efficient liquid phase exfoliation and ion intercalation based exfoliation.¹⁷⁻²⁰ Ion intercalation based exfoliation is especially intriguing, as it can induce a phase transition from

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Most of the research on TMDs HER catalysis has been devoted to MoS_2 and WS_2 . A variety of methods have been developed for the enhancement of HER performance of these compounds.²²⁻²⁸ As far as ion intercalation based exfoliation goes, n-butyllithium is the most commonly used intercalant.^{14, 29, 30} Aromatic based exfoliation agents such as sodium naphtalenide have also been shown to produce single layer sheets with a high yield.^{31, 32} Aside from the aforementioned 2H -> 1T phase transition, the increased catalytic activity also stems from the increased amount of edges, which are the HER active sites.^{22, 23, 33} In fact, the approach of increasing the edge site concentration via decreasing size of the catalyst is very fashionable.³⁴⁻³⁶

Despite the promising results, many of the TMDs family members remain unexplored in terms of HER catalysis. Most of the reports deal with MoS₂ and WS₂ and their composites with conductive substrates such as graphene.^{37, 22, 27, 38-41} Lately, research on other TMDs including molybdenum and tungsten diselenides has begun to proliferate.^{42, 43} However, very little attention has been paid to molybdenum and tungsten ditellurides. As of now, there is only one paper dealing with molybdenum and tungsten ditellurides.⁴⁴ Since that paper deals with liquid phase exfoliation, there is still a knowledge gap about performance of chemically exfoliated MoTe₂ and WTe₂. Despite the fact that their electrochemical properties are relatively unexplored, MoTe₂ and WTe₂ have been intensively studied for some of their outstanding physical properties. For example they are both so-called type-II Weyl semimetals which gives rise to extraordinary physical properties.^{45, 46} WTe₂ can also exhibit superconducting properties and very high magnetoresistance.^{47, 48}

In this work we demonstrate the influence of chemical exfoliation of $MoTe_2$ and WTe_2 on the HER catalytical properties. For this purpose we have incorporated two commonly used exfoliation reagents – n-butyllithium and sodium naphtalenide. Thorough characterization revealed strong tendency towards oxidation after exfoliation of both $MoTe_2$ and WTe_2 . The knowledge acquired from the inherent electrochemistry investigation allowed for the extraction of potentials used for the oxidative/reductive pretreatment aiming for further enhancement of calatytical properties. The schematic drawing of tellurides exfoliation procedure is shown on **Scheme 1**.



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Scheme 1. The schematic drawing of exfoliation procedure based on lithium intercalation and subsequent exfoliation by reaction with water.

RESULTS AND DISCUSSION

In this paper we show the relations between electrocatalytic activity of layered ditellurides and their structure as well as their degree of exfoliation. Significantly contrasting properties are observed on the hydrogen evolution reaction (HER) catalysis of chemically exfoliated transition metal ditellurides, namely MoTe₂ and WTe₂. For more detailed comparison, bulk materials are described too. Two of the previously reported exfoliation reagents were used to intercalate and subsequently exfoliate these materials. One of them, n-butyllithium is commonly used for the exfoliation of transition metal dichalcogenides (TMDs). The other one, sodium naphtalenide has also been previously reported to be suitable for high yield exfoliation of TMDs, especially in the case of layered transition metal disulfides.

A variety of analytical techniques including scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), Raman spectroscopy and X-ray photoelectron spectroscopy were employed to carefully characterize the materials from the viewpoint of composition and structure. The results extracted from inherent electrochemistry measurements were used to probe the potential activation of materials via oxidation/reduction. Samples in this work are referred to on the basis of procedure used for exfoliation (Bulk, BuLi and Naph) and eventually the reductive/oxidative electrochemical treatment (red.; ox.).

Electron micrographs depicting the morphology of molybdenum and tungsten ditellurides are shown in **Figure 1**.



Figure 1. SEM micrographs of bulk and exfoliated MoTe₂ (top) and WTe₂ (bottom). Scale bars correspond to $5 \mu m$.

