SUPPORTING INFORMATION

Advances in Oxychalcogenide Materials for Hydrogen Evolution Photocatalysis in Aqueous Media

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Table S1. Comparison of the different structural and physical properties of Oxysulfide materials

Compounds	Bandgap magnitude & Nature	Semiconduction type	Cation choice	Coordination environment & Anion ratio	Polar units ?	Polar Structure?	H_2 or O_2 production ?	Reference
$Sr_6Cd_2Sb_6S_{10}O_7$	Indirect (1.89 eV)	n-type	Sb^{3+}	SbS_5 $SbOS_4$ SbO_3	Yes	Yes (*Cm*)	H_2 & O_2 (theory)	DOI : 10.1021/acs.inorgchem.2c03040
$Sm_2Ti_2S_2O_5$	Indirect (2 eV)	n-type	Ti^{4+}	TiO_5	Yes	No (*I*4/*mmm*)	H_2 & O_2 (measured)	DOI : 10.1021/ja0269643

$Y_2Ti_2O_5S_2$	- (1.9 eV)	n-type	Ti^{4+}	TiO_5	Yes	No (*I4/mmm*)	H_2 & O_2 (measured)	DOI : 10.1038/s41563-019-0399-z
Layered - $LaOInS_2$	Direct (~2.64 eV)	-	In^{3+}	InS_6	Yes	$P2_1/m$	H_2 & O_2 (measured)	DOI :10.1039/c7ta04440b DOI :10.1246/cl.2007.854
α - $LaOInS_2$	- (~2.7 eV)	p-type	In^{3+}	InS_5O InS_4 InS_6	Yes	*Pmcn*	H_2 & O_2 (theory)	DOI : 10.1039/C9CC09797J
$La_5In_3S_9O_3$	- (2.60 eV)	p-type	In^{3+}	InS_4	Yes	*Pbcm*	H_2 & O_2 (measured)	DOI : 10.1016/j.jssc.2003.10.012 DOI : 10.1246/cl.2007.854
LaCuOS	Direct (3.2 eV)	p-type	Cu^{2+}	CuS_4	No	*P4/nmm*	-	DOI : 10.1063/1.1319507
PrCuOS	Direct (3.03 eV)	p-type	Cu^{2+}	CuS_4	No	*P4/nmm*	-	DOI : 10.1021/cm030175i
NdCuOS	Direct (2.98 eV)	p-type	Cu^{2+}	CuS_4	No	*P4/nmm*	-	DOI : 10.1021/cm030175i
LaAgOS	Direct (2.50 eV)	p-type	Ag^{+}	AgS_4	No	*P4/nmm*	-	DOI : 10.1002/smtd.202201368
$LaGaS_2O$	Indirect (3 eV)	n-type	Ga^{3+}	GaS_2O_2	No	*Pmca*	Anodic photocurrent under UV light	DOI :10.1021/jp802153t
La_3GaS_5O	Direct (2.3 eV)	n-type	Ga^{3+}	GaS_4	No	No (*Pnma*)	H_2 or O_2 Under visible light (measured)	DOI :10.1021/jp802153t
$CeInOS_2$	Direct (2.41 eV)	-	In^{3+}	InS_6	Yes	$P2_1/m$	H_2 (measured)	DOI : 10.1039/c9dt01562k
$PrInOS_2$	Direct (2.43 eV)	-	In^{3+}	InS_6	Yes	$P2_1/m$	H_2 (measured)	DOI : 10.1039/c9dt01562k
$La_2O_2Fe_2OS_2$	Direct (0.19 eV)	-	Fe^{2+}	FeO_2S_4	No	No (*I4/mmm*)	-	DOI: 10.1103/PhysRevLett.104.216405 DOI: 10.1103/PhysRevB.86.125122
SrZnSO	Direct (3.1 eV)	p-type	Zn^{2+}	ZnS_3O	Yes	Yes ($P6_3mc$)	H_2 (theory)	DOI : 10.1016/j.apcatb.2017.12.006

