SUPPLEMENTARY INFORMATION

FOR

Catalytic Properties of Group 4 Transition Metal Dichalcogenides (MX_2; M = Ti, Zr, Hf; X = S, Se, Te)

Rou Jun Toh,[a] Zdenek Sofer[b] and Martin Pumera[a]*

[a]*Division of Chemistry & Biological Chemistry School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore.*

[b]*Department of Inorganic Chemistry, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic*

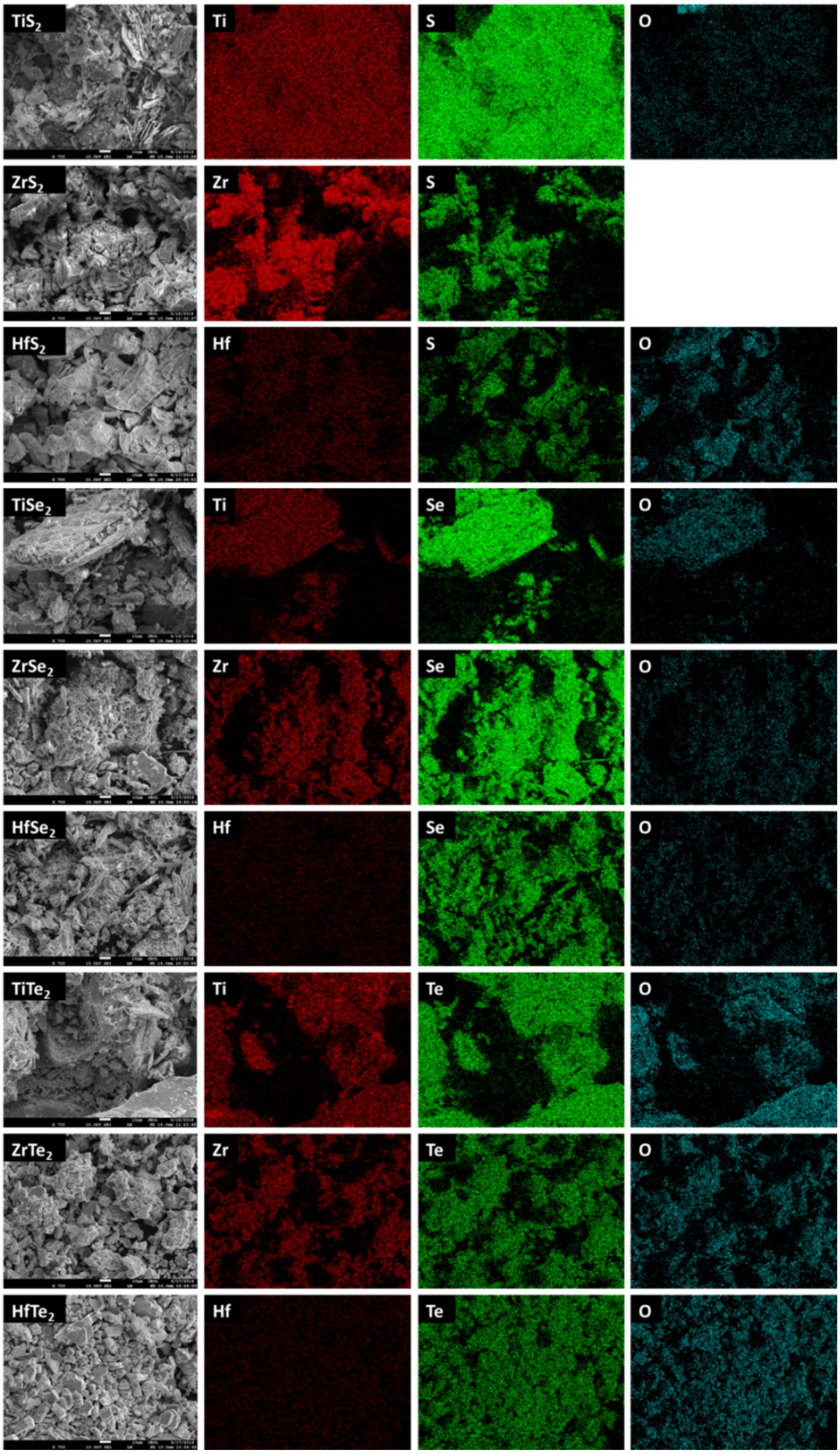

Figure S1. Scanning electron micrographs and corresponding energy-dispersive X-ray maps of group 4 TMDs. Scale bars represent 10 µm.