A striking transition from large regularly shaped crystals of bulk material to wrinkled small crystallites of exfoliated materials was clearly observed. SEM micrographs documented the successful exfoliation using n-butyllithium and sodium naphtalenide reagents. However, most of the wrinkling formed during the exfoliation was observed only on the edges of relatively large sheets. This was especially apparent in the case of WTe₂ BuLi suggesting that the yield of single to few-layered sheets was much lower than in the case of transition metal sulfides, where the use of same exfoliation reagents led to high yield of single to few-layered sheets.³¹

Composition as well as elemental distribution was measured by SEM-EDS. Element distribution maps are shown in **Figure S1** and the composition is summarized in **Table 1**. The maps revealed homogeneous distribution for all the samples, but there was a tremendous increase in oxygen content contrasting with the oxygen free bulk materials. Such an increase is most likely related to an increased surface area introduced by the exfoliation. Even though

ACS Catalysis

this is quite typical for chemically exfoliated TMDs, such a high oxygen content indicated higher susceptibility of molybdenum and tungsten tellurides toward oxidation, compared to other TMDs.¹

Further characterization was performed with TEM and HR-TEM (Figure 2). The individual exfoliated plates with single and few layer thickness exhibit lateral sizes in the range from hundred of nanometers up to few microns. Elemental distribution map measurement performed by EDS (Figure S2) shows homogeneous distribution of elements without any evidence of phase separation and decomposition.



Figure 2. TEM and HR-TEM images of TMDs with SAED insert. The scale bar on TEM images correspond to 1 μ m and 500 nm (MoTe₂ Naph) and the scale bar on HR-TEM image corresponds to 5 nm.

Table 1. Composition of bulk and exfoliated Molybdenum and Tungsten ditellurides obtained

 by EDS.

Sample M (at. %) Te (at. %) O (at. %) Te/M

MoTe ₂ Bulk	31.3	68.7	0.0	2.20
MoTe ₂ BuLi	16.9	39.3	43.9	2.33
MoTe ₂ Naph	21.7	53.6	24.7	2.47
WTe ₂ Bulk	31.7	68.3	0.0	2.15
WTe ₂ BuLi	23.0	50.7	26.4	2.21
WTe ₂ Naph	24.2	49.0	26.8	2.02

X-ray diffraction (XRD) was used to verify the phase purity of both synthesized bulk and exfoliated molybdenum and tungsten tellurides. The XRD patterns are shown in **Figure S3** together with structures of MoTe₂ and WTe₂. Pure 2H phases were successfully synthesized for both bulk materials. Exfoliation by both n-butyllithium and sodium naphtalenide led to a partial decomposition into tellurium and the corresponding telluride. However, the degree of decomposition was very low in all cases (approximate concentration of Te lower than 5 wt. %). Despite the high concentration of oxygen (EDS and XPS), no reflections related to the oxides were detected. This indicates the presence of amorphous oxides only. Although the reflections of exfoliated tellurides are quite sharp and narrow, we attribute this to restacking which is quite typical for TMDs. It was shown by SEM that significant wrinkling and lowering of sheet size took place during the exfoliation.

Raman spectroscopy was employed for further structural characterization of $MoTe_2$ and WTe_2 . Raman spectra of $MoTe_2$ in the 160-400 cm⁻¹ region are shown in the left part of **Figure 3**. Several modes were found in this region. An in-plane mode at ~ 235 cm⁻¹ denoted as E_{2g}^1 and out-of-plane mode at ~ 174 cm⁻¹ denoted as A_{1g} were observed in MoTe₂ bulk and MoTe₂ Naph samples.^{49, 50} A_{1g} mode was not observed in the MoTe₂ BuLi sample. This was caused by an overlap with an intense peak with a maximum at~130 cm⁻¹ which is not

completely shown in the region displayed in **Figure 3**. Raman spectrum over a wider range of wavenumbers is shown in the supporting information (**Figure S4**). Apart from the peak at 130 cm⁻¹, several additional peaks were identified in the MoTe₂ BuLi Raman spectrum: an intense peak at ~ 119 cm⁻¹ and two peaks at ~ 820 and 995 cm⁻¹ which are related to the presence of MoO_3 .⁵¹ None of these peaks were detected in other MoTe₂ spectra. This is also in good agreement with the high concentration of oxygen in the MoTe₂ BuLi sample (see EDS discussed previously and XPS discussed in the following sections). Additional peak denoted as B_{2g} was observed in the Raman spectrum of MoTe₂ Naph. This peak appears neither in Raman spectrum of the bulk nor in the single layer MoTe₂ suggesting that MoTe₂ Naph sample was composed of few layers thick sheets.⁵² The absence of this peak in the Raman spectrum of MoTe₂ BuLi may indicate that this material was composed of atomically thin sheets that do not possess this phonon vibration.⁵²



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Figure 3. Raman spectra of bulk and exfoliated MoTe₂ (left) and WTe₂ (right).

