Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information for "Metallic and anti-metallic properties of hydrogen adsorbed AnO_2 (An = Th, U, and Pu) surfaces"

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1 Occupation matrix control calculations for UO_2 and PuO_2

To ensure the reproducibility of our calculation, we would like to present the occupation matrices (OMs) here. These OMs are obtained by enumerating the diagonal OM as the initial OM and performing electronic minimization. The energy profiles of these calculations for UO_2 and PuO_2 are given by Figs. 1 and 2, respectively. Various final electronic states emerge from these self-consistent PBE+U calculations and they strongly depend on the input diagonal OM, which is denoted by a binary number in the square bracket, i.e., the occupancy of the f orbital. Note that the OM with the spin being opposite with the moment is negligible and set as the null matrix here. For the lowest-energy state of UO_2, the OMs of final states are given by

$$\begin{pmatrix} 0.03 & 0.00 & -0.01 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.04 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ -0.01 & 0.00 & 0.03 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.99 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.04 & 0.00 & 0.04 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.16 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.04 & 0.00 & 0.99 \end{pmatrix},$$

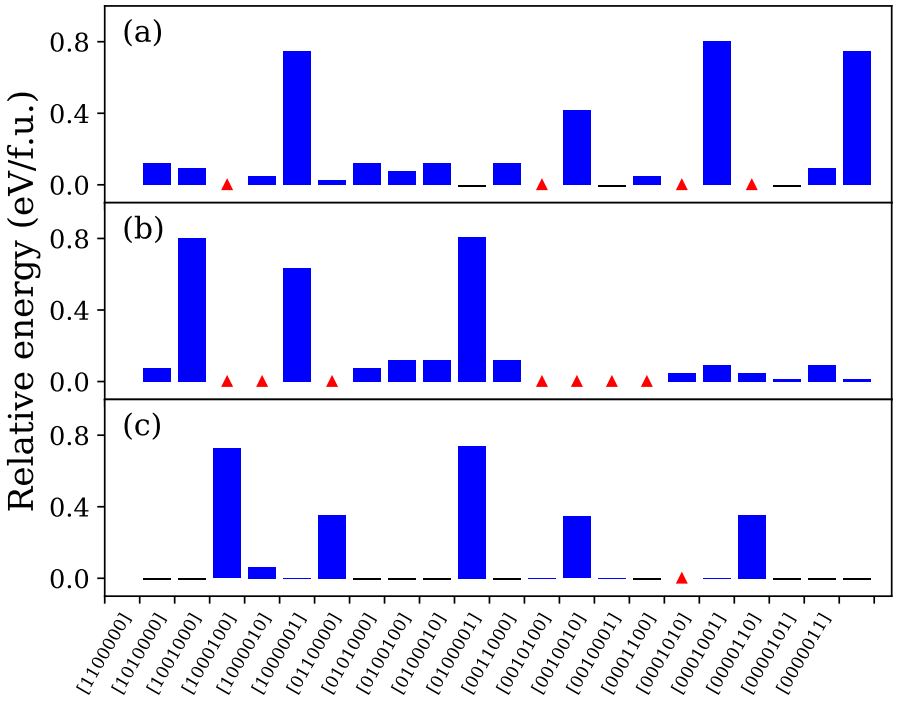

Figure 1 The energy profile of occupation matrix control calculation for (a) "tetragonal-100", (b) "tetragonal-110", and (c) "hexagonal" bulk unit cell of UO_2. The lowest-energy state is labeled by the red triangle.

$$\begin{pmatrix} 0.68 & 0.00 & 0.40 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.04 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.40 & 0.00 & 0.48 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.59 & 0.00 & -0.47 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.03 & 0.00 & 0.01 \\ 0.00 & 0.00 & 0.00 & -0.47 & 0.00 & 0.43 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.01 & 0.00 & 0.03 \end{pmatrix},$$