Material	Ti at. %	Zr at. %	Hf at. %	S at. %	Se at. %	Te at. %	C at. %	O at. %	Al at. %	Si at. %
TiS_2	27.19	-	-	41.07	-	-	14.23	16.95	0.32	0.24
ZrS_2	-	27.00	-	29.47	-	-	28.70	14.43	0.39	-
HfS_2	-	-	20.22	15.76	-	-	23.06	40.97	-	-
$TiSe_2$	17.06	-	-	-	25.55	-	19.21	36.36	-	1.82
$ZrSe_2$	-	9.91	-	-	21.40	-	50.94	17.75	-	-
$HfSe_2$	-	-	10.34	-	20.61	-	47.35	21.70	-	-
$TiTe_2$	23.30	-	-	-	-	34.65	-	41.08	0.98	-
$ZrTe_2$	-	12.66	-	-	-	30.30	19.15	37.88	-	-
$HfTe_2$	-	-	11.25	-	-	25.34	23.96	39.45	-	-

Figure S2. Elemental compositions of group 4 TMD materials based on energy-dispersive X-ray spectroscopy.

Material	Surface Chalcogen / Metal Ratio		
	Before electrochemical treatment	After reductive treatment	After oxidative treatment
TiS_2	1.41	Loss of TiS_2	Loss of TiS_2
ZrS_2	0.77	Loss of ZrS_2	-
HfS_2	0.43	-	-
$TiSe_2$	1.67	Loss of $TiSe_2$	Loss of $TiSe_2$
$ZrSe_2$	0.88	Loss of $ZrSe_2$	Loss of $ZrSe_2$
$HfSe_2$	0.80	1.15	0.99
$TiTe_2$	3.78	Loss of $TiTe_2$	Loss of $TiTe_2$
$ZrTe_2$	5.08	Loss of $ZrTe_2$	Loss of $ZrTe_2$
$HfTe_2$	4.16	Loss of $HfTe_2$	Loss of $HfTe_2$

Figure S3. Tabulated chalcogen-to-metal ratios of group 4 TMD materials before and electrochemical treatments based on high resolution X-ray photoelectron spectroscopy.

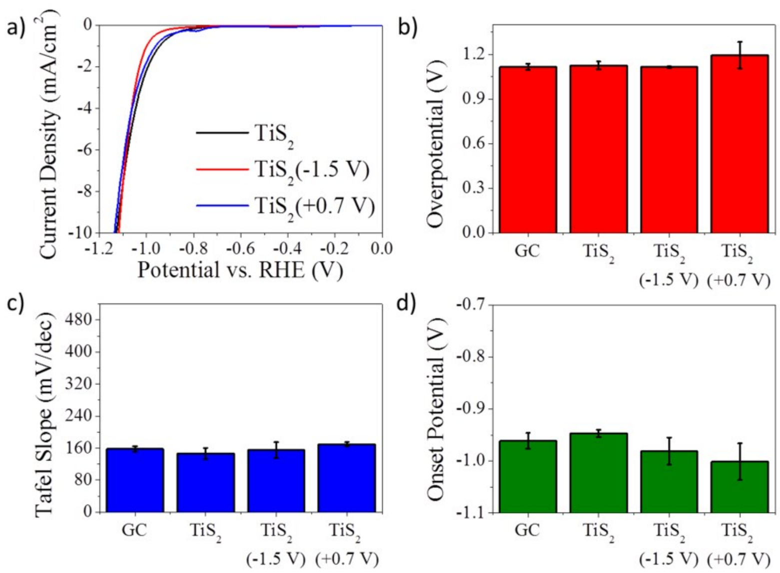

Figure S4. The effect of electrochemical treatment on HER performance of TiS_2. (a) Linear sweep voltammograms for HER in acidic electrolyte on TiS_2 (black line), TiS_2 after -1.5 V treatment (red line) and TiS_2 after +0.7 V treatment (blue line) deposited on a GC electrode. Presented in the bar charts 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.