Raman spectra of WTe₂ are shown in the right part of **Figure 3**. Four peaks were detected in the 100 - 250 cm⁻¹wavenumber region. These peaks located at ca. 213, 164, 143 and 124 cm⁻¹ are denoted as A₁⁹, A₁⁷, A₁⁴ and A₁³, respectively.⁵³ Even though the peak positions are in good agreement with the literature for all WTe₂ samples, the peak intensity ratios are in good agreement only for bulk WTe₂. We observed significant lowering of A₁⁹ mode intensity while the remainder of the modes exhibited an increase in intensity as well as strong broadening, which was especially apparent for WTe₂ Naph sample. We have not observed any softening of the modes associated with the decreased number of layers below five layers reported in the literature.⁵³ We suggest that the strong broadening of individual modes was related to the decrease of lateral size of individual sheets which was observed by SEM.

In the next step, surface composition was examined by X-ray photoelectron spectroscopy (XPS). Survey spectra (**Figure S5**) were firstly recorded. The composition extracted from the survey spectra and the chalcogen to metal ratios are summarized in **Table S1**. The carbon shown in the results originates from adventitious carbon and hydrocarbon/CO₂ contamination. An increase in oxygen concentration can be seen for both exfoliated MoTe₂ and WTe₂ samples. This is related to the increase of surface area, which allows faster surface oxidation. The susceptibility of MoTe₂ and WTe₂ towards oxidation has already been reported previously.^{53, 54} The chalcogen to metal ratios also revealed that the exfoliation produces tellurium rich surface in the case of MoTe₂ and metal rich surface in the case of WTe₂.

Page 11 of 30





Figure 4. High-resolution XPS spectra of a) MoTe₂ Mo 3d, b) WTe₂ W 4f, c) MoTe₂ Te 3d and d) WTe₂ Te 3d.

High resolution core-level spectra were further recorded for Mo 3d, W 4f and Te 3d states (**Figure 4**). Firstly, deconvolution of Mo 3d spectrum in **Figure 4a** revealed the presence of two oxidation states in both bulk and exfoliated MoTe₂. $Mo3^{4+} 3d_{5/2}$ and $Mo^{4+} 3d_{3/2}$ pair at ca. 228.7 eV and 231.8 eV, respectively, was attributed to MoTe₂ whereas the pair located at ca. 232.8 eV and 236 eV was attributed to molybdenum in Mo⁶⁺ oxidation state (MoO₃ typical for TMDs). A dramatic increase of Mo⁶⁺ peaks intensity can be clearly seen

especially in the case of MoTe₂ BuLi. This is in good agreement with EDS and Raman spectroscopy measurements (see previous sections) and further confirms the susceptibility of MoTe₂ towards oxidation. Interestingly, intercalation and subsequent exfoliation does not induce any phase transition from 2H to 1T. However, this has been previously reported for some others TMDs.¹ The concentrations of the individual valence states are summarized in **Table S2.** Figure 4b displays the high resolution core-level spectra of W 4f state. Similarly to Mo 3d, two pairs of peaks were detected in the W 4f spectra, namely W^{4+} 4f_{7/2} together with W^{4+} 4f_{5/2} at ca. 31.7 and 33.9 eV, respectively, from 2H WTe₂, and W^{6+} 4f_{7/2} together with W⁶⁺ 4f_{5/2} at ca. 35.5 and 37.7 eV, respectively, from WO₃. Additionally, a new pair of peaks, originating from 1T WTe₂, was observed at slightly lower binding energies than 2H WTe₂. This is in high contrast with MoTe₂, in which no 1T phase was observed. Moreover, it can be seen from Table S2 that most of the WTe₂ is in the form of 1T phase, especially in the case of WTe₂ Naph. This suggests that the exfoliation process of WTe₂ is highly favorable for the 2H -> 1T phase transformation. On the other hand, an increase of W⁶⁺ concentration can be seen in the case of exfoliated WTe₂ as well. This was again attributed to an increased surface area and higher degree of oxidation introduced during the exfoliation. Finally, Te 3d core-level spectra of MoTe₂ and WTe₂ are displayed in Figure 4c and Figure 4d, respectively. A very similar trend to that observed in Mo 3d and W 4f spectra can be seen here. In contrast to a low concentration of TeO₂ in bulk materials, the exfoliated samples exhibited an increased concentration of oxidized species. Generally, n-butyllithium exfoliation route seemed to result in more oxidized materials than sodium naphtalenide exfoliation route for both MoTe₂ and WTe₂. Despite the expectations, the increased degree of oxidation does not necessarily lead to a decrease of HER catalytic properties as will be discussed in the following sections.

