Supporting Information: Theoretical Investigation of Ta_2O_5, TaON and Ta_3N_5: Electronic Band Structures and Absolute Band Edges

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1. Details of phonon calculations

The longitudinal optical (LO) phonon, *i.e.* the vibrational mode which leads to the most significant polarization and electron-phonon coupling, is calculated in the following procedure:

(a) Calculate the phonon frequency at Γ point (in Frölich model, only Γ point frequency is needed), by density functional perturbation theory (DFPT), which has been implemented in VASP package. [1][2][3]

(b) Do a non-analytical term correction (NAC) to the frequency calculated in (a). One should notice that the frequency directly calculated by DFPT does not include the contribution of LO-TO splitting, which, however, is crucial for accurate determination of the frequency in ionic crystal. [4] Therefore we have taken this effect into account by the formula,

$$D_{\alpha\beta}(jj',\mathbf{q}\to\mathbf{0}) = D_{\alpha\beta}(jj',\mathbf{q}=\mathbf{0}) + \frac{1}{\sqrt{m_j m_{j'}}}\frac{4\pi}{\Omega_0}\frac{[\sum_{\gamma} q_\gamma Z^*_{j,\gamma\alpha}][\sum_{\gamma'} q_{\gamma'} Z^*_{j',\gamma'\beta}]}{\sum_{\alpha\beta} q_\alpha \epsilon^{\infty}_{\alpha\beta} q_\beta},$$

where Born effective charge Z^* and high-frequency dielectric tensor $\epsilon^{\infty}_{\alpha\beta}$ have been calculated in (a).

(c) Choose the largest phonon frequency as ω_{LO}, since it gives the largest polarization.

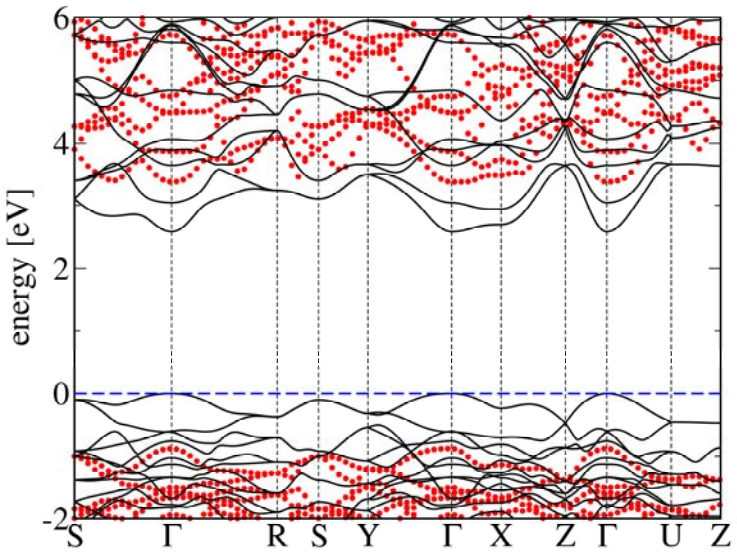

Figure S1 Band structures of β'-Ta_2O_5. The black lines denote the results from PBEsol and the red dots denote the results from G_0W_0@PBEsol. The VBM from PBEsol is taken as the Fermi level. For comparison, the Brillouin path is chosen as same as the case in β-Ta_2O_5.

