Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Transition-metal monochalcogenide nanowires: High-efficient bi-functional catalysts for oxygen evolution/reduction reactions

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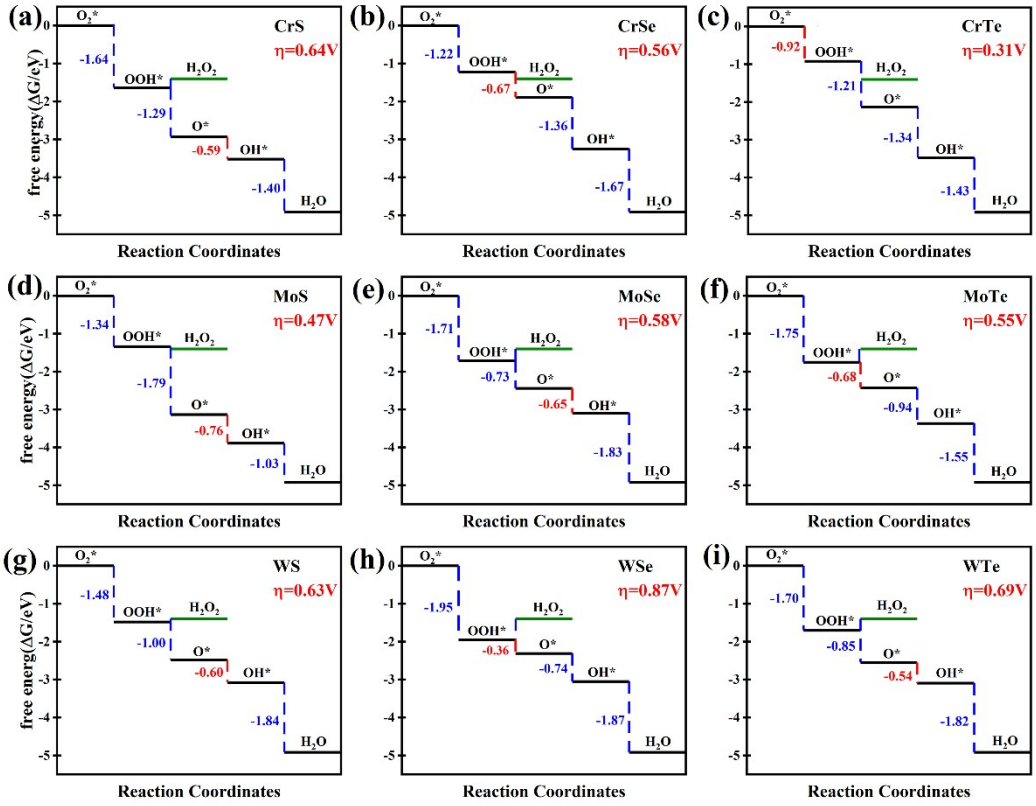

Fig. S1. Free energy figures of (a) CrS, (b) CrSe, (c) CrTe, (d) MoS, (e) MoSe, (f) MoTe, (g) WS, (h) WSe, and (i) WTe for ORR process at zero potential (U = 0), where the elementary reaction with ΔG in red represents the potential-determining step.