In the next step, we performed inherent electrochemistry measurements. This is highly advantageous for the extraction of electrochemical potentials used for electrochemical

ACS Catalysis

activation treatment (oxidation/reduction). Cyclic voltammetry curves for both anodic and cathodic scans in a phosphate buffer solution are shown in **Figure 5** for MoTe₂ and **Figure 6** for WTe₂. From the CV curves, potentials used for electrochemical oxidation/reduction pretreatment were identified. Potentials higher/lower by ca. 0.2 V than the most positive/negative oxidation/reduction peak were used.

Firstly for the MoTe₂ Bulk, a peak at ca. 0.55 V followed by an inconspicuous reduction peak at ca. -0.84 V emerges in the anodic scan. This oxidation peak was shifted to about 0.37 V in the following scans. Similarly, the same oxidation and reduction peaks were present in the cathodic scans with the exception of the reduction peak at -0.84 V which only emerged in the following scans. This suggested that the reduction peak is related to the reduction of moieties formed during the oxidation at 0.55 V/0.37 V. From the literature and our previous work we can conclude that the oxidation peak can be at least partially ascribed to an oxidation process of tellurium.^{55, 56} For more detailed investigation, we also performed XPS measurements after electrochemical oxidation/reduction with the results shown in Figure S6 and summarized in Tables S3 and S4. The increase in TeO₂ concentration in MoTe₂ Bulk ox. is quite unsurprising. However, the striking TeO₂ concentration increase for MoTe₂ Bulk red. was unexpected. This may be a result of a metastable intermediate formation which is readily oxidized under exposure to ambient atmosphere. The HR XPS spectra of Mo 3d revealed changes in Mo⁶⁺ concentration. A complete reduction to Mo⁴⁺ in MoTe₂ Bulk red. and a slight increase of Mo⁶⁺ in MoTe₂ Bulk ox. can be seen. This indicates that the oxidation observed in the CV curves may be an overlap of Te and Mo oxidations.

The situation becomes much more complex in case of n-butyllithium and sodium naphtalenide exfoliated MoTe₂. Obviously, exfoliation introduces new oxidizable/reducible moieties, which is apparent from the broadening of oxidation peak at 0.55V and appearance of new reduction peaks. The similarity of CV curves for both MoTe₂ BuLi and MoTe₂ Naph

makes it apparent that both routes produce similar reducible/oxidizable moieties. However, reduction peaks are less intensive in the case of MoTe₂ Naph and the analysis of XPS spectra (**Figure S6** and **Table S4**) revealed, that both Te and Mo are more easily reduced in the case of MoTe₂ Naph. The smaller current indicates fewer reducible species which were shown to be likely metastable and tend to oxidize under ambient conditions.



Figure 5. Inherent electrochemistry measurements of bulk and exfoliated MoTe₂. Conditions: PBS (pH 7.2), scan rate 0.1 V/s.

The WTe₂ Bulk behavior was very similar to that of MoTe₂ Bulk and the comparison revealed only one additional peak at ca. -1.5 V. Since the difference is in the metal element, we expect that this signal originated from tungsten. The XPS spectra after electrochemical oxidation/reduction (**Figure S7** and **Tables S6 and S7**) revealed an increased concentration of W⁶⁺ in both reduced and oxidized WTe₂ Bulk. This was in contrast to MoTe₂ Bulk which was successfully reduced by cathodic potentials. As expected, this was even more pronounced for

ACS Catalysis

 WTe_2 Bulk ox. The analysis of Te 3d spectra also showed an increase in TeO₂ concentration, which was also very well apparent by the emergence of a new pair of peaks in the W 4f spectra. This was not observed in the untreated materials.

Inspection of the complex CV curves of WTe₂ BuLi and WTe₂ Naph revealed that the exfoliation of WTe₂ introduced new oxidizable/reducible moieties. Firstly, an increase in current was clearly apparent for both exfoliated samples. Additionally, the reduction peak previously observed at about -1.5 V shifted to about -1 V in both anodic and cathodic scans suggesting either an activation of reducible moieties or a presence of new ones. Moreover, the oxidation peak at about 0.4 V and the reduction peak are related to each other. It is obvious from **Figure 6** that the oxidation current increased significantly after sweeping to negative potentials. This suggested a reversible oxidation of products formed by the electrochemical reduction. The complexity of the surface chemistry was mostly pronounced in the WTe₂ Naph sample which exhibited multiple oxidation peaks (anodic scan) and multiple reduction peaks (cathodic scan).