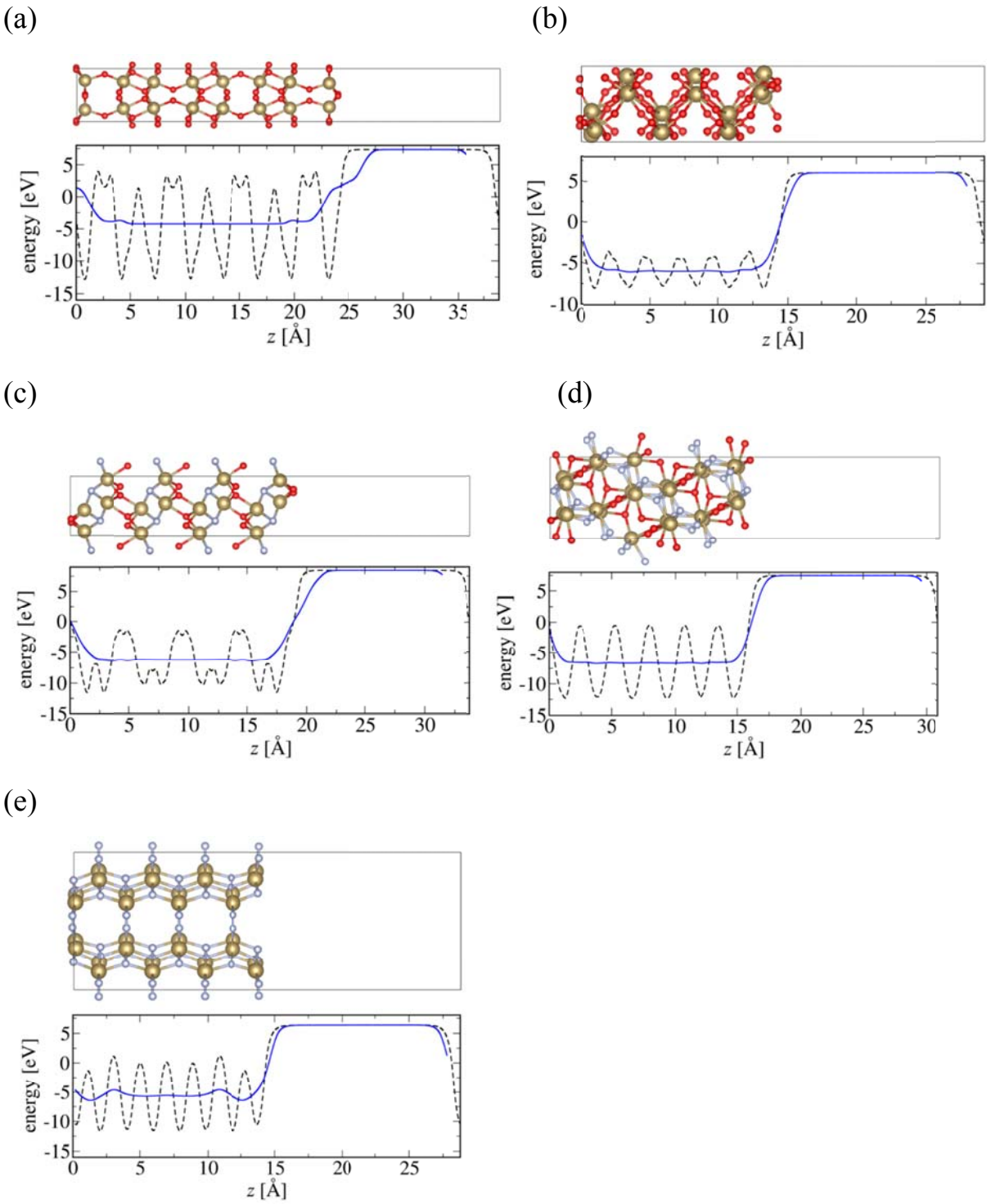

Figure S2 Surface structures and the corresponding macroscopic electrostatic potentials for: a) ε-Ta_2O_5-(100); b) ε-Ta_2O_5-(010)-O, c) TaON-(100)-O, d) TaON-(111)-O, e) Ta_3N_5-(100). Black dashed line indicates the electrostatic potential averaged over the *xy*-plane of the slab and blue line indicates the further average over the bulk period along *z* direction.

Table S1 Convergence test of surface energy with respect to slab thickness for a few energetically competitive surfaces. The units of thickness and surface energy are Å and J/m^2 respectively.

Species	Thickness1	Energy1	Thickness2	Energy2
ε-Ta_2O_5-(010)-O	14.1	1.134	19.0	1.135
β-TaON-(100)-O	18.9	1.438	23.7	1.438
β-TaON-(111)-O	16.0	1.532	21.4	1.534
β-Ta_3N_5-(100)	13.6	1.410	15.6	1.412

References

[1] Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-energy Calculations Using a Plane-wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169.

[2] Gajdoš, M.; Hummer, K.; Kresse, G.; Furthmüller, J.; Bechstedt, F. Linear Optical Properties in the Projector-augmented Wave Methodology. *Phys. Rev. B* **2006**, *73*, 045112.

[3] Shishkin, M.; Kresse, G. Implementation and Performance of the Frequency-dependent GW Method with the PAW Framework. *Phys. Rev. B* **2006**, *74*, 035101.

[4] Grosso, G.; Parravicini, G. P. *Solid State Physics, Second Edition*, Academic Press: Oxford, UK, 2014.