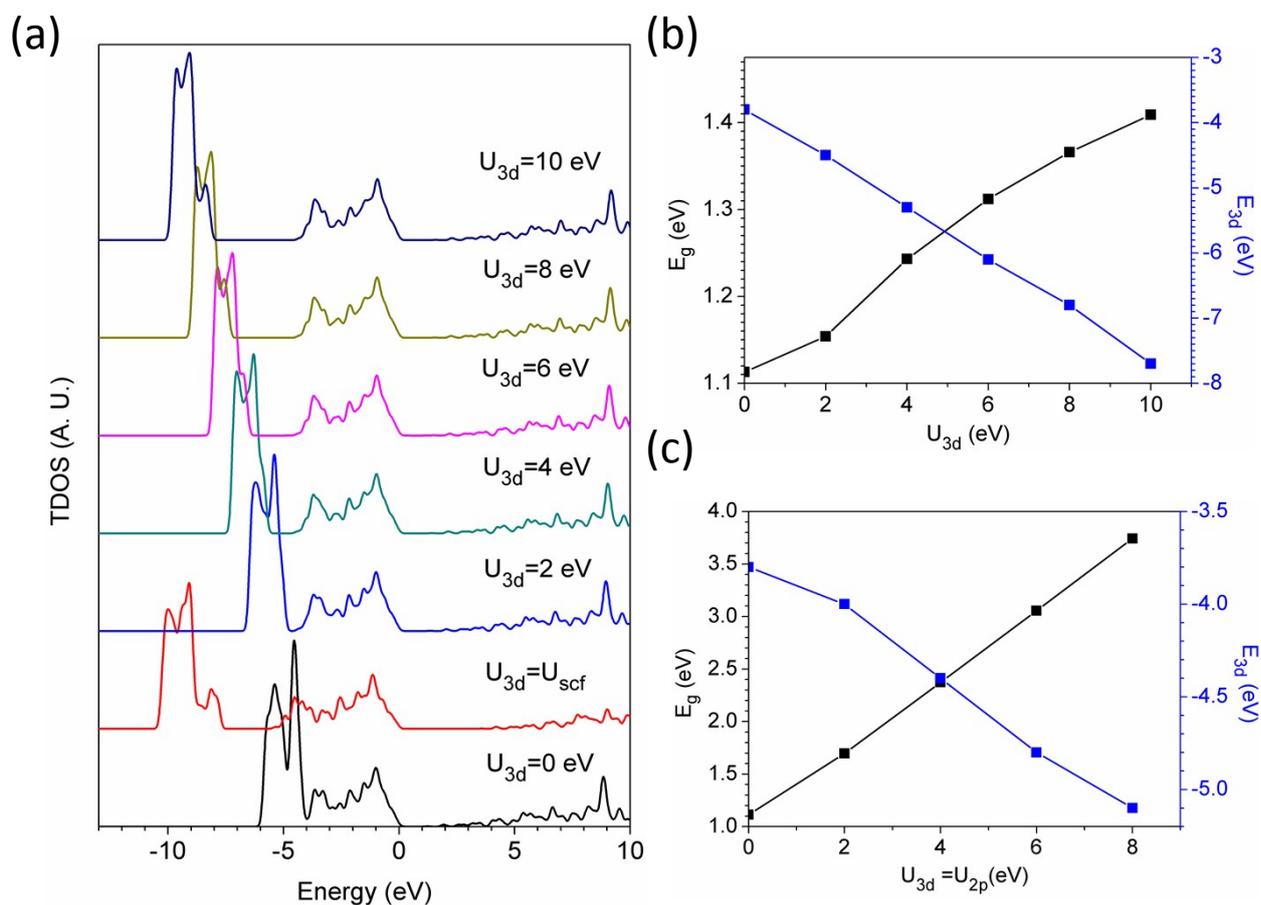


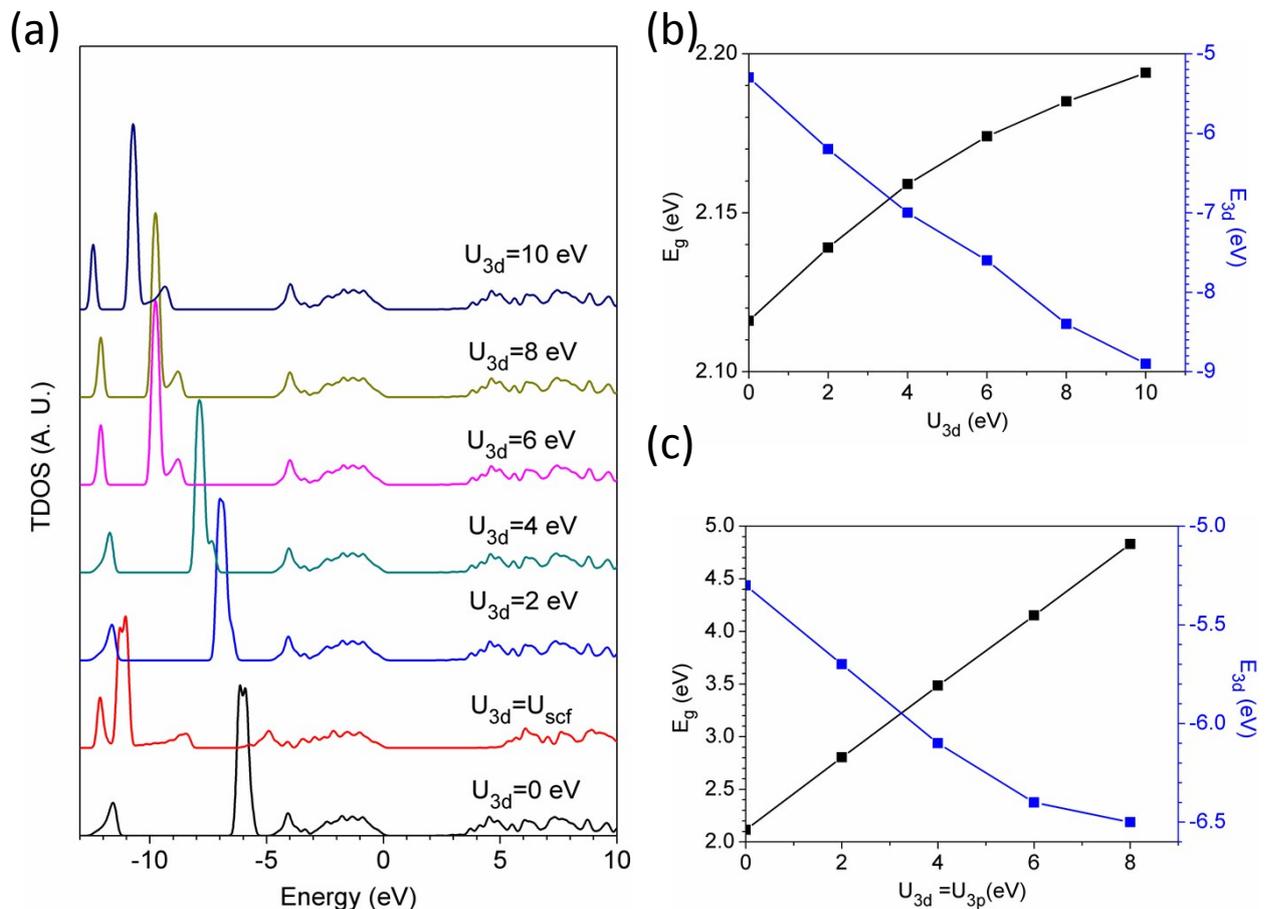
### Supplemental Information

We have further taken the standard PBE+U calculations with manually empirical tuning the band gap of ZnO with different input Hubbard-U parameters on Zn-3d and O-2p orbitals (Figure S1 (a)). Figure S1 (b) shows the parameters on Zn-3d orbitals only, while the Figure S1 (c) shows the parameters on both Zn-3d and O-2p orbitals with equivalent input values. From Figure S1 (b), we see that the band gap of WZ-ZnO monotonically increases from 1.113 eV to 1.409 eV from  $U_{3d}=0$  eV increase to  $U_{3d}=10$  eV. The contribution of the Hubbard-U on 3d orbital of Zn site