XPS spectra again revealed a high instability and susceptibility of the exfoliated WTe₂ towards oxidation. While an increase of the oxidized species is apparent in WTe₂ BuLi red. and WTe₂ Naph red., a complete oxidation is observed for samples treated with anodic potentials.



Figure 6. Inherent electrochemistry measurements of bulk and exfoliated WTe₂. Conditions: PBS (pH 7.2), scan rate 0.1 V/s.

Finally, the exfoliated molybdenum and tungsten ditellurides were tested for their hydrogen evolution reaction (HER) catalytical activity. The bulk material as well as bare glassy carbon (GC) and Pt/C catalyst measurements are included for comparison. AOverpotential at -10 mA.cm⁻² was used to compare the individual samples. Results of HER measurements are shown in **Figure 7**. Because of their low surface area and thus lower amount of HER actives sites, both bulk MoTe₂ and WTe₂ exhibited the largest overpotentials. Electrochemically untreated MoTe₂ Bulk exhibited an overpotential of -0.75 V which increased to -0.80 V for MoTe₂ Bulk red. and -0.90 V for MoTe₂ Bulk ox. becoming even worse catalyst than the bare GC electrode. WTe₂ in its untreated bulk form showed a slightly higher catalytic activity (-0.64 V) than the bulk MoTe₂, but electrochemical treatment led again to slightly higher overpotentials. The difference between oxidized and reduced bulk

ACS Catalysis

WTe₂ was negligible with overpotentials of -0.68 V and -0.69 V for WTe₂ Bulk red. and WTe₂ Bulk ox., respectively.

Exfoliation invoked a dramatic increase in HER catalytic activity, which was very well documented by the overpotential decrease. We attribute this to an increase in surface area introduced during the exfoliation and a presence of 1T phase in the exfoliated WTe₂. BuLi exfoliated MoTe₂ and Naph exfoliated MoTe₂ exhibit the respective overpotentials -0.38 V and -0.40 V. Interestingly, both electrochemical oxidation and reduction have a minute influence on the catalytical activity especially in the case of MoTe₂ where only a slightly higher overpotential can be observed for MoTe₂ BuLi red. This effect was a bit more pronounced in the case of MoTe₂ Naph with a little higher difference between the performance of untreated and electrochemically treated samples. The XPS analysis discussed in the previous section revealed dramatic changes in the surface composition. The fact that HER activity remained nearly the same suggests that even the oxidized surface of MoTe₂ may serve as a HER catalyst and that the activity is hindered only to a minimal degree. This was strikingly different from MoS₂ where the treatment with oxidative potentials led to worsening of HER activity. The catalytic activity of molybdenum and tellurium oxides also has to be taken into account and asks for more attention in the future.

We performed density functional theory (DFT) calculation of hydrogen bonding onto edges of MoTe₂ and WTe₂ to elucidate their activity for HER. Intrinsic activity for HER can be assessed by the Gibbs free energy of the adsorbed H (ΔG_H), because a material with (nearly) thermoneutral ΔG_H (i.e. $\Delta G_H \approx 0$ eV) is expected to be effective for HER.⁵⁷ Pt/C is, by far, the best electrocatalyst and its ΔG_H has been found to be almost perfectly thermoneutral.⁵⁸ We focus on the metal edge of MoTe₂ and WTe₂, since the edges have been found to be active facets for molybdenum and tungsten disulfides, whereas the (0001) basal planes have been found to be inert.^{23, 42} Our calculations reveal that the bare metal edges (i.e.