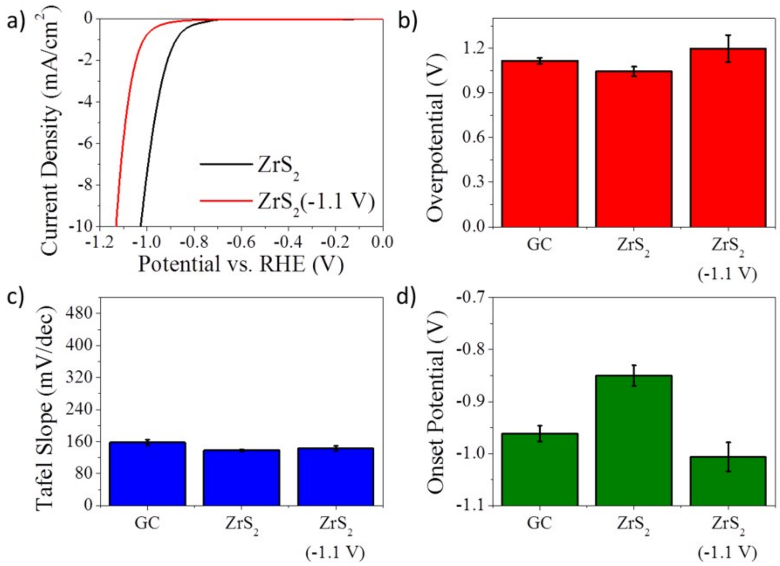

Figure S5. The effect of electrochemical treatment on HER performance of ZrS_2. (a) Linear sweep voltammograms for HER in acidic electrolyte on ZrS_2 (black line) and ZrS_2 after -1.1 V treatment (red line) deposited on a GC electrode. Presented in the bar charts are the averages of the (b) overpotential 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.

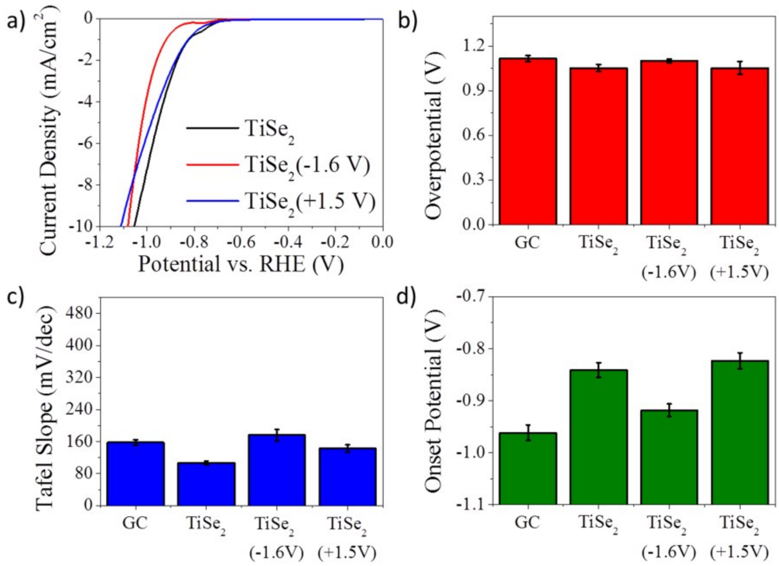

Figure S6. The effect of electrochemical treatment on HER performance of $TiSe_2$. (a) Linear sweep voltammograms for HER in acidic electrolyte on $TiSe_2$ (black line), $TiSe_2$ after -1.6 V treatment (red line) and $TiSe_2$ after +1.5 V treatment (blue line) deposited on a GC electrode. Presented in 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.