$SrZn_2S_2O$	Direct (3.86 eV)	n-type	Zn^{2+}	ZnS_3O	Yes	Yes (*$Pmn2_1$*)	H_2 & O_2 (measured)	DOI: 10.1039/C9DT03699G
CaCoSO	Indirect (0.4 eV)	p-type	Co^{2+}	CoS_3O	Yes	Yes (*$P6_3mc$*)	-	DOI : 10.1016/j.materresbull.2017.05.041
CaZnSO	Direct (3.7 eV)	p-type	Zn^{2+}	ZnS_3O	Yes	Yes (*$P6_3mc$*)	H_2 (theory)	DOI : 10.1016/j.apcatb.2017.12.006
BaCoSO	- (1.3 eV)	-	Co^{2+}	CoS_2O_2	No	(*Cmcm*)	-	DOI :10.1103/PhysRevB.100.205130
CaFeSO	Indirect (1.6 eV)	-	Fe^{2+}	FeS_3O	Yes	Yes (*$P6_3mc$*)	-	DOI : 10.1103/PhysRevMaterials.1.034406
BaZnSO	Direct (3.9 eV)	-	Zn^{2+}	ZnS_2O_2	No	(*Cmcm*)	-	DOI :10.1021/ic051240o
BiCuOS	Indirect (1.1 eV)	p-type	Cu^{2+}	CuS_4	No	*P4/nmm*	Decomposition of pollutant (CR) aqueous under visible light: 55 % in 70 mins	DOI :10.3390/ma8031043 DOI : 10.3390/ma11030447
BiAgOS	Indirect (1.5 eV)	p-type	Ag^{+}	AgS_4	No	*P4/nmm*	-	DOI : 10.1021/acs.chemmater.7b02664
$Ln_2Ti_2S_2O_5$ (Ln = Sm, Gd, Tb, Dy, Ho and Er)	Indirect (2.13-1.94 eV)	-	Ti^{4+}	$TiSO_5$	Yes	No (*I4/mmm*)	H_2 & O_2 under visible light (measured)	DOI :10.1021/jp036890x
$La_5Ti_2CuS_5O_7$	Indirect (2.02 eV)	p-type	Ti^{4+} Cu^{+}	TiO_4S_2 TiO_5S CuS_4	Yes	No (*Pnma*)	H_2 & O_2 (measured)	DOI: 10.1039/c2cp43132g
$La_5Ti_2AgS_5O_7$	Indirect (2.17 eV)	p-type	Ti^{4+} Ag^{+}	TiO_4S_2 TiO_5S AgS_4	Yes	No (*Pnma*)	H_2 & O_2 (measured)	DOI: 10.1039/c2cp43132g
$Sr_2Cu_2ZnO_2S_2$	- (2.7 eV)	p-type	Cu^{2+} Zn^{2+}	CuS_4 ZnO_4	No	No (*I4/nmm*)	-	DOI :10.1021/cm0105864
Sr_2CuGaO_3S	- (2.6 eV)	p-type	Cu^{2+} Ga^{3+}	CuS_4 GaO_5	No Yes	*P4/nmm*	-	DOI : 10.1021/cm0007813
Sr_2CuInO_3S	- (2.3 eV)	p-type	Cu^{2+} In^{3+}	CuS_4 InO_5	No Yes	*P4/nmm*	-	DOI : 10.1021/cm0007813