metal edge at 0% Te coverage) are unstable, because they have a very high energy and undergo serious structural changes, which disrupt the nanostripe. The adsorption of tellurium monomer atoms (i.e. 50% Te coverage) is necessary to stabilize the edge. It should be noted that the specific structure (the coverage of chalcogen atoms on the edge) depends mainly on the chemical potential of tellurium containing species under the operating conditions and can seriously affect the calculated adsorption enthalpies.⁵⁹ The resulting Gibbs free energy of adsorbed H is 0.57 eV and 0.34 eV for the metal edge of MoTe₂ and WTe₂, respectively. In comparison, molybdenum disulfide and diselenide have respective ΔG_H of -0.36 eV and 0.02 eV for the equivalent adsorption at 25 % hydrogen coverage of the Mo-edge.^{42, 57} Tungsten disulfide and diselenide have $\Delta G_{\rm H}$ of -0.04 eV and 0.17 eV under the same circumstances, respectively. The hydrogen atom thus binds to the tellurium monomer atoms at the metal edge, but the bond is weaker than the H-S bond in analogous molybdenum and tungsten dichalcogenides. A similar trend of an increased adsorption enthalpy as one descends through the group of dichalcogenides has been recently calculated for platinum dichalcogenides.⁵⁵ Increasing the size of chalcogen atom (in the sequence S, Se, Te), the bonding orbitals become larger and more diffused and, consequently, the bond between the atom and the hydrogen weakens. As a result, both MoTe₂ and WTe₂ should intrinsically exhibit HER performance inferior to that of their disulfides and diselenides, which can adsorb hydrogen more effectively ($\Delta G_{\rm H}$ close to zero). It should be emphasized, that our calculations are of a model character, and have therefore inherent limitations. One of limitations is the computational model, which represents catalytic site as an ideally straight edge in vacuum, i.e. the roles of lattice imperfections, edge curvature, and solvent effects are neglected. Moreover, although the $\Delta G_{\rm H}$ has been widely considered to be a useful indicator for the catalytic activity, it describes only equilibrium thermodynamics of the reaction and may not be directly related to the activation barrier for HER.⁶⁰

ACS Catalysis

Compared to MoTe₂, the WTe₂ seems to offer a lot more possibilities in terms of possible electrochemical activation. While the exfoliated MoTe₂ after electrochemical treatment exhibited nearly the same activity, there were major differences in untreated and electrochemically treated WTe₂. WTe₂ BuLi with an overpotential of -0.60 V showed only a minor improvement over bulk WTe₂ but became much more active after electrochemical treatment. The overpotentials lowered down to -0.55 V for WTe₂ BuLi red. and even more down to -0.40 V for WTe₂ BuLi ox. This was quite surprising if we consider the XPS results which revealed that the surface of this material was fully corroded. Therefore, the catalytic activity of surface oxides may play even more important role than in the case of MoTe₂. Finally, WTe₂ BuLi. However, in this case, the electrochemical treatment did not lead to an improvement of HER catalytic activity. On one hand, WTe₂ Naph ox. was also revealed to be fully corroded but still outperformed WTe₂ Naph red.. This again calls for more attention on how the presence of surface oxides influences the overall HER performance of TMDs.



Figure 7. HER performance measured by LSV in 0.5M H₂SO₄ with a slow scan rate of 2 mV/s. Average overpotential values are shown in the right part of the figure. Error bars are based on triplicate measurements.

Finally, Tafel slopes extracted from the LSV curves are displayed and compared in **Figure 8**. As a benchmark for potential application performance, Tafel slopes are of high importance. Values of Tafel slopes around 150 mV/dec of both MoTe₂ Bulk and WTe₂ Bulk showcased their small HER catalytic activity, which is not enhanced neither by electrochemical oxidation nor reduction. The exfoliated MoTe₂ samples exhibited Tafel slope of 57 mV/dec and 47 mV/dec for MoTe₂ BuLi and MoTe₂ Naph, respectively, showcasing the major improvement in comparison with the Bulk sample. Only minimal differences in Tafel slope values can be observed for electrochemically treated samples. This is in good agreement with LSV measurements. WTe₂ BuLi and WTe₂ Naph (56 mV/dec and 58 mV/dec, respectively) Tafel slopes also follow the overall HER activity very well. The improvement of WTe₂ ox. HER activity was also confirmed by the decrease of Tafel slope to 42 mV/dec.



Figure 8. Tafel slopes extracted from LSV measurements. Average values and error bars are based on triplicate measurements.

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Conclusion

In summary, we have thoroughly characterized bulk and chemically exfoliated MoTe₂ and WTe₂ and tested their activity towards hydrogen evolution reaction. The feasibility of electrochemical activation via the oxidation or reduction was also inspected. Exfoliation using both n-butyllithium and sodium naphtalenide led to a dramatic increase in oxygen content. We attributed this to an increased rate of oxidation caused by increased surface area observed by SEM. XPS analysis revealed that both metals as well as tellurium were oxidized during the process of exfoliation. The degree of oxidation of the individual elements was strongly dependent on the exfoliation route.

