Supplementary Information:

Understanding the advantage of hexagonal WO_3 as an efficient photoanode for solar water splitting: A first-principles perspective

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TABLE S1. Surface free energies of various considered h-WO_3 surface structures with diverse orientations and terminations at corresponding stoichiometric ratio $R_{W/O}$, which is the ratio of the number of W atoms to that of oxygen in the surface structure. A stoichiometric surface will have $R_{W/O} = 2$. Surface energies at both the oxygen-lean (γ_O-lean) and oxygen-rich (γ_O-rich) limits are reported in eV/Å^2. Each surface unit cell (0001), (10$\bar{1}$0), and, (11$\bar{2}$0) areas correspond to 48.191, 28.607, and, 49.549 in Å^2.

Surfaces		$R_{W/O}$	γ_O-lean		γ_O-rich	
			relax	unrelax	relax	unrelax
(0001)	WO_6	0.316	0.175	0.201	0.078	0.105
	WO_5	0.353	0.011	0.074	0.108	0.170
(10$\bar{1}$0)	W_aO_6	0.304	0.205	0.219	0.097	0.111
	W_aO_5	0.333	0.041	0.106	0.041	0.106
	W_aO_4	0.368	0.048	0.104	0.157	0.213
	W_bO_6	0.314	0.198	0.228	0.089	0.120
	W_bO_{5a}	0.355	0.014	0.089	0.123	0.197
	W_bO_{5b}	0.333	0.081	0.229	0.081	0.229
	W_bO_4	0.379	0.085	0.181	0.302	0.398
(11$\bar{2}$0)	W_aO_6	0.311	0.231	0.259	0.105	0.134
	W_aO_5	0.322	0.123	0.190	0.061	0.127
	W_aO_4	0.333	0.075	0.168	0.075	0.168
	W_bO_6	0.309	0.232	0.253	0.106	0.128
	W_bO_5	0.333	0.044	0.126	0.044	0.126
	W_bO_4	0.362	0.052	0.117	0.177	0.242