and

$$\begin{pmatrix} 0.25 & 0.00 & -0.15 & 0.08 & 0.00 & 0.28 & 0.00 \\ 0.00 & 0.38 & 0.00 & 0.00 & -0.37 & 0.00 & 0.27 \\ -0.15 & 0.00 & 0.18 & -0.14 & 0.00 & -0.29 & 0.00 \\ 0.08 & 0.00 & -0.14 & 0.23 & 0.00 & 0.26 & 0.00 \\ 0.00 & -0.37 & 0.00 & 0.00 & 0.43 & 0.00 & -0.29 \\ 0.28 & 0.00 & -0.29 & 0.26 & 0.00 & 0.56 & 0.00 \\ 0.00 & 0.27 & 0.00 & 0.00 & -0.29 & 0.00 & 0.25 \end{pmatrix},$$

for "tetragonal-100", "tetragonal-110", and "hexagonal" bulk unit cell, respectively. For PuO_2, the OMs are given by

$$\begin{pmatrix} 0.32 & 0.00 & 0.41 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 1.02 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.41 & 0.00 & 0.77 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.94 & 0.00 & -0.24 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.14 & 0.00 & -0.26 \\ 0.00 & 0.00 & 0.00 & -0.24 & 0.00 & 0.27 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & -0.26 & 0.00 & 0.93 \end{pmatrix},$$

$$\begin{pmatrix} 0.45 & 0.00 & 0.39 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 1.02 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.39 & 0.00 & 0.76 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.89 & 0.00 & -0.32 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.15 & 0.00 & -0.25 \\ 0.00 & 0.00 & 0.00 & -0.32 & 0.00 & 0.18 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & -0.25 & 0.00 & 0.94 \end{pmatrix},$$

and

$$\begin{pmatrix} 0.39 & 0.00 & 0.00 & 0.36 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.60 & 0.00 & 0.00 & 0.47 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.48 & 0.00 & 0.00 & 0.47 & 0.00 \\ 0.36 & 0.00 & 0.00 & 0.81 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.47 & 0.00 & 0.00 & 0.48 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.47 & 0.00 & 0.00 & 0.60 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 1.01 \end{pmatrix},$$

for "tetragonal-100", "tetragonal-110", and "hexagonal" bulk unit cell, respectively.

2 Electronic structures of AnO_2 surfaces

The orbital- and slab-projected density of states (DOS) are shown in Figs. 3, 4, and 5, for ThO_2, UO_2, and PuO_2, respectively. All the stoichiometric AnO_2 surfaces exhibit an insulating character but the character such as band gap is totally different. The band gap of (111) surface is very close to that of bulk but greater than those of (100) and (110) surface. As can be seen in Figure 3, the valence and conduction bands are dominated by O $2p$ and Th $5f$ states, respectively. For (111) surface, the peaks appear below the Fermi level for the projected DOS of the outer plane and there is no strong modification for surface electronic structure. For (100) and (110) surface, the dangling surface band appear in the conduction band of the outer plane, which contribute the decrease of band gap. This difference may stem from the symmetry of slab model. The (111) slab model is trigonal with space group $P\bar{3}m1$ (No. 164) while the other two slab models are orthorhombic with space group *Pmmn* (No. 56). Note that this symmetry would be further broken by setting the AFM ordering for UO_2 and PuO_2. For UO_2, both the valence and conduction bands are dominated by U $5f$ states and thus there is no strong modification between surface and bulk bands. Thus the effect of surface termination is small. FOr PuO_2, the valence band are contributed by Pu $5f$ and O $2p$ states and for O $2p$ state in the surface. For (111) surface, the additional peaks appear below the Fermi level, being similar to ThO_2. The substantial decrease of (100) surface band gap is attributed to the emergent O $2p$ peaks around the Fermi level.