Presence of various reducible/oxidizable surface moieties in the exfoliated molybdenum and tungsten ditellurides was detected by the inherent electrochemistry measurements. A variety of different characteristic signals also clearly shows that these moieties were dependent on used exfoliation agent. With the use of potentials inferred from the inherent electrochemistry measurements, we have tested the materials for possible enhancement of catalytic properties. Surface analysis after electrochemical treatment revealed a very high susceptibility of molybdenum, tungsten as well as tellurite towards oxidation.

Finally HER catalytic activities were determined for all of the studied materials. HER performance was significantly enhanced in the case of MoTe₂ exfoliated with both n-butyllithium and sodium naphtalenide and both materials performed similarly even after both electrochemical treatments. More pronounced enhancement was observed for WTe₂ exfoliated with sodium naphtalenide. On the other hand, n-butyllithium exfoliated WTe₂ showed much more promising possibilities for electrochemical pretreatment activation surpassing the sodium naphtalenide exfoliated WTe₂. Interestingly, despite the very high degree of corrosion, these materials, especially MoTe₂, retain their high HER activity. This is

of high importance, because the loss of catalytic activity due to surface corrosion is not an issue in this case.

EXPERIMENTAL

Materials

Molybdenum powder (99.9%) and tungsten powder (99.9%) were obtained from Alfa Aesar, Germany. Tellurium (99.999%) was obtained from Mateck, Germany. N-butyllithium (2.5 M in hexanes) and sodium (99.9%) were obtained from Sigma-Aldrich, Czech Republic. Naphthalene and tetrahydrofuran (THF) were obtained from Penta, Czech Republic.

Synthesis procedures

MoTe₂ and WTe₂ were prepared by synthesis from elements in evacuated quartz glass ampoules. Stoichiometric amount of Mo (for MoTe₂), W (for WTe₂) and Te corresponding to 10g of ditellurides was placed in quartz glass ampoule (100x15mm; 2mm wall thickness) and evacuated on the base pressure of $1x10^{-3}$ Pa. Subsequently, quartz ampoule was melt sealed by oxygen-hydrogen welding torch. The sample was heated to 600 °C for 48 hours. Ampoule content was mechanically mixed for 10 minutes and heated to 800 °C for 48 hours and then to 850 °C for 12 hours after the first heating procedure. All heating and cooling rates were 5 °C/min.

Prepared TMDs were then prepared by chemical exfoliation method. Glovebox with an Argon atmosphere was used for the exfoliation process. Prior to exfoliation, powder samples were dried at 70 °C for 24h. After cooling down to room temperature, samples were loaded into the glovebox. Lithium intercalation was performed by stirring 1g of individual TMD with excess (1.5x moles compared to TMD) of n-butyllithium solution (hexane). Sodium naphtalenide solution used for exfoliation of 1g of TMD powder was prepared by mixing sodium metal with naphthalene in dried tetrahydrofuran. Glass coated magnetic stir bars were used to avoid

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fluorine contamination. Intercalated TMDs were then filtered *via* 0.45 µm nylon membrane. 30 mL of hexane or 30mL of tetrahydrofuran was used to wash lithium or sodium intercalated TMDs, respectively. The exfoliated materials were then dispersed in 100 mL of water (under inert Argon atmosphere) and ultrasonicated for 15 min. Purification was performed by dialysis and filtration. Prior to any further use, materials were dried in vacuum oven at 50 °C for 48h.

Characterizations

Scanning electron microscope (SEM) equipped with FEG source (Tescan Lyra dual beam microscope) was used for morphology measurements. Energy dispersive spectroscopy (EDS) analyzer (X-MaxN) with a 20 mm² SDD detector (Oxford instruments) was used for the measurements of composition. Data were evaluated using AZtecEnergy software. Before the measurement, samples were placed onto a conductive carbon tape. All measurements were carried out with 15 kV acceleration voltage.

An inVia Raman microscope (Renishaw, England) with a CCD detector was used for Raman spectroscopy in backscattering geometry. A Nd-YAG laser (532 nm, 50 mW) with 50x magnification objective was used for measurements. Instrument calibration was performed with a silicon reference which gives a peak centre at 520 cm⁻¹ and a resolution of less than 1 cm⁻¹. In order to avoid radiation damage, laser power output used for this measurement was kept at 5 mW.

X-ray powder diffraction data were collected at room temperature on Bruker D8 Discoverer powder diffractometer (Bruker, Germany) with parafocusing Bragg–Brentano geometry using CuK α radiation ($\lambda = 0.15418$ nm, U = 40 kV, I = 40 mA). Data were scanned over the angular range 5-90° (2 θ) with a step size of 0.019° (2 θ). Data evaluation was performed in the software package EVA.