$Sr_3Cu_2Sc_2O_5S_2$	Direct (3.1 eV)	p-type	Cu^{2+} Sc^{3+}	CuS_4 ScO_5	No Yes	No (*I4/nmm*)	-	DOI : 10.1063/1.2817643
$La_2SnO_2S_3$	- (3 eV)	n-type	Sn^{4+}	SnS_4	Yes	No (*Pbnm*)	-	DOI : 10.1107/S0108270185004978
$RE_2M_2S_3O_4$ (RE = Y, Tm; M = Zr, Hf)	Direct (2.95 – 2.80 – 2.93 eV)	-	M^{4+}	MS_3O_4	No	No (*Pbam*)	-	DOI : 10.1039/D1CC00351H
$Sm_3NbS_3O_4$	Direct (2.68 eV)	-	Sm^{3+} Nb^{5+}	$[NbS_2O_4]^{7-}$	Yes	Yes ($Pna2_1$)	-	DOI: 10.1021/acs.inorgchem.1c01634
$Gd_3NbS_3O_4$	Direct (2.74 eV)	-	Gd^{3+} Nb^{5+}	$[NbS_2O_4]^{7-}$	Yes	Yes ($Pna2_1$)	-	DOI: 10.1021/acs.inorgchem.1c01634
$Dy_3NbS_3O_4$	Direct (2.72 eV)	-	Dy^{3+} Nb^{5+}	$[NbS_3O_4]^{9-}$	No	No (*Pnma*)	-	DOI: 10.1021/acs.inorgchem.1c01634
$A_2GeGa_2OS_6$ (A = Ca, Sr)	Indirect (3.15 eV)	-	Ga^{3+}		No	($P\bar{4}2_1m$)	-	DOI: 10.1021/acsami.2c04422
$Sr_2CdGe_2OS_6$	Indirect (3.62 eV)	-	Cd^{2+}	CdS_4 GeS_3O	No Yes	($P\bar{4}2_1m$)	-	DOI : 10.1021/acsami.2c04422 DOI : 10.1021/acs.chemmater.2c00385
$Sr_2ZnGe_2OS_6$	Indirect (3.73 eV)	-	Zn^{2+}	ZnS_4 GeS_3O	No Yes	($P\bar{4}2_1m$)	-	DOI : 10.1021/acsami.2c04422 DOI : 10.1021/acs.chemmater.2c00385
$Sr_2MnGe_2OS_6$	Indirect (3.51 eV)	-	Mn^{2+}	MnS_4 GeS_3O	No Yes	($P\bar{4}2_1m$)	-	DOI : 10.1021/acsami.2c04422 DOI : 10.1021/acs.chemmater.2c00385
$LnMGa_3S_6O$ (Ln = La, Pr, and Nd; M = Ca and Sr)	Direct (3.21-3.27 eV)	-	Ln^{3+} M^{2+} Ga^{3+}	$(Ln/M)S_7O$ GaS_3O GaS_4	Yes	($P\bar{4}2_1m$)	-	DOI : 10.1021/acsami.2c11199
$Sr_2CoGe_2OS_6$	Indirect (2.77 eV)	-	Co^{2+}	CoS_4 Ge_2OS_6	?	($P\bar{4}2_1m$)	-	DOI: 10.1021/acs.inorgchem.2c03283
$Ba_5Ga_2SiO_4S_6$	Direct (4.03 eV)	-	Ba^{2+} Ga^{3+}	$[Ga_2SiO_4S_6]$ clusters made of corner-sharing $[SiO_4]$ and $[GaOS_3]$ tetrahedra	?	(*Cc*)	-	DOI: 10.1021/acs.inorgchem.2c03577
$Ba_2SnSSi_2O_7$ Fresnoite - type	- (> 4.00 eV)	-	Ba^{2+} Sn^{4+}	SnO_4S	?	(*P4bm*)	-	DOI: 10.1039/d2qm00621a