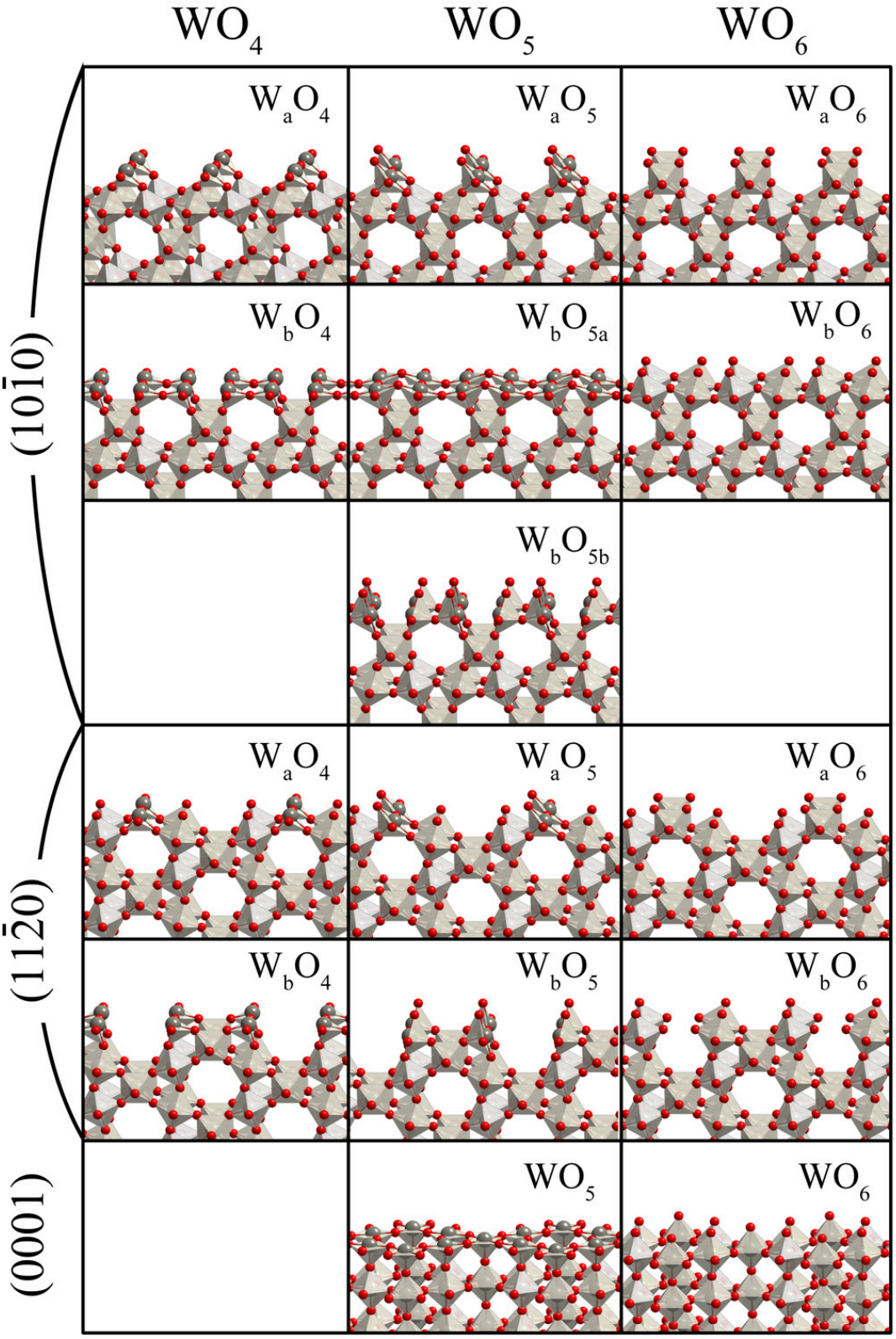


FIG. S1. (Color online) Surface structures of h-WO_3 before structural relaxation.