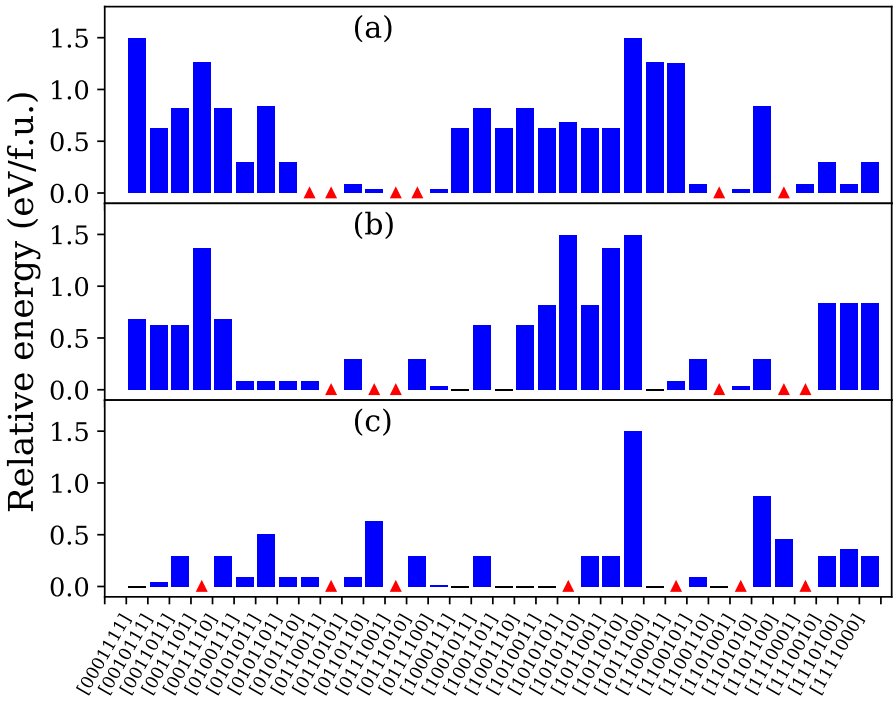

Figure 2 The energy profile of occupation matrix control calculation for (a) "tetragonal-100", (b) "tetragonal-110", and (c) "hexagonal" bulk unit cell of PuO_2. The lowest-energy state is labeled by the red triangle.

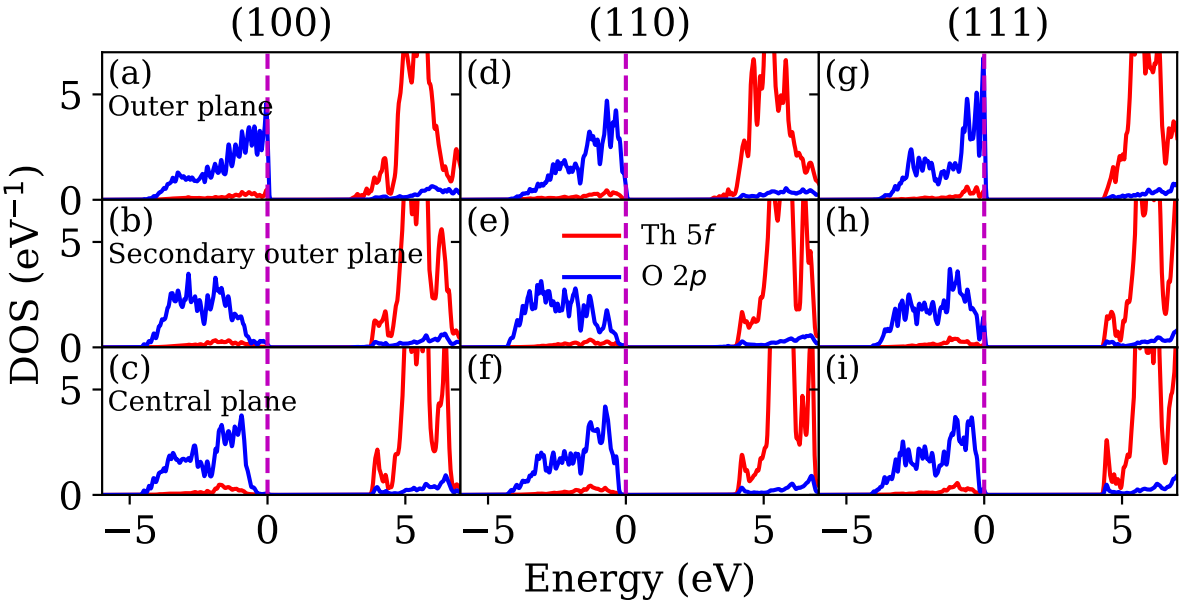

Figure 3 The $5f$ and $2p$-projected and slab-projected DOS of ThO_2 for (a-c) (110), (d-f) (110), and (g-i) (111) surface. The panels (a,d,g), (b,e,h), (c,f,i) corresponds to the slab-projected DOS of outer, secondary outer, and central plane, respectively.