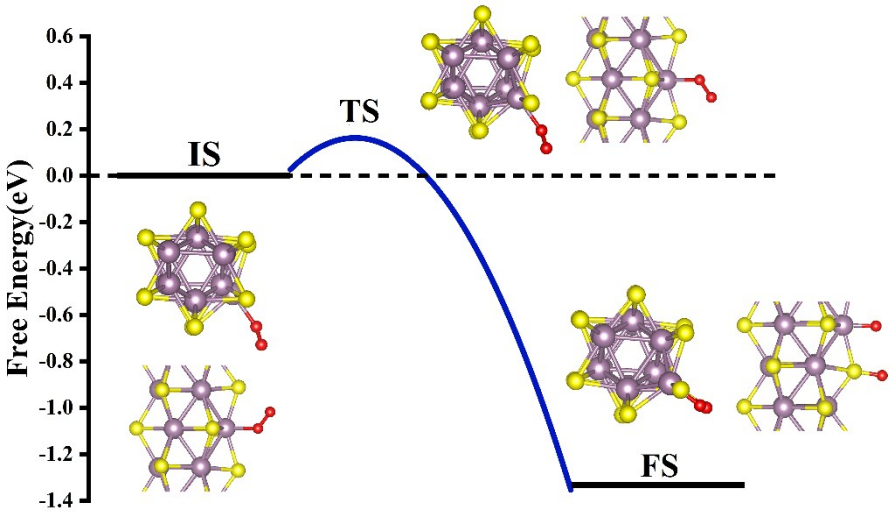

Fig. S2. Energy profile for the O_2 dissociation on MoS nanowires.

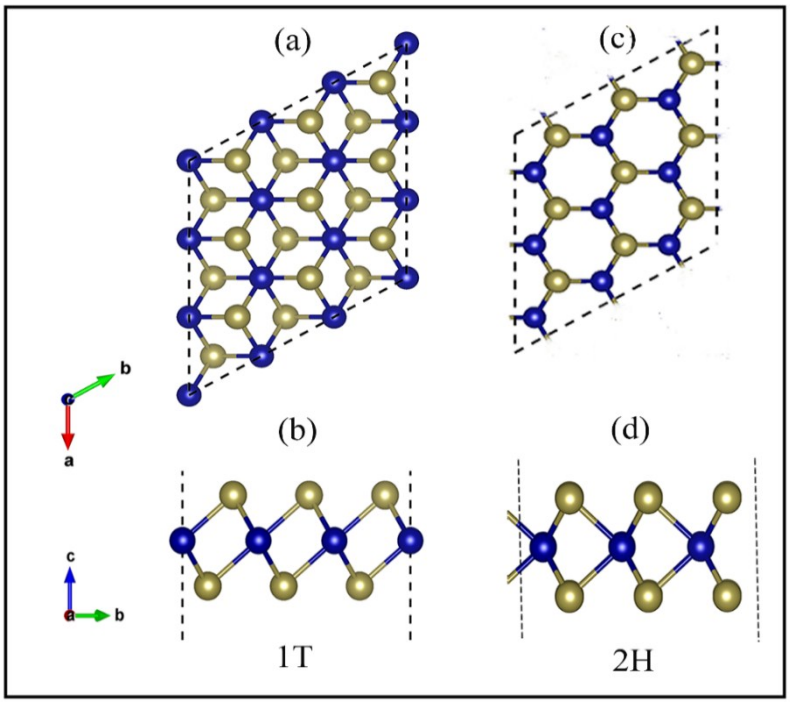

Fig. S3. The representative structures of 2D $CrTe_2$ monolayers in 3×3×1supercells: (a) top and (b) side views of 1T phase, (c) top and (d) side view of 2H phase. The blue and yellow atom represent metal and chalcogen atoms, respectively.

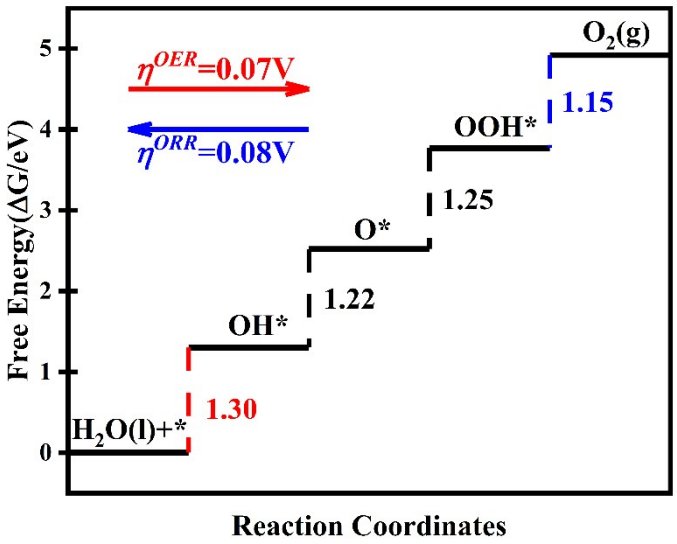

Fig. S4 Free energy diagram of CrTe NW obtained by involving solvent effect. The solvent effect was taken into account by using an implicit solvation model with the dielectric constant of 78.54 (water).