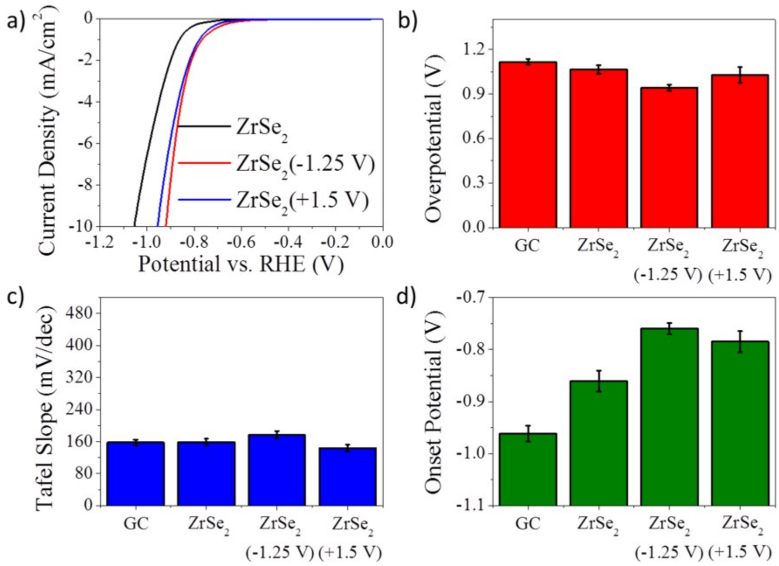

Figure S7. The effect of electrochemical treatment on HER performance of $ZrSe_2$. (a) Linear sweep voltammograms for HER in acidic electrolyte on $ZrSe_2$ (black line), $ZrSe_2$ after -1.25 V treatment (red line) and $ZrSe_2$ after +1.5 V treatment (blue line) deposited on a GC electrode. Presented 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.

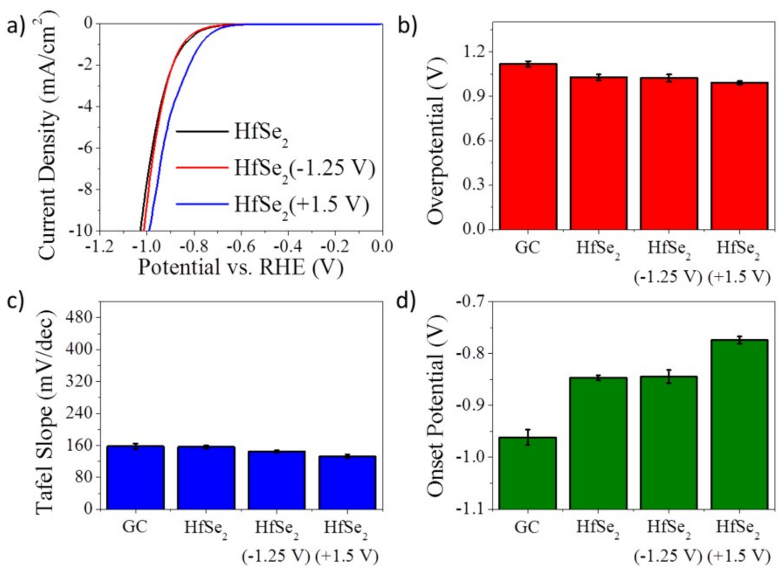

Figure S8. The effect of electrochemical treatment on HER performance of $HfSe_2$. (a) Linear sweep voltammograms for HER in acidic electrolyte on $HfSe_2$ (black line), $HfSe_2$ after -1.25 V treatment (red line) and $HfSe_2$ after +1.5 V treatment (blue line) deposited on a GC electrode. Presented 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.

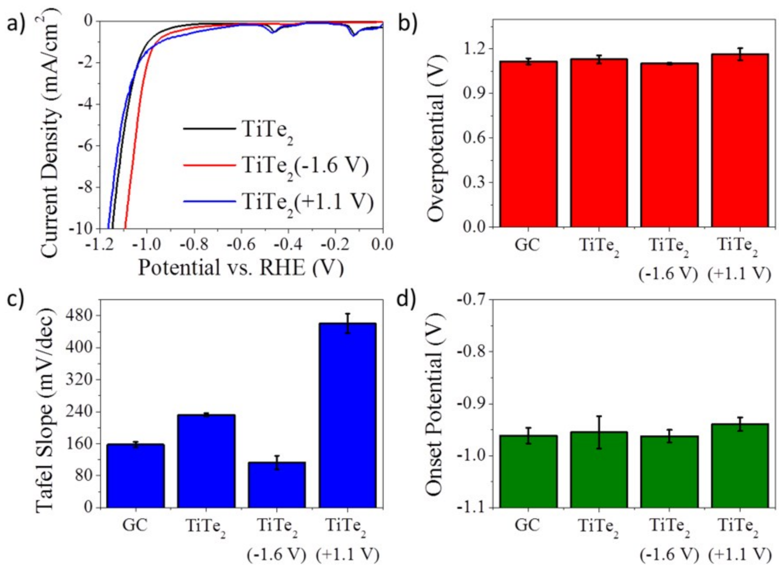

Figure S9. The effect of electrochemical treatment on HER performance of $TiTe_2$. (a) Linear sweep voltammograms for HER in acidic electrolyte on $TiTe_2$ (black line), $TiTe_2$ after -1.6 V treatment (red line) and $TiTe_2$ after +1.1 V treatment (blue line) deposited on a GC electrode. Presented in 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.