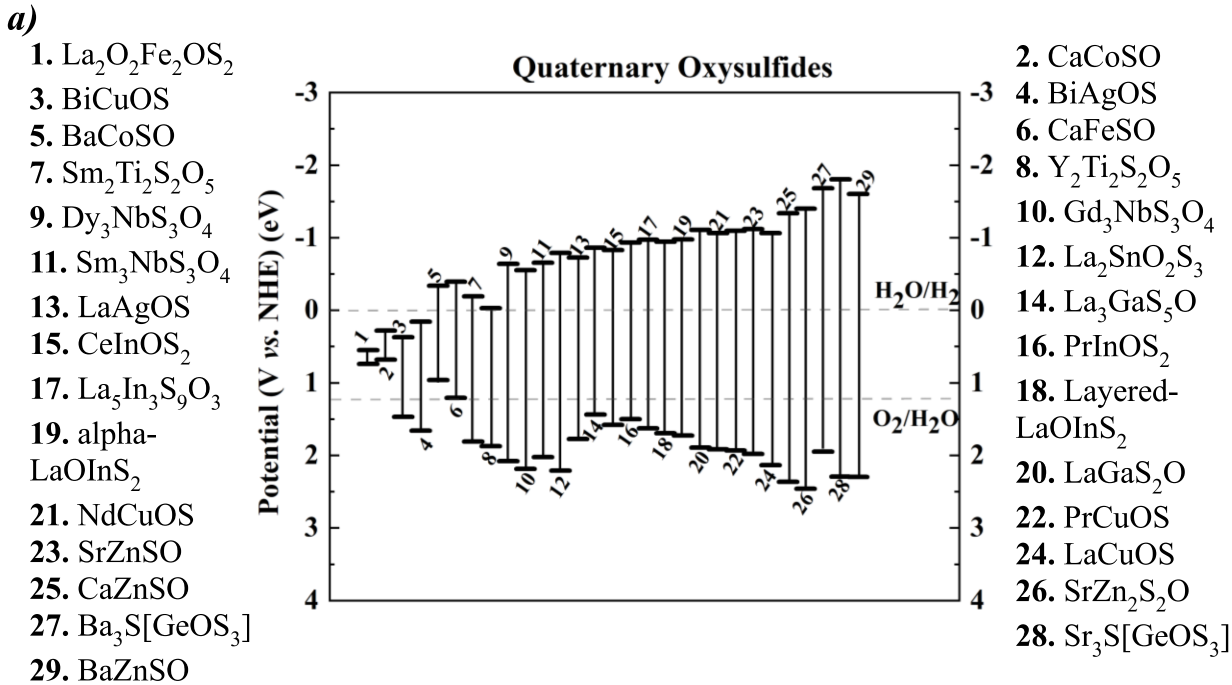
$[Sr_3VO_4][GaS_3]$ 0D	Direct (2.23 eV-DFT)	-	Ga^{3+} V^{5+}	$[Ga_2Q_6]^{6-}$ dimers, $[VO_4]^{5+}$ tetrahedra		No ($P2_1/c$)	-	DOI: 10.1039/d2qi01160c
$[Sr_3VO_4][InS_3]$ 1D	Indirect (2.13 eV-DFT)	-	In^{3+} V^{5+}	$_\infty[InQ_3]^{3-}$ chains, $[VO_4]^{5+}$ tetrahedra		Yes ($Pmc2_1$)	-	DOI: 10.1039/d2qi01160c
$Ae_3S[GeOS_3]$(Ae=Ba, Sr) Antiperovskite structure	Direct (3.63 eV Ba) (4.10 eV Sr)	-		$[GeOS_3]$ $[SAe_6]$	Yes	Yes ($Pca2_1$)	-	DOI: 10.1002/advs.202204755
$La_3NbS_2O_5$	- (2.13-2.17 eV-sulfurization synthesis) (2.26 eV- solid-state synthesis)	-	La^{3+} Nb^{5+}		Yes	No ($I4/mmm$)	H_2 (measured)	DOI: 10.1016/S1003-6326(13)62780-6
$Sn_2Nb_2O_{7-x}S_x$	2.1 eV	n-type	Sn^{4+} Nb^{5+}	Sn_2O chains Nb_2O_6 octahedra		No ($Fd3m$)	H_2 & O_2 (measured)	DOI: 10.1016/j.jphotochem.2023.114895
$ZnO_{0.6}S_{0.4}$	Direct 2.03 eV	-	Zn^{2+}					DOI: 10.1016/j.chemosphere.2017.05.112
$Zn(Zn,Ni,In)_2(O,S)_{4-x}$	Direct 2.81 eV (0 mol% Ni) 2.91 eV (5 mol% Ni) 2.90 eV (10 mol% Ni) 2.90 eV (20 mol% Ni)	-	Zn^{2+} Ni^{2+}				H_2 (measured)	DOI: 10.1021/acsaem.1c03200
$(Bi, Ce)_2(O, S)_{3-x}$	Direct 1.73 eV (0.0 N_2H_4) 1.69 eV (0.2 N_2H_4) 1.66 eV (0.4 N_2H_4) 1.59 eV (0.6 N_2H_4)	n-type	Ce^{3+}/Ce^{4+}		-	No ($Pbnm$)	H_2 (measured)	DOI : 10.1039/d2ta09780j