presents a trend of down-shifting of the  $t_{2g}$  component of Zn-3d orbitals ( $E_{3d}$ ), which is 7.5 eV below the VBM ( $E_V-7.5$  eV) measured by experiments [1, 2]. The  $E_{3d}$  level is linearly updated from  $E_V-3.8$  eV to  $E_V-7.7$  eV with input  $U_{3d}$  from 0 eV to 10 eV. From Figure S1 (c), we turn to consider the contribution of Hubbard-U on O-2p orbitals in ZnO. This is consistent to the view of Lany and Zunger for stabilizing the localized hole states [3-6]. The band gap linearly increases from 1.113 eV to 3.743 eV when  $U_{3d}=U_{2p}=0$  eV increases to  $U_{3d}=U_{2p}=8$  eV gradually. The consideration of the O-2p contribution leads to a different variation behavior of  $E_{3d}$  levels of Zn-sites. It decreases the level from  $E_V-3.8$  eV to  $E_V-5.1$  eV below the VBM monotonically. The method we introduced here is also consistent with the result from the work by another group [7].



**Figure S1.** (a) TDOS comparison of wz-ZnO by PBE+U calculation with chosen U parameters form 0 eV to 10 eV as well as self-consistently determined  $U_{scf}$ . (b) The variation behaviors of band gap and 3d orbital level calculated by PBE+U calculations from the range of  $U_{3d}=0$  eV to 10 eV. (c) The variation behaviors of band gap and 3d orbital level calculated by PBE+U calculations from the range of  $U_{3d}=U_{2p}=0$  eV to 8 eV.