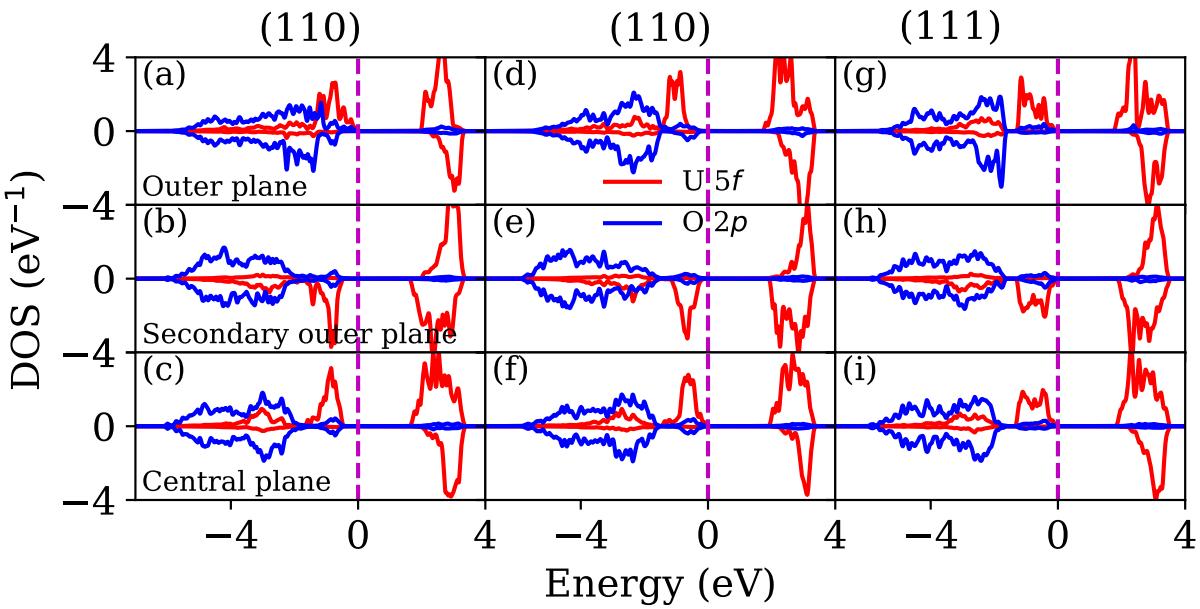

Figure 4 The 5f and 2p-projected and slab-projected DOS of UO_2 for (a-c) (110), (d-f) (110), and (g-i) (111) surface. The panels (a,d,g), (b,e,h), (c,f,i) corresponds to the slab-projected DOS of outer, secondary outer, and central plane, respectively.