Table S2. Comparison of the different structural and physical properties of Oxyselenide materials

Compounds	**Bandgap magnitude & Nature**	**Semiconduction type**	**Cation choice**	**Coordination environment & Anion ratio**	**Polar units ?**	**Polar Structure?**	**H_2 or O_2 production ?**	**Reference**
LaCuOSe	Direct (2.8 eV)	p-type	Cu^{2+}	$CuSe_4$	No	*P4/nmm*	-	DOI : 10.1021/acsaem.2c00590
LaAgOSe	Direct (2.50 eV)	p-type	Ag^{+}	$AgSe_4$	No	*P4/nmm*	-	DOI : 10.1002/smtd.202201368
BiCuOSe	Indirect (0.8 eV)	p-type	Cu^{2+}	$CuSe_4$	No	*P4/nmm*	Degradation of organic contaminants in solar light	DOI : 10.3390/ma8031043 DOI : 10.3390/ma11030447
CaFeSeO	Indirect (1.8 eV)	n-type	Fe^{2+}	$FeSe_2O_2$	Yes	($Cmc2_1$ *Pmcn*)	-	DOI : 10.1021/acs.chemmater.5b02164 DOI : 10.1021/acs.inorgchem.6b01951
$La_2CdO_2Se_2$	Direct (3.3 eV)	n-type	La^{3+} Cd^{2+}	La_4O $CdSe_4$	No	$P4_2/nmc$	-	DOI :10.1021/jp048722q
$La_2O_2Fe_2OSe_2$	Direct (0.17 eV)	-	Fe^{2+}	FeO_2Se_4	No	No (*I4/mmm*)	-	DOI: 10.1103/PhysRevLett.104.216405 DOI: 10.1103/PhysRevB.86.125122
$Sr_6Cd_2Sb_6Se_{10}O_6$	Indirect (1.55 eV)	p-type	Sb^{3+}	$SbSe_5$ $SbOSe_4$ SbO_3	Yes	Yes (*Cm*)	-	DOI : 10.1002/anie.202206816
$Sr_2Sb_2Se_3O_2$	Direct (1.7 eV)	-	Sb^{3+}	SbOSe4	Yes	$P2_1/mc$	-	DOI : 10.1021/acs.chemmater.5b04536
$[Sr_3VO_4][GaSe_3]$ 0D	Indirect (2.51 eV)	-	Ga^{3+} V^{5+}	$[Ga_2Q_6]^{6-}$ dimers, $[VO_4]^{5+}$ tetrahedra		No ($P2_1/c$)	-	DOI : 10.1039/d2qi01160c
$[Sr_3VO_4][InSe_3]$ 1D	Indirect (2.62 eV)	-	In^{3+} V^{5+}	$_\infty[InQ_3]^{3-}$ chains, $[VO_4]^{5+}$ tetrahedra		Yes ($Pmc2_1$)	-	DOI : 10.1039/d2qi01160c
$Ae_3Se[GeOSe_3]$(Ae=Ba, Sr) Antiperovskite structure	Direct (3.52 eV Ba) (3.50 eV Sr)	-		$[GeOSe_3]$ $[SeAe_6]$	Yes	Yes ($Pca2_1$)	-	DOI: 10.1002/advs.202204755

Table S3. Comparison of the different structural and physical properties of Oxytelluride materials