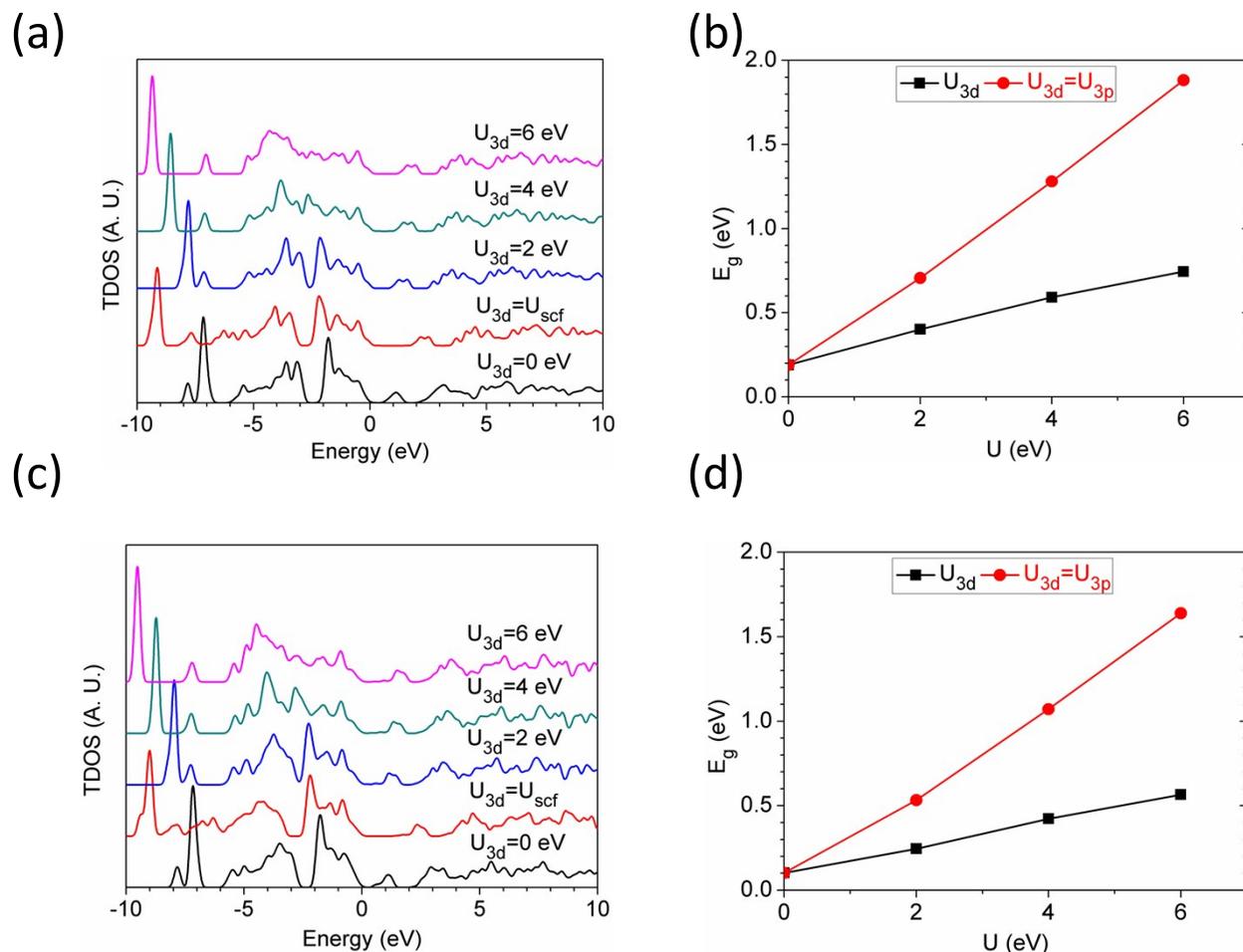
In the  $U$  dependence test on primitive cell of ZB-ZnS lattice as shown in Figure S2 (a), we find the consideration of  $U$  parameter solely adding on Zn-3d orbital has limited improvement on the band structure, which can be also seen in Figure S2 (b). The band gap of ZnS has increased from 2.116 eV to 2.194 eV which are still evidently underestimated compared to experimental value. On the contrast, the  $E_{3d}$  level of Zn-3d orbital is overestimated from  $E_V-5.3$  eV to  $E_V-8.9$  eV with  $U_{3d}$  value from 0 eV to 10 eV respectively. Figure S2 (c) shows the dependence on the collective contribution of  $U_{3d}$  and  $U_{3p}$  parameters. The band gap increases from 2.116 eV to 4.830 eV when  $U_{3d}=U_{3p}=0$  eV increases to  $U_{3d}=U_{3p}=8$  eV gradually. The  $E_{3d}$  level is also illustrating an improved estimation. The additional contribution of the S-3p orbital correction by Hubbard- $U$  parameter shows an improvement on the band gap and  $E_{3d}$  calculations, but also acting more sensitively with compared to the case of O-2p in ZnO calculations above.



**Figure S2.** (a) TDOS comparison of zb-ZnS by PBE+U calculation with chosen  $U$  parameters form 0 eV to 10 eV as well as self-consistently determined  $U_{scf}$ . (b) The variation behaviors of band gap and 3d orbital level calculated by PBE+U calculations from the range of  $U_{3d}=0$  eV to 10 eV. (c) The variation behaviors of band gap and 3d orbital level calculated by PBE+U calculations from the range of  $U_{3d}=U_{3p}=0$  eV to 8 eV.