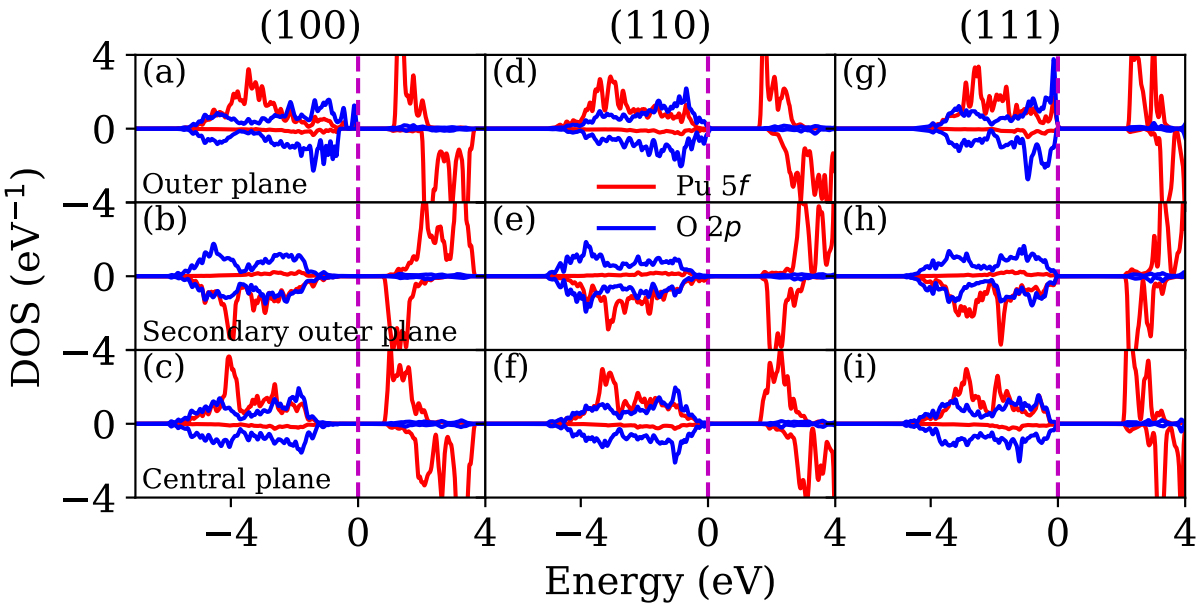

Figure 5 The 5f and 2p-projected and slab-projected DOS of PuO_2 for (a-c) (110), (d-f) (110), and (g-i) (111) surface. The panels (a,d,g), (b,e,h), (c,f,i) corresponds to the slab-projected DOS of outer, secondary outer, and central plane, respectively.

3 Electronic structures of hydrogen-adsorbed AnO_2 surfaces

In this appendix, some band structures of hydrogen adsorbed AnO_2 surface are given. Figure 6 and 7 show the band structures and DOS of ThO_2 (100) surface, respectively. Figure 8 and 9 show the band structures and DOS of ThO_2 (111) surface, respectively. Figure 10 and 11 show the band structures and DOS of UO_2 (100) surface, respectively. Figure 12 and 13 show the band structures and DOS of UO_2 (110) surface, respectively. Figure 14 and 15 show the band structures and DOS of PuO_2 (100) surface, respectively. Figure 16 and 17 show the band structures and DOS of PuO_2 (110) surface, respectively.

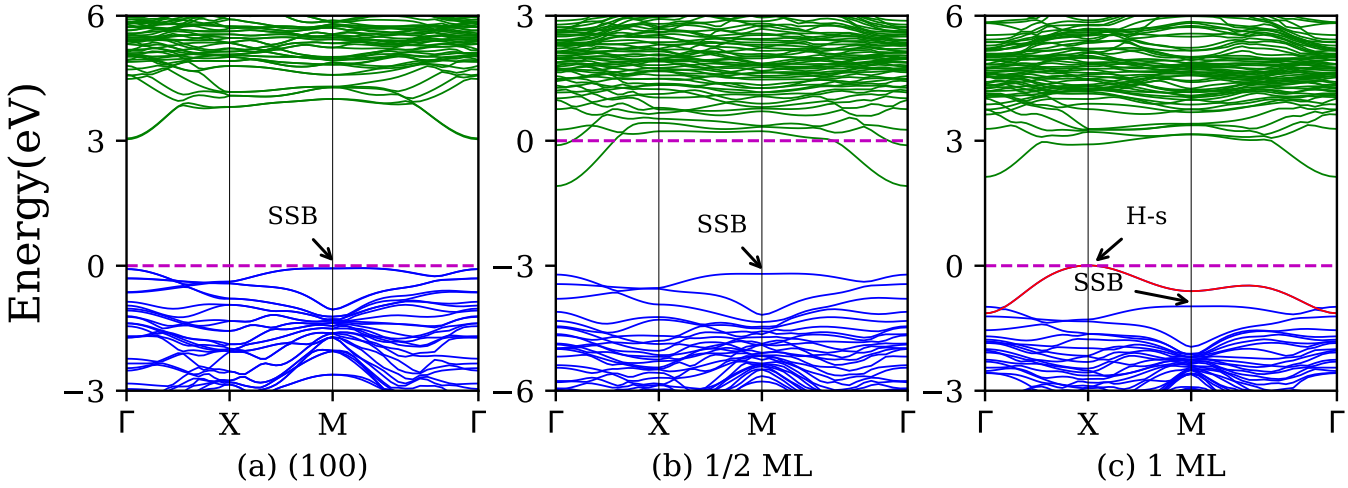

Figure 6 The band structures of (a) clean, (b) 1/2 ML, and (c) 1 ML hydrogen-adsorbed ThO_2 (100) surface. The Fermi level is denoted by the horizontal dashed line and surface-state bands are labelled by arrows.