Compounds	**Bandgap magnitude & Nature**	**Semiconduction type**	**Cation choice**	**Coordination environment & Anion ratio**	**Polar units ?**	**Polar Structure?**	**H_2 or O_2 production ?**	**Reference**
BiCuOTe	Indirect (0.5 eV)	p-type	Cu^{2+}	$CuTe_4$	No	*P4/nmm*	-	DOI : 10.1016/j.solidstatesciences.2016.05.012
$Ba_3Yb_2O_5Te$	Direct (2.2 eV)	-	Yb^{3+}	YbO_5	Yes	*P4/mmm*	-	DOI : 10.1016/j.jssc.2013.04.030
La_2O_2Te	Indirect (2.7 eV)	-	La^{3+}	La_4O	Yes	No (*I4/mmm*)	-	DOI : 10.1021/acs.inorgchem.2c02287
Pr_2O_2Te	Indirect (2.6 eV)	-	Pr^{3+}	Pr_4O	Yes	No (*I4/mmm*)	-	DOI : 10.1021/acs.inorgchem.2c02287
Ce_2O_2Te	Indirect (2.1 eV)	-	Ce^{3+}	Ce_4O	Yes	No (*I4/mmm*)	-	DOI : 10.1021/acs.inorgchem.2c02287
LaCuOTe	Direct (2.4 eV)	p-type	Cu^{2+}	$CuTe_4$	No	*P4/nmm*	-	DOI : 10.1021/acsaem.2c00590



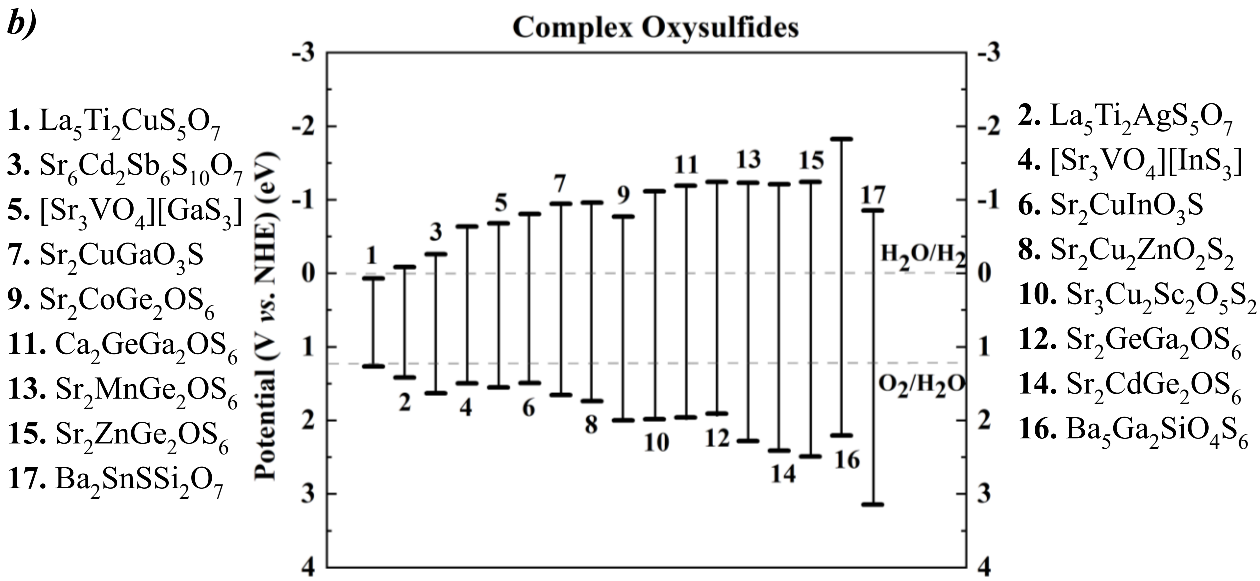


Figure S1 : Estimated band edge positions using the empirical method of (a) Quaternary Oxysulfides and (b) Complex Oxysulfides.