Table S1 The OER/ORR overpotentials of CrTe NWs under tensile strain (ε).

ε	0%	1%	3%	5%
η^{OER} (V)	0.20	0.18	0.28	0.24
η^{ORR} (V)	0.31	0.28	0.37	0.38

Table S2. Optimized lattice constant, band gap (E_g), active site, overpotential and electron transfer from metal to chalcogen atom (ΔQ) of monolayer MX_2.

	structure	lattice constant(Å)	band gap(eV)	active site	η^{OER}(V)	η^{ORR}(V)	electron transfer(e)
CrS_2	1T	3.06	Metal	S	1.96	1.32	0.51
	2H	3.04	0.94	S	0.96	1.82	0.50
$CrSe_2$	1T	3.20	Metal	Se	1.09	0.80	0.43
	2H	3.20	0.76	Se	1.26	1.25	0.42
$CrTe_2$	1T	3.47	Metal	Te	2.35	1.29	0.31
	2H	3.56	0.59	Te	0.53	0.68	0.30
MoS_2	1T	3.20	Metal	S	2.38	1.50	0.56
	2H	3.18	1.62	S	1.54	2.14	0.53
$MoSe_2$	1T	3.29	Metal	Se	1.04	0.88	0.42
	2H	3.32	1.44	Se	1.45	1.56	0.42
$MoTe_2$	1T	3.47	Metal	Te	2.11	1.31	0.25
	2H	3.52	1.14	Te	0.99	0.99	0.25
WS_2	1T	3.21	Metal	S	2.48	1.98	0.65
	2H	3.18	1.8	S	1.65	2.16	0.60
WSe_2	1T	3.33	Metal	Se	1.25	2.08	0.48
	2H	3.33	1.48	Se	1.51	1.82	0.47
WTe_2	1T	3.53	Metal	Te	2.39	1.88	0.27
	2H	3.87	0.99	Te	1.03	1.29	0.27

ORR Mechanism

The dissociative mechanism pathways are generally the following equations (S1-S5):

$$* + O_2(g) \rightarrow O* + O* \quad \text{(S1)}$$

$$O* + H^+ + e^- \rightarrow OH* \quad \text{(S2)}$$

$$O* + H^+ + e^- \rightarrow OH* \quad \text{(S3)}$$

$$OH* + H^+ + e^- \rightarrow H_2O(l) \quad \text{(S4)}$$

$$OH* + H^+ + e^- \rightarrow * + H_2O(l) \quad \text{(S5)}$$

In associative mechanism, ORR follows the following steps:

$$* + O_2(g) \rightarrow O_2^* \quad \text{(S6)}$$

$$O_2^* + H^+ + e^- \rightarrow OOH* \quad \text{(S7)}$$

$$OOH* + H^+ + e^- \rightarrow O* + H_2O(l) \quad \text{(S8)}$$

$$O* + H^+ + e^- \rightarrow OH* \quad \text{(S9)}$$

$$OH* + H^+ + e^- \rightarrow * + H_2O(l) \quad \text{(S10)}$$

The formation energies are calculated with following equations:

$$\Delta E_{OH*} = E_{NW\text{-}OH} - E_{NW} - (E_{H2O} - 0.5E_{H2}) \quad \text{(S11)}$$

$$\Delta E_{O*} = E_{NW\text{-}O} - E_{NW} - (E_{H2O} - E_{H2}) \quad \text{(S12)}$$

$$\Delta E_{OOH*} = E_{NW\text{-}OOH} - E_{NW} - (2E_{H2O} - 1.5E_{H2}) \quad \text{(S13)}$$

where E_{NW} is the ground state energy of the nanowires before adsorption, $E_{NW\text{-}OH}$,

E_{NW-O}, E_{NW-OOH} are the ground state energies of nanowires absorbed with O*, OH*, and OOH*, respectively. E_{H2O} and E_{H2} are the energies of single isolated H_2O and H_2 molecules in the liquid and gas phase, respectively.