SUPPLEMENTARY INFORMATION

FOR

Catalytic Properties of Group 4 Transition Metal Dichalcogenides (MX$_2$; M = Ti, Zr, Hf; X = S, Se, Te)

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Figure S1. Scanning electron micrographs and corresponding energy-dispersive X-ray maps of group 4 TMDs. Scale bars represent 10 μm.
Figure S2. Elemental compositions of group 4 TMD materials based on energy-dispersive X-ray spectroscopy.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ti at. %</th>
<th>Zr at. %</th>
<th>Hf at. %</th>
<th>S at. %</th>
<th>Se at. %</th>
<th>Te at. %</th>
<th>C at. %</th>
<th>O at. %</th>
<th>Al at. %</th>
<th>Si at. %</th>
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<tbody>
<tr>
<td>TiS₂</td>
<td>27.19</td>
<td>-</td>
<td>41.07</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>14.23</td>
<td>16.95</td>
<td>0.32</td>
<td>0.24</td>
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<tr>
<td>ZrS₂</td>
<td>- 27.00</td>
<td>29.47</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>28.70</td>
<td>14.43</td>
<td>0.39</td>
<td>-</td>
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<tr>
<td>HfS₂</td>
<td>-</td>
<td>-</td>
<td>20.22</td>
<td>15.76</td>
<td>-</td>
<td>-</td>
<td>23.06</td>
<td>40.97</td>
<td>-</td>
<td>-</td>
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<tr>
<td>TiSe₂</td>
<td>17.06</td>
<td>-</td>
<td>-</td>
<td>25.55</td>
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<td>19.21</td>
<td>36.36</td>
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<tr>
<td>ZrSe₂</td>
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<td>-</td>
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<td>17.75</td>
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<tr>
<td>HfSe₂</td>
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<td>-</td>
<td>10.34</td>
<td>20.61</td>
<td>-</td>
<td>47.35</td>
<td>21.70</td>
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<tr>
<td>TiTe₂</td>
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<td>-</td>
<td>-</td>
<td>34.65</td>
<td>-</td>
<td>41.08</td>
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<tr>
<td>ZrTe₂</td>
<td>- 12.66</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30.30</td>
<td>19.15</td>
<td>37.88</td>
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<tr>
<td>HfTe₂</td>
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<td>-</td>
<td>11.25</td>
<td>-</td>
<td>25.34</td>
<td>23.96</td>
<td>39.45</td>
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Figure S3. Tabulated chalcogen-to-metal ratios of group 4 TMD materials before and electrochemical treatments based on high resolution X-ray photoelectron spectroscopy.
**Figure S4.** The effect of electrochemical treatment on HER performance of TiS\(_2\). (a) Linear sweep voltammograms for HER in acidic electrolyte on TiS\(_2\) (black line), TiS\(_2\) after -1.5 V treatment (red line) and TiS\(_2\) after +0.7 V treatment (blue line) deposited on a GC electrode. Presented in the bar charts are the averages of the (b) overpotential at -10 mA cm\(^{-2}\) current density, (c) Tafel slopes and (d) HER onset potential, with their corresponding error bars for bare GC and TiS\(_2\) before and after electrochemical treatment.

**Figure S5.** The effect of electrochemical treatment on HER performance of ZrS\(_2\). (a) Linear sweep voltammograms for HER in acidic electrolyte on ZrS\(_2\) (black line) and ZrS\(_2\) after -1.1 V treatment (red line) deposited on a GC electrode. Presented in the bar charts are the averages of the (b) overpotential at -10 mA cm\(^{-2}\) current density, (c) Tafel slopes and (d) HER onset potential, with their corresponding error bars for bare GC and ZrS\(_2\) before and after electrochemical treatment.
Figure S6. The effect of electrochemical treatment on HER performance of TiSe$_2$. (a) Linear sweep voltammograms for HER in acidic electrolyte on TiSe$_2$ (black line), TiSe$_2$ after -1.6 V treatment (red line) and TiSe$_2$ after +1.5 V treatment (blue line) deposited on a GC electrode. Presented in the bar charts are the averages of the (b) overpotential at -10 mA cm$^{-2}$ current density, (c) Tafel slopes and (d) HER onset potential, with their corresponding error bars for bare GC and TiSe$_2$ before and after electrochemical treatment.

Figure S7. The effect of electrochemical treatment on HER performance of ZrSe$_2$. (a) Linear sweep voltammograms for HER in acidic electrolyte on ZrSe$_2$ (black line), ZrSe$_2$ after -1.25 V treatment (red line) and ZrSe$_2$ after +1.5 V treatment (blue line) deposited on a GC electrode. Presented in the bar charts are the averages of the (b) overpotential at -10 mA cm$^{-2}$ current density, (c) Tafel slopes and (d) HER onset potential, with their corresponding error bars for bare GC and ZrSe$_2$ before and after electrochemical treatment.
**Figure S8.** The effect of electrochemical treatment on HER performance of HfSe$_2$. (a) Linear sweep voltammograms for HER in acidic electrolyte on HfSe$_2$ (black line), HfSe$_2$ after -1.25 V treatment (red line) and HfSe$_2$ after +1.5 V treatment (blue line) deposited on a GC electrode. Presented in the bar charts are the averages of the (b) overpotential at -10 mA cm$^{-2}$ current density, (c) Tafel slopes and (d) HER onset potential, with their corresponding error bars for bare GC and HfSe$_2$ before and after electrochemical treatment.

**Figure S9.** The effect of electrochemical treatment on HER performance of TiTe$_2$. (a) Linear sweep voltammograms for HER in acidic electrolyte on TiTe$_2$ (black line), TiTe$_2$ after -1.6 V treatment (red line) and TiTe$_2$ after +1.1 V treatment (blue line) deposited on a GC electrode. Presented in the bar charts are the averages of the (b) overpotential at -10 mA cm$^{-2}$ current density, (c) Tafel slopes and (d) HER onset potential, with their corresponding error bars for bare GC and TiTe$_2$ before and after electrochemical treatment.
**Figure S10.** The effect of electrochemical treatment on HER performance of ZrTe$_2$. (a) Linear sweep voltammograms for HER in acidic electrolyte on ZrTe$_2$ (black line), ZrTe$_2$ after -1.6 V treatment (red line) and ZrTe$_2$ after +1.1 V treatment (blue line) deposited on a GC electrode. Presented in the bar charts are the averages of the (b) overpotential at -10 mA cm$^{-2}$ current density, (c) Tafel slopes and (d) HER onset potential, with their corresponding error bars for bare GC and ZrTe$_2$ before and after electrochemical treatment.

**Figure S11.** The effect of electrochemical treatment on HER performance of HfTe$_2$. (a) Linear sweep voltammograms for HER in acidic electrolyte on HfTe$_2$ (black line), HfTe$_2$ after -1.6 V treatment (red line) and HfTe$_2$ after +1.1 V treatment (blue line) deposited on a GC electrode. Presented in the bar charts are the averages of the (b) overpotential at -10 mA cm$^{-2}$ current density, (c) Tafel slopes and (d) HER onset potential, with their corresponding error bars for bare GC and HfTe$_2$ before and after electrochemical treatment.