ESCAProbeP (Omicron Nanotechnology Ltd, Germany) spectrometer with a monochromatic aluminium X-ray radiation source (1486.7 eV) was used High resolution X-ray photoelectron spectroscopy (XPS). Firstly, wide-scan survey spectra of all elements were collected. High-resolution C 1s, Mo 3d, W 4f and Te 3d core level spectra were also recorded. Relative sensitivity factors were used to evaluate the element concentrations. Samples were placed onto conductive carbon tape and the electron gun was used to eliminate sample charging during measurement (1-5 V).

The electrochemical characterization was performed by cyclic voltammetry using potentiostat PGSTAT204 (Metrohm Autolab B.V., The Netherlands) with three electrode setup. Glassy carbon working electrode (GC), glass carbon auxiliary electrode (GC) and saturated Ag/AgCl reference electrode were obtained from Gamry (USA). For the inherent electrochemistry measurements a 1 μ l of 1 mg/ml of TMD suspension was drop-casted onto the surface of GC electrode and dried to obtain a homogeneous layer. CV curves were then measured in an argon purged 50 mM phosphate buffer solution with a scan rate of 0.1 V/s. A new portion of material was applied before every measurement. GC electrode was cleaned by polishing (0.05 μ m alumina) before every measurement. Hydrogen evolution reaction (HER) was performed in argon purged 0.5 M H₂SO₄ solution with a scan rate of 2 mV/s. All the measurements were performed three times, always with a new portion of material drop-casted on the GC electrode. For the electrochemical treatment measurements, materials were reduced/oxidized at potentials specific for each material, rinsed in distilled water, dried and then used for individual measurements with conditions described above.

DFT calculations

DFT calculations were performed using the projector-augmented wave method implemented in the Vienna Ab initio Simulation Package (VASP).^{61, 62} The energy cutoff for the plane-wave expansion was set to 350 eV. We used optimized van der Waals functional

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optB86b-vdW functional,⁶³ which works very well for both covalent and van der Waals bonds in layered materials.⁶⁴ We considered the adsorption of hydrogen onto the surface and edge sites of single layered ditellurides. The surface (basal plane) was modeled by a 4x4 supercell (16 Mo or W atoms) in connection with $3x_3x_1$ k-point sampling. The layers were separated by 18 Å of vacuum. The edge was modeled by a 4x4 nanostripe, i.e. it contained four atoms along the edge and the nanostripe was four atoms wide. The nanostripe model of the ascleaved edge of the 2H structure exposed both telluride terminated edge and metal terminated edge. We focused on the metal terminated edge. We used 50 % Te coverage of the metal edge for both MoTe₂ and WTe₂ to stabilize dangling bonds at the edge. The Brillouin zone of the one-dimensional nanostripe was sampled by $1x_3x_1$ k-points where three k-points belonged to the only direction in which the cell was periodically repeated. As the edge were 25%, 50%, 75%, and 100%. The differential energy of adsorption ΔE was calculated as

 $\Delta E = E_{TOT}(nH^*) - E_{TOT}[(n-1)H^*] - 1/2 E_{TOT}(H_2)$

The Gibbs free-energy of the adsorption atomic hydrogen (ΔG) was obtained as

 $\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S_H$

where, ΔE_{ZPE} and ΔS_H was the difference in zero point energy, and entropy between the adsorbed hydrogen and hydrogen in the gas phase. These thermal corrections were found to be independent of particular adsorption site, and thus ΔG at standard condition was determined by ΔE plus a thermal correction constant of 0.29 eV.⁵⁷

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ASSOCIATED CONTENT

Supporting information.

The EDS maps of exfoliated and non-exfoliated tellurides obtained by SEM and TEM, X-ray diffractograms, Raman spectra of MoTe₂ BuLi, XPS survey spectra, high resolution Mo 3d, W 4f and Te 4f spectra and composition obtained by XPS, composition of tellurides after electrochemical pretreatment obtained by XPS.

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AUTHOR CONTRIBUTIONS

M. P. and Z. S. planned and supervised the project. J. L., P. V. and V. M. and D. S. planned and conducted the experiments. P. L. performed DFT calculations. The manuscript was written through contribution of all authors.

COMPETITING FINANTIAL INTERESTS

The authors declare no competing financial interests.

ACS Catalysis

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