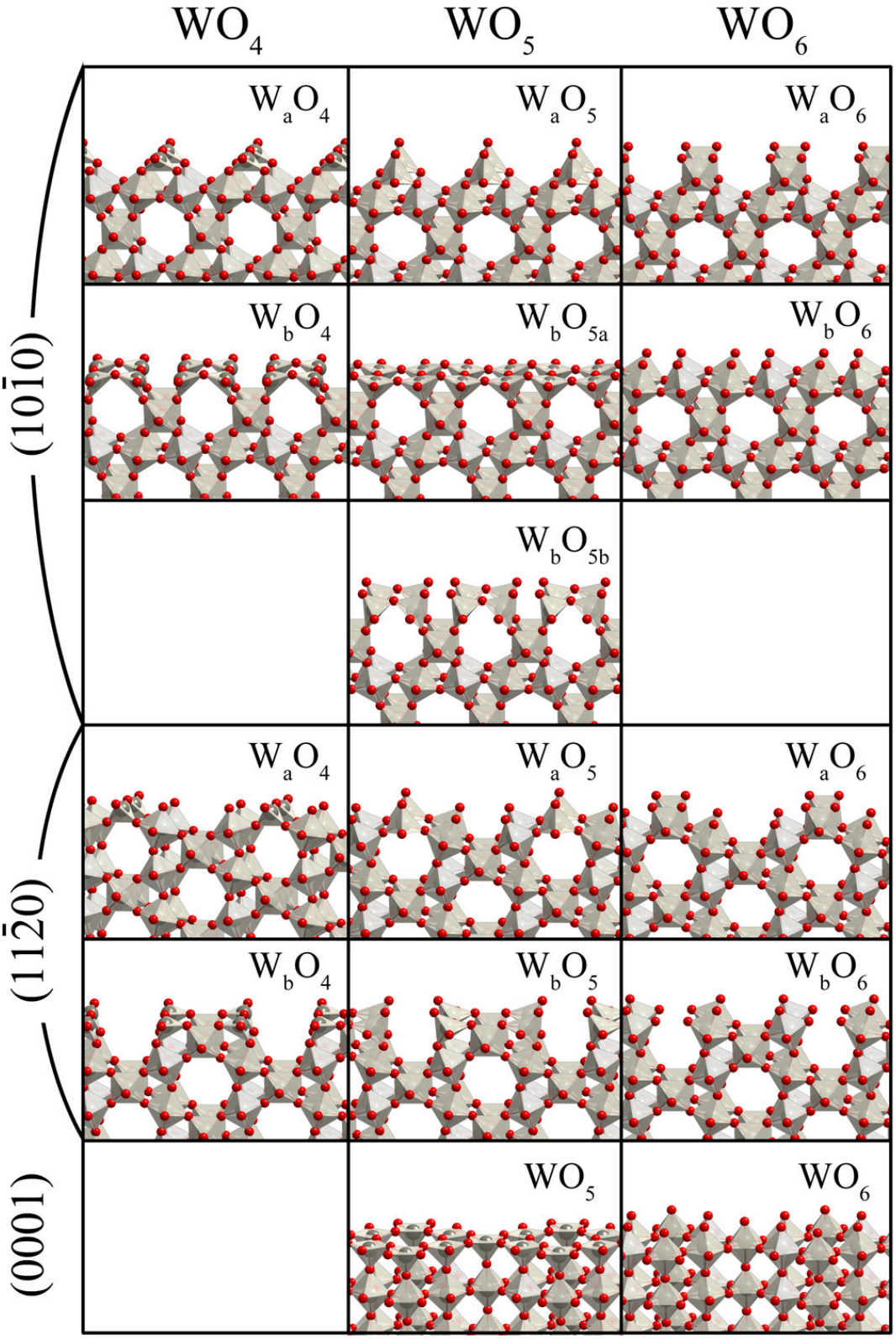


FIG. S2. (Color online) Surface structures of h-WO_3 after structural relaxation.

TABLE S2. PBE results of surface free energies in various considered h-WO_3 surface structures with diverse orientations and terminations at corresponding stoichiometric ratio $R_{W/O}$, which is the ratio of the number of W atoms to that of oxygen in the surface structure. A stoichiometric surface will have $R_{W/O} = 2$. Surface energies at both the oxygen-lean (γ_O-lean) and oxygen-rich (γ_O-rich) limits are reported in eV/Å^2. Each surface unit cell (0001), (10$\bar{1}$0), and, (11$\bar{2}$0) areas correspond to 48.287, 28.669, and, 49.656 in Å^2.

Surfaces		$R_{W/O}$	γ_O-lean		γ_O-rich	
			relax	unrelax	relax	unrelax
(0001)	WO_6	0.316	0.159	0.188	0.072	0.100
	WO_5	0.353	0.003	0.064	0.090	0.151
(10$\bar{1}$0)	W_aO_6	0.304	0.191	0.204	0.093	0.106
	W_aO_5	0.333	0.030	0.094	0.030	0.094
	W_aO_4	0.368	0.039	0.094	0.137	0.192
	W_bO_6	0.314	0.182	0.215	0.084	0.117
	W_bO_{5a}	0.355	0.001	0.078	0.099	0.176
	W_bO_{5b}	0.333	0.064	0.214	0.064	0.214
	W_bO_4	0.379	0.073	0.176	0.269	0.372
(11$\bar{2}$0)	W_aO_6	0.311	0.214	0.244	0.100	0.131
	W_aO_5	0.322	0.107	0.177	0.050	0.120
	W_aO_4	0.333	0.062	0.150	0.062	0.150
	W_bO_6	0.309	0.215	0.237	0.102	0.124
	W_bO_5	0.333	0.032	0.115	0.032	0.115
	W_bO_4	0.362	0.041	0.108	0.154	0.221