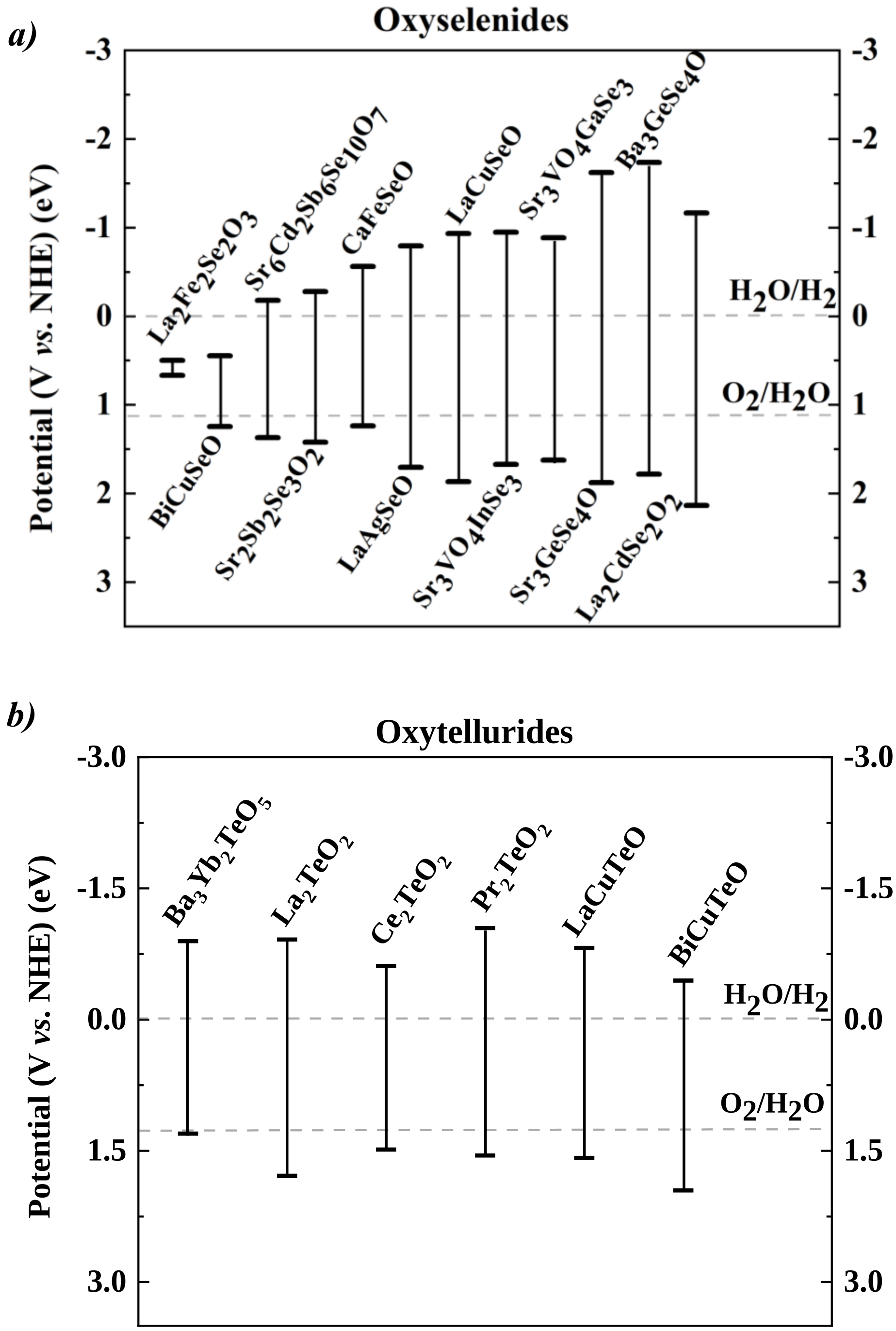


Figure S2 : Estimated band edge positions using the empirical method of (a) Oxyselenides and (b) Oxytellurides.