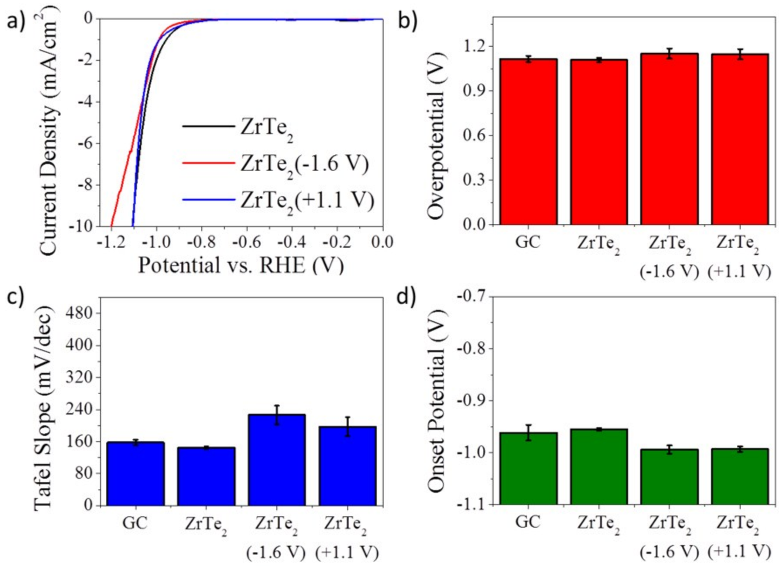

Figure S10. The effect of electrochemical treatment on HER performance of $ZrTe_2$. (a) Linear sweep voltammograms for HER in acidic electrolyte on $ZrTe_2$ (black line), $ZrTe_2$ after -1.6 V treatment (red line) and $ZrTe_2$ after +1.1 V treatment (blue line) deposited on a GC electrode. Presented 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.

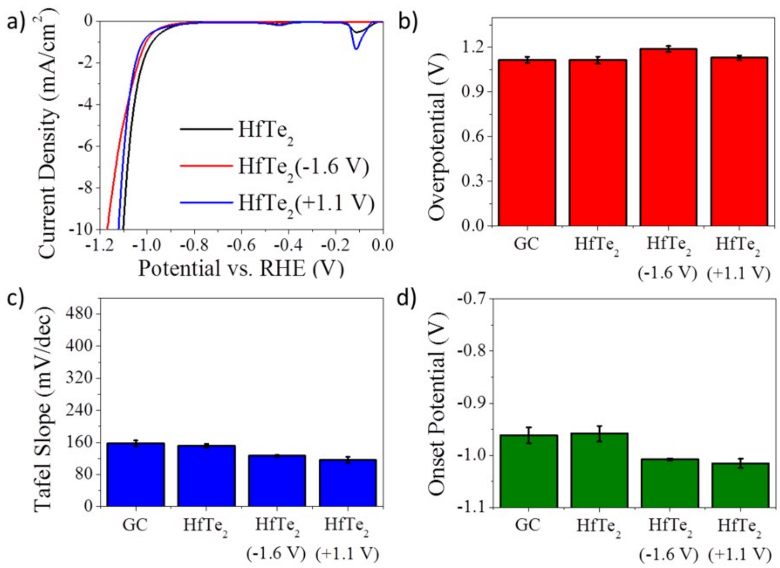

Figure S11. The effect of electrochemical treatment on HER performance of $HfTe_2$. (a) Linear sweep voltammograms for HER in acidic electrolyte on $HfTe_2$ (black line), $HfTe_2$ after -1.6 V treatment (red line) and $HfTe_2$ after +1.1 V treatment (blue line) deposited on a GC electrode. Presented 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.