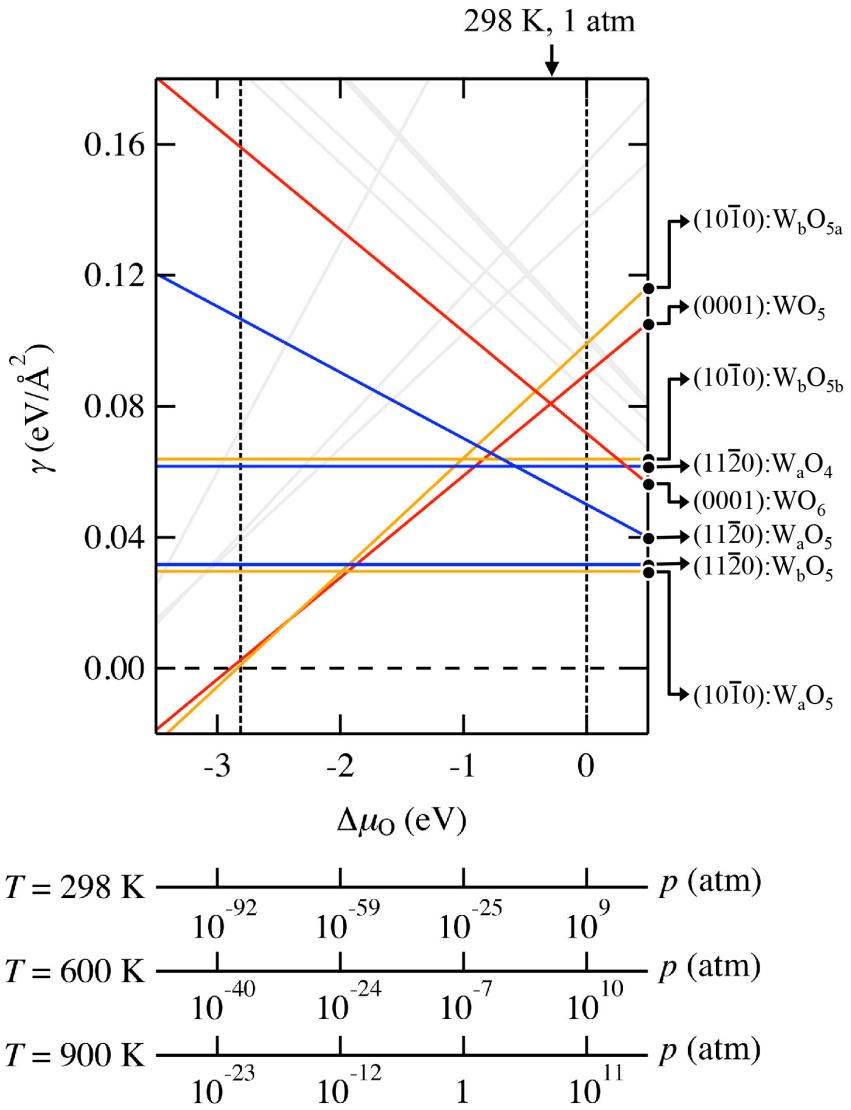
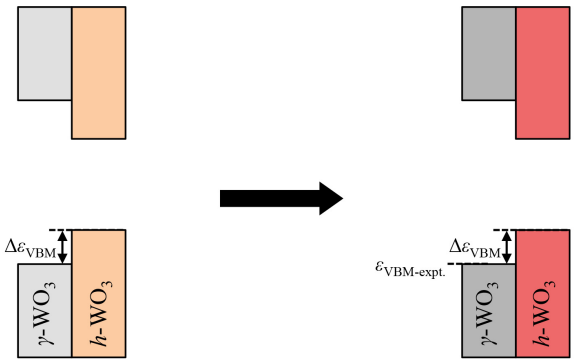


FIG. S3. (Color online) PBE results of calculated surface free energy (as a function of the change in the chemical potential of oxygen, $\Delta\mu_O$) of most lowest low-index surfaces of h-WO_3, with the corresponding temperature and pressure are shown in lower panel. Relatively stable structures and less stable structures are depicted in color lines and in grey lines, respectively.

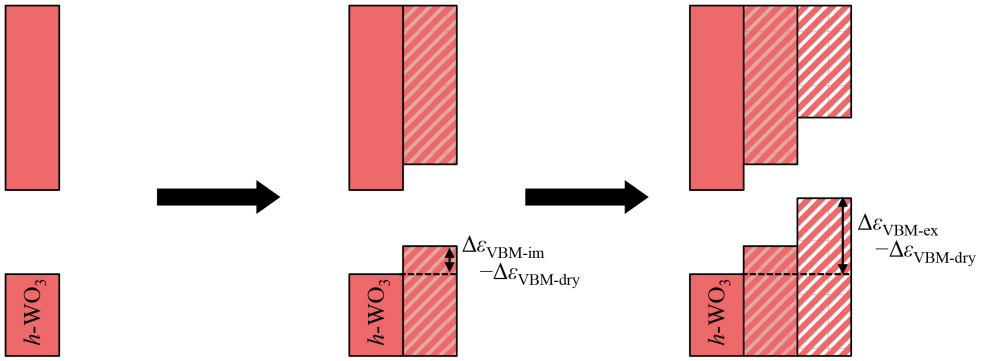
(1) Experimental correction



(a) Theoretically calculated band offsets ($\Delta\varepsilon_{\mathrm{VBM}}$) of bulk γ-WO_3 and h-WO_3

(b) Experimentally measured VBM level of γ-WO_3 ($\varepsilon_{\mathrm{VBM\text{-}expt.}}$) and applied $\Delta\varepsilon_{\mathrm{VBM}}$ to estimate the VBM of h-WO_3

(2) Theoretical correction



(a) Theoretically calculated h-WO_3 surface band edge position in the vacuum environment

(b) Theoretically calculated h-WO_3 surface band edge position with the implicit solvation model

(c) Apply theoretical reference of VBM shift in W-O system by using explicit solvation model

FIG. S4. (Color online) Methodologies of the corrections used in the manuscript for band edge positions of h-WO_3.