For the calculations on the KS (kesterite) and WZ (wurtzite) lattices of CZTS ( $Cu_2ZnSnS_4$ ) compounds, the trend of variation on the band gap dependent on the choice of  $U$  parameters towards slowly to the suggested observed value ( $\sim 1.4$  eV) [8, 9]. For the cases of  $U$  parameters applied on the Cu-3d and Zn-3d orbitals of KS-CZTS (Figure S3 (a) and (b)), the band gap increases from 0.190 eV to 0.745 eV from  $U_d=0$  eV to  $U_d=6$  eV respectively. With further importing the contribution of S-3p orbitals with applied  $U$ , the band gap of KS-CZTS has increased from 0.190 eV to 1.882 eV with range from  $U_{3d}=U_{3p}=0$  eV to 6 eV respectively.

The trend in WZ-CZTS lattice is similar (Figure S3 (c) and (d)). The calculated band gap increases from 0.102 eV to 0.565 eV when  $U_{3d}$  is given from 0 eV to 6 eV on both 3d orbitals of Cu and Zn sites. Further contribution of S-3p orbitals with U gives an improvement on the band gap from 0.102 eV to 1.639 eV from  $U_{3d}=U_{3p}=0$  eV to 6 eV respectively.

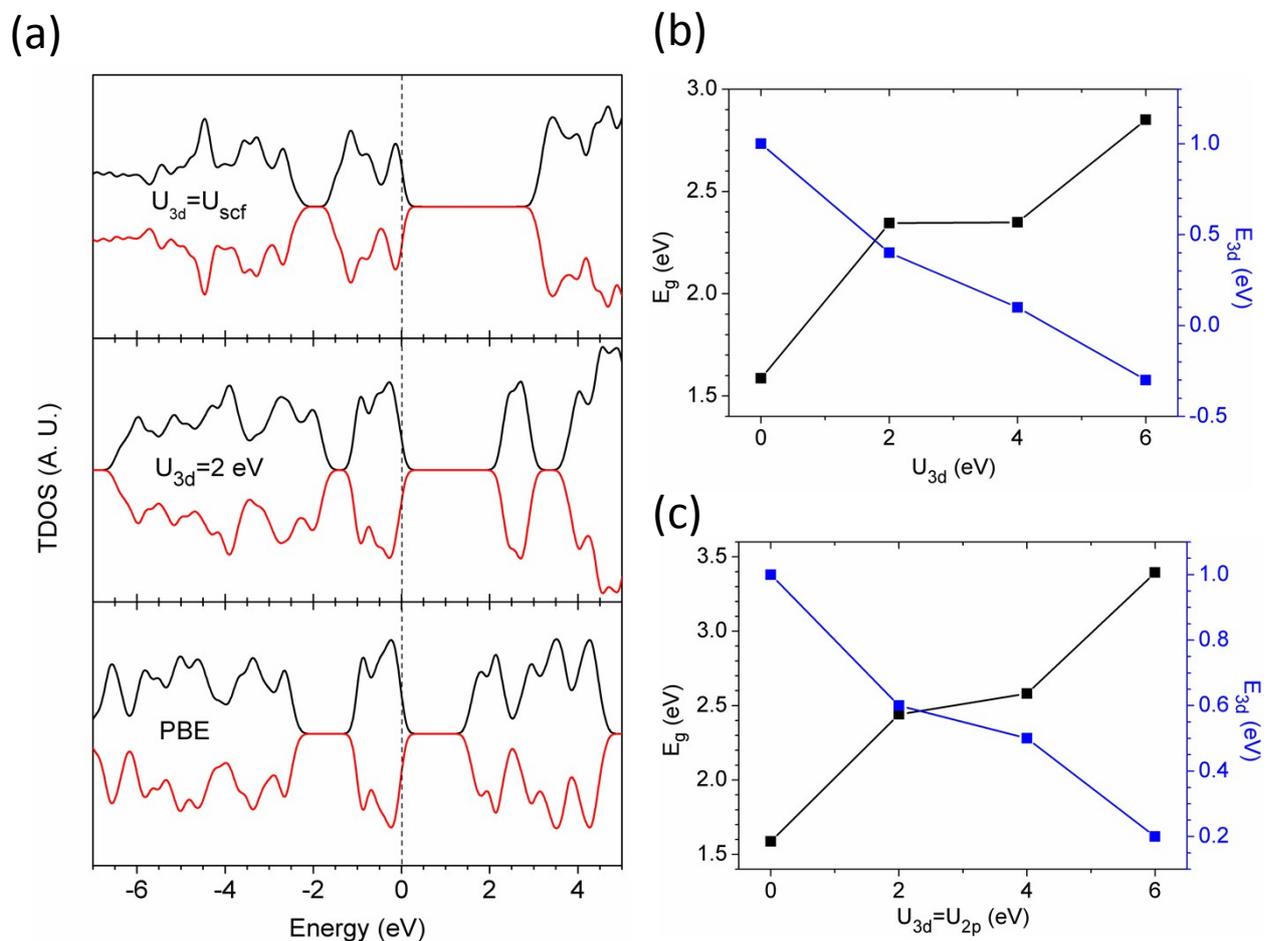


**Figure S3.** (a) TDOS comparison of KS-CZTS by PBE+U calculation with chosen U parameters from 0 eV to 6 eV as well as self-consistently determined  $U_{scf}$ . (b) The variation behaviors of band gap and 3d orbital level calculated by PBE+U calculations from the range of  $U_{3d}=U_{3p}=0$  eV to 6 eV for KS-CZTS. (c) TDOS comparison of WZ-CZTS by PBE+U calculation with chosen U parameters from 0 eV to 6 eV as well as self-consistently determined  $U_{scf}$ . (d) The variation behaviors of band gap and 3d orbital level calculated by PBE+U calculations from the range of  $U_{3d}=U_{3p}=0$  eV to 6 eV for WZ-CZTS.

Our standard band gap calculations on these closed-shell solids that, the plain PBE calculations has vastly underestimate its band gap no matter the system intrinsically has a wide or narrow band gap. Further Hubbard U corrections on the band structure show that the standard PBE+U calculations cost amount of time to empirically tune the value approaching to experimental band gap with many uncertainty at the meanwhile. This would be rather difficult to guarantee and balance the efficiency and accuracy for unknown novel materials under extreme physicochemical conditions or extraordinary environments. Only when the U parameters have been self-consistently determined, the PBE+U calculations can obviously give a satisfied band gap within an acceptable range for further applications.

We have also carried out an investigation of the U dependence in PBE+U calculations for the process of band gap tuning, as shown in Figure S4 (a). As discussed above, the band gap

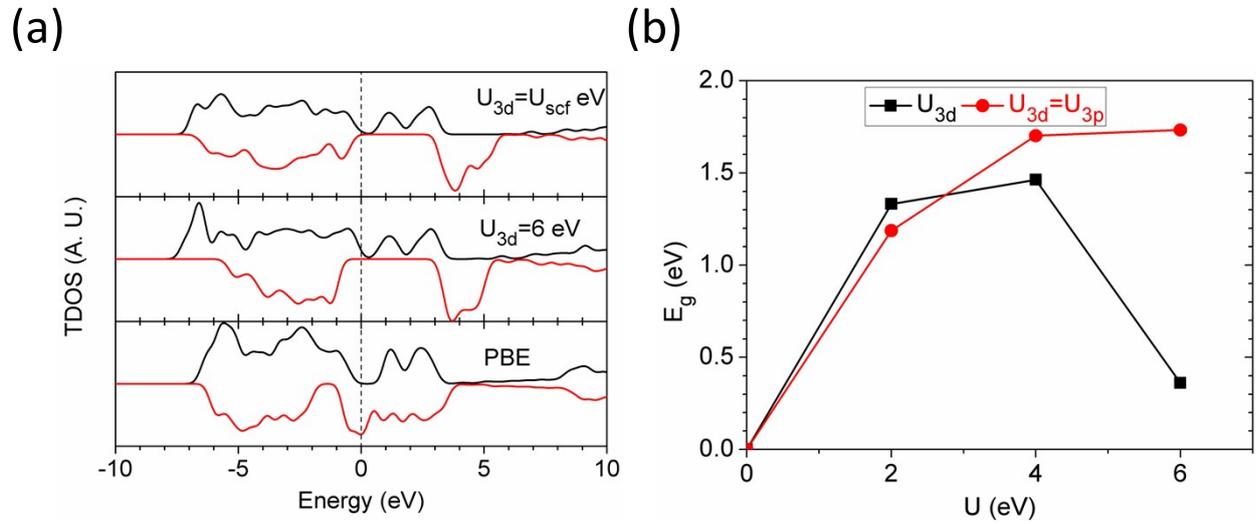
of Cr<sub>2</sub>O<sub>3</sub> in AFM phase is mainly sourced from the splitting between filled (Cr-3d) and empty (Cr-3d\*) 3d levels Cr sites. It seems to be an efficient way to apply the Hubbard-U parameter on Cr-3d orbital only. However, this will increase the Coulomb repulsive 3d-3d\* orbitals of Cr sites and suppress the repulsive interactions between Cr-3d and O-2p orbitals at the same time, as shown in Figure S4 (b). The band gap changes from 1.587 eV to 2.850 eV with range from  $U_{3d}=0$  eV to 6 eV. But this reduces the energetic distance between Cr-3d and O-2p orbitals from  $E_V+1.0$  eV to  $E_V-0.3$  eV. The negative value ( $E_{3d}=-0.3$  eV) denotes the overlapping between Cr-3d and O-2p orbitals. Figure S4 (c) shows the additional contributions of O-2p orbitals with U. The band gap has increased from 1.587 eV to 3.394 eV with range from  $U_{3d}=U_{2p}=0$  eV to 6 eV respectively. Meanwhile, this process also shows a decrease of occupied Cr-3d orbital level positions with respect the top of valence band maximum (VBM) of Cr<sub>2</sub>O<sub>3</sub>, which is from  $E_V+1.0$  eV to  $E_V+0.2$  eV accordingly.



**Figure S4.** (a) TDOS comparison of Cr<sub>2</sub>O<sub>3</sub> by PBE+U calculation with chosen U parameters from 0 eV to 6 eV as well as self-consistently determined  $U_{scf}$ . (b) The variation behaviors of band gap and 3d orbital level calculated by PBE+U calculations from the range of  $U_{3d}=0$  eV to 6 eV. (c) The variation behaviors of band gap and 3d orbital level calculated by PBE+U calculations from the range of  $U_{3d}=U_{2p}=0$  eV to 6 eV.

In the calculation test on the Co<sub>3</sub>V<sub>8</sub>O<sub>4</sub>, we find that such ferromagnetic compound has an interesting variation behavior in band gap with response to the input Hubbard-U parameters. As show in Figure S5 (a) that, plain PBE calculation shows the structure to be metallic without opening a gap near the  $E_F$  (0 eV). With increasing Hubbard-U parameters, the band gap firstly increases from 0 eV to 4 eV and then decrease after 4eV for the choice of U

(Figure S5 (b)). In this compound, the main difficulty is to provide a relatively small band gap for reflecting its semi-metallic behavior.



**Figure S5.** (a) TDOS comparison of  $\text{Co}_3\text{V}_8\text{O}_4$  by PBE+U calculation with chosen U parameters from 0 eV to 6 eV as well as self-consistently determined  $U_{scf}$ . (b) The variation behaviors of band gap and 3d orbital level calculated by PBE+U calculations from the range of  $U_{3d}=0$  eV to 6 eV. (c) The variation behaviors of band gap and 3d orbital level calculated by PBE+U calculations from the range of  $U_{3d}=U_{2p}=0$  eV to 6 eV.

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