Supporting Information

Thermodynamic Oxidation and Reduction Potentials of Photocatalytic Semiconductors in Aqueous Solution

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Table S1. The band edge positions (VBM and CBM) of semiconductors listed in Figure 3, and the possible reduction and oxidation reactions and the corresponding potentials from which Φ^{re} and Φ^{ox} are determined. Except those stated in the Notes column, the band edge positions of the semiconductors are collected from Ref. [11, 23, 24] and the Gibbs free energy data of the reactants and products used for calculating the potentials are collected from Ref. [20, 21]. When the reactants and products have different phases (crystal, solution or gas), the phase with the lowest Gibbs free energy under 298.15 K and 1 Bar is considered in the calculation. The band edge positions and potentials are relative to NHE in V. The (*) sign in the potentials column shows the potentials are independent on the pH value, the (**) sign shows the potentials depend on the pH value but do not follow the Nernstian relation, and all other potentials with no signs follow the Nernstian relation. VBO means the valence band offset.

	VBM	CBM	Reaction	Potential	Notes
Si	0.42	-0.76	**$Si+2H_2->SiH_4$**	**-0.15**	
			$Si+2H_2O->SiO_2+2H_2$	**-0.99**	
Ge	-0.16	-0.90	**$Ge+2H_2->GeH_4$**	**-0.29**	
			$Ge+2H_2O->GeO_2+2H_2$	**-0.12**	
SiC	1.40	-1.00	**$SiC+2H_2->CH_4+Si$**	**-0.03**	
			$SiC+2H_2->SiH_4+C$	-0.31	
			$SiC+4H_2->SiH_4+CH_4$	-0.09	
			$SiC+4H_2O->SiO_2+CO_2+4H_2$	**-0.31**	
ZnS	2.10	-1.72	**$ZnS+H_2->Zn+H_2S$**	**-0.87**	
			$ZnS+H_2O->ZnO+S+H_2$	0.61	
			$ZnS+5H_2O->ZnO+2H^++(SO_4)^{2-}+4H_2$	0.42 (**)	
			$ZnS+4H_2O->Zn^{2+}+(SO_4)^{2-}+4H_2$	**0.33**	
CdS	1.79	-0.72	**$CdS+H_2->Cd+H_2S$**	**-0.64**	
			$CdS+5H_2O->CdO+2H^++(SO_4)^{2-}+4H_2$	0.48 (**)	
			$CdS+4H_2O->CdSO_4+4H_2$	**0.37**	
ZnSe	1.53	-1.31	**$ZnSe+H_2->Zn+H_2Se$**	**-0.93**	
			$ZnSe+H_2O->ZnO+Se+H_2$	**0.41**	
			$ZnSe+5H_2O->ZnO+H_2SeO_4+4H_2$	0.87	
CdSe	1.32	-0.59	**$CdSe+H_2->Cd+H_2Se$**	**-0.69**	The Gibbs free energy of CdSe is approximated by its calculated formation energy (-1.5 eV/f.u.), without the entropy contribution.
			$CdSe+H_2O->CdO+Se+H_2$	**0.65**	
CdTe	0.68	-0.90	**$CdTe+H_2->Cd+H_2Te$**	**-0.92**	
			$CdTe+H_2O->CdO+Te+H_2$	**0.52**	
$CuGaS_2$	1.05	-1.38	$2CuGaS_2+3H_2->Cu_2S+2Ga+3H_2S$	-0.99	The band alignment is determined

			$2CuGaS_2+H_2$->$2Cu+Ga_2S_3+H_2S$ **$CuGaS_2+2H_2$->$Cu+Ga+2H_2S$**	-1.36 **-0.81**	based on the calculated VBO($ZnS/CuGaS_2$)=1.15 eV and the experimental band gap 2.43 eV. The Gibbs free energy of $CuGaS_2$ is approximated by its formation energy (-4.36 eV/f.u., cited from Ref. [S1]), without the entropy contribution.
			$2CuGaS_2+4H_2O$->$Cu_2O+Ga_2O_3+4S+4H_2$ $2CuGaS_2+5H_2O$->$2CuO+Ga_2O_3+4S+5H_2$ **$2CuGaS_2+20H_2O$->$Cu_2O+Ga_2O_3+8H^+$+$4(SO_4)^{2-}$+$16H_2$**	0.73 0.71 **0.45 (**)**	
Cu_2ZnGeS_4	1.07	-1.21	$Cu_2ZnGeS_4+4H_2$->$2Cu+Zn+Ge+4H_2S$ **$Cu_2ZnGeS_4+H_2$->$Cu_2S+ZnS+GeS+H_2S$**	-0.40 **-0.25**	The band alignment is determined based on the calculated VBO($CuGaS_2/Cu_2ZnGeS_4$)=-0.02 eV, and the band gap (2.28 eV) of Cu_2ZnGeS_4 cited from Ref. [S2]. The Gibbs free energy of Cu_2ZnGeS_4 is approximated by its calculated formation energy (-5.39 eV/f.u.), without the entropy contribution.
			$Cu_2ZnGeS_4+20H_2O$->$Cu_2O+ZnO+GeO_2+8H^+$ +$4(SO_4)^{2-}$+$16H_2$ $Cu_2ZnGeS_4+21H_2O$->$2CuO+ZnO+GeO_2+8H^+$+ $4(SO_4)^{2-}+17H_2$	**0.39 (**)** 0.41 (**)	
Cu_2ZnSnS_4	0.78	-0.72	$Cu_2ZnSnS_4+4H_2$->$2Cu+Zn+Sn+4H_2S$ **$Cu_2ZnSnS_4+H_2$->$Cu_2S+ZnS+SnS+H_2S$**	-0.38 **-0.06**	The band alignment is determined based on the calculated VBO($CuGaS_2/Cu_2ZnSnS_4$)=0.34 eV, and the experimental band gap 1.5 eV. The Gibbs free energy of Cu_2ZnSnS_4 is approximated by its calculated formation energy (-5.35 eV/f.u.), without the entropy contribution.
			$Cu_2ZnSnS_4+20H_2O$->$Cu_2O+ZnO+SnO_2+8H^+$ +$4(SO_4)^{2-}$+$16H_2$	**0.39 (**)**	
GaN	2.31	-1.21	**$2GaN+3H_2$->$2Ga+2NH_3$**	**-0.28**	The formation energy (-129.289 kJ/mol) and entropy (34.120 J/mol/K) of GaN are cited from Ref. [S3].
			$2GaN+3H_2O$->$Ga_2O_3+N_2+3H_2$	**-0.15**	
			$2GaN+9H_2O$->$Ga_2O_3+2H^+$+$2(NO_3)^-$+$8H_2$	0.76 (**)	
AlP	1.84	-0.70	**$2AlP+3H_2$->$2Al+2PH_3$**	**-0.55**	The Gibbs free energy of AlP is approximated by its formation energy, without the entropy contribution.
			$2AlP+3H_2O$->$Al_2O_3+2P+3H_2$	**-1.00**	
			$2AlP+11H_2O$->$Al_2O_3+2H_3PO_4+8H_2$	-0.60	
GaP	1.09	-1.25	**$2GaP+3H_2$->$2Ga+2PH_3$**	**-0.27**	The Gibbs free energy of GaP is approximated by its formation energy, without the entropy contribution.
			$2GaP+3H_2O$->$Ga_2O_3+2P+3H_2$	**-0.28**	
$ZnGeP_2$	1.15	-1.05	**$2ZnGeP_2+3H_2$->$2Zn+2GeP+2PH_3$**	**-0.14**	The band alignment is determined based on the VBO($GaP/ZnGeP_2$)=-0.06 eV cited from Ref. [S4]. The Gibbs free energy of $ZnGeP_2$ is approximated by its calculated formation energy (-1.24 eV/f.u.), without the entropy contribution.
			$ZnGeP_2+3H_2$->$Zn+Ge+2PH_3$	-0.49	
			$ZnGeP_2+3H_2O$->$ZnO+GeO_2+2P+3H_2$	**0.11**	
InP	0.72	-0.70	**$2InP+3H_2$->$2In+2PH_3$**	**-0.31**	
			$2InP+3H_2O$->$In_2O_3+2P+3H_2$	**0.06**	
AlAs	1.14	-1.11	**$2AlAs+3H_2$->$2Al+2AsH_3$**	**-0.60**	The Gibbs free energy of AlAs is approximated by its formation energy (-1.22 eV/f.u.), without the
			$2AlAs+3H_2O$->$Al_2O_3+2As+3H_2$	**-1.16**	

					entropy contribution.
GaAs	0.54	-0.98	**$2GaAs+3H_2$->$2Ga+2AsH_3$**	**-0.47**	
			$2GaAs+3H_2O$->$Ga_2O_3+2As+3H_2$	**-0.26**	
Ta_2O_5	3.48	-0.42	**$Ta_2O_5+5H_2$->$2Ta+5H_2O$**	**-0.75**	
			$2Ta_2O_5+20H^+$+$20Cl^-$->$4TaCl_5+10H_2+5O_2$	**1.79 (*)**	
Ta_3N_5	1.57	-0.53	**$2Ta_3N_5+15H_2$->$6Ta+10NH_3$**	-0.42	The Gibbs free energy of Ta_3N_5 is approximated by its calculated formation energy (-9.03 eV/f.u.), without the entropy contribution.
			$2Ta_3N_5+15H_2O$->$3Ta_2O_5+5N_2+15H_2$	**-0.27**	
			$2Ta_3N_5+45H_2O$->$3Ta_2O_5+10H^+$+$10(NO_3)^-$ +$40H_2$	0.71 (**)	
TaON	2.15	-0.35	$2TaON+5H_2$->$2Ta+2H_2O+2NH_3$	-0.58	The Gibbs free energy of TaON is approximated by its calculated formation energy (-6.27 eV/f.u.), without the entropy contribution.
			$10TaON+15H_2$->$2Ta_2O_5+6Ta+10NH_3$	**-0.47**	
			$5TaON+5H_2$->$Ta_3N_5+2Ta+5H_2O$	-0.81	
			$2TaON+3H_2O$->$Ta_2O_5+N_2+3H_2$	**-0.23**	
			$2TaON+9H_2O$->$Ta_2O_5+2H^+$+$2(NO_3)^-$+$8H_2$	0.73 (**)	
TiO_2	3.38	0.15	TiO_2+2H_2->$Ti+2H_2O$	-1.07	
			TiO_2+H_2->$TiO+H_2O$	**-0.81**	
			TiO_2+4H^++$4Cl^-$->$TiCl_4+2H_2+O_2$	**1.75 (*)**	
$BaTiO_3$	3.81	0.43	$BaTiO_3+H_2$->$Ba+TiO_2+H_2O$	-2.31	
			$BaTiO_3+H_2$->$BaO+TiO+H_2O$	-1.66	
			$BaTiO_3+2H_2$->$BaO+Ti+2H_2O$	-1.50	
			$BaTiO_3+2H_2$->$Ba+TiO+2H_2O$	-1.56	
			$BaTiO_3+3H_2$->$Ba+Ti+3H_2O$	**-1.49**	
			$2BaTiO_3+12H^+$+$12Cl^-$->$2BaCl_2+2TiCl_4+6H_2+3O_2$	**1.41 (*)**	
$FeTiO_3$	3.33	0.43	**$FeTiO_3+H_2$->$Fe+TiO_2+H_2O$**	**-0.27**	
			$FeTiO_3+H_2$->$FeO+TiO+H_2O$	-1.01	
			$FeTiO_3+2H_2$->$Fe+TiO+2H_2O$	-0.54	
			$2FeTiO_3+12H^+$+$8Cl^-$->$2Fe^{2+}$+$2TiCl_4+6H_2+3O_2$	1.60 (*)	
			$2FeTiO_3+14H^+$+$8Cl^-$->$2Fe^{3+}$+$2TiCl_4+7H_2+3O_2$	1.52 (*)	
			$2FeTiO_3+6H^+$->$2Fe^{3+}+2TiO_2+H_2+2H_2O$	**1.17 (*)**	
WO_3	3.22	0.53	WO_3+H_2->WO_2+H_2O	0.04	
			WO_3+3H_2->$W+3H_2O$	**-0.09**	
			$2WO_3+12H^+$+$12Cl^-$->$2WCl_6+6H_2+3O_2$	**1.89 (*)**	
$CuWO_4$	2.65	0.40	**$2CuWO_4+H_2$->$Cu_2O+2WO_3+H_2O$**	**-0.08**	The band alignment is cited from Ref. [S5]. The Gibbs free energy of $CuWO_4$ is approximated by its formation energy, without the entropy contribution.
			$CuWO_4+H_2$->$Cu+WO_3+H_2O$	0.20	
			$CuWO_4+2H_2$->$Cu+WO_2+2H_2O$	0.12	
			$CuWO_4+8H^+$+$8Cl^-$->$CuCl_2+WCl_6+4H_2+2O_2$	**1.78 (*)**	
Cu_2O	1.30	-0.70	**Cu_2O+H_2->$2Cu+H_2O$**	**0.47**	The band alignment is cited from Ref. [S6].
			Cu_2O+H_2O>$2CuO+H_2$	0.64	
			Cu_2O+4H^++$4Cl^-$>$2CuCl_2+H_2+H_2O$	**0.43 (*)**	
			Cu_2O+3H_2O>$2Cu(OH)_2+H_2$	0.58	
PbO	3.23	0.46	**$PbO+H_2$->$Pb+H_2O$**	**0.25**	

			$PbO+H_2O->PbO_2+H_2$ **$2PbO+4H^++4Cl^-->2PbCl_2+2H_2+O_2$**	1.08 **0.71 (*)**	
ZnO	3.58	0.17	**$ZnO+H_2->Zn+H_2O$**	**-0.43**	
			$2ZnO+4H^+->2Zn^{2+}+2H_2+O_2$	**0.90 (*)**	
SnO_2	4.07	0.51	**$SnO_2+H_2->SnO+H_2O$**	**-0.14**	
			$SnO_2+4H^++4Cl^-->SnCl_4+2H_2+O_2$	**1.56 (*)**	
Fe_2O_3	2.90	0.58	**$Fe_2O_3+H_2->2FeO+H_2O$** $Fe_2O_3+3H_2->2Fe+3H_2O$	**-0.01** -0.05	
			$2Fe_2O_3+12H^+->4Fe^{3+}+6H_2+3O_2$	**1.27 (*)**	
$BiFeO_3$	2.63	0.44	$2BiFeO_3+3H_2->2Bi+Fe_2O_3+3H_2O$ **$2BiFeO_3+H_2->Bi_2O_3+2FeO+H_2O$** $BiFeO_3+2H_2->Bi+FeO+2H_2O$	0.26 **-0.36** 0.19	The band alignment is cited from Ref. [S7]. The Gibbs free energy of $BiFeO_3$ is approximated by its formation energy (-768.4 kJ/mol) cited from Ref. [S8], without the entropy contribution.
			$2BiFeO_3+12H^++12Cl^-->2BiCl_3+2FeCl_3+6H_2+3O_2$	**1.36 (*)**	
$BiVO_4$	2.10	-0.30	$2BiVO_4+3H_2->2Bi+V_2O_5+3H_2O$ $2BiVO_4+H_2->Bi_2O_3+2VO_2+H_2O$ **$2BiVO_4+5H_2->Bi_2O_3+2V+5H_2O$** $BiVO_4+4H_2->Bi+V+4H_2O$	0.26 0.42 **-0.31** -0.05	The band alignment is cited from Ref. [S9]. The Gibbs free energy of $BiVO_4$ is approximated by its calculated formation energy (-11.78 eV/f.u.), without the entropy contribution.
			$4BiVO_4+12H^++12Cl^-->4BiCl_3+2V_2O_5+6H_2+3O_2$ $2BiVO_4+12H^++12Cl^-->2BiCl_3+2VOCl_3+6H_2+3O_2$	**1.24 (*)** 1.37 (*)	
Co_3O_4	1.02	-1.16	**$Co_3O_4+H_2->3CoO+H_2O$** $Co_3O_4+4H_2->3Co+4H_2O$	**0.55** 0.23	The band alignment is cited from Ref. [S10].
			$2Co_3O_4+18H+->6Co^{3+}+8H_2O+H_2$ $Co_3O_4+9HF->3CoF_3+4H_2O+0.5H_2$	**2.33 (*)** 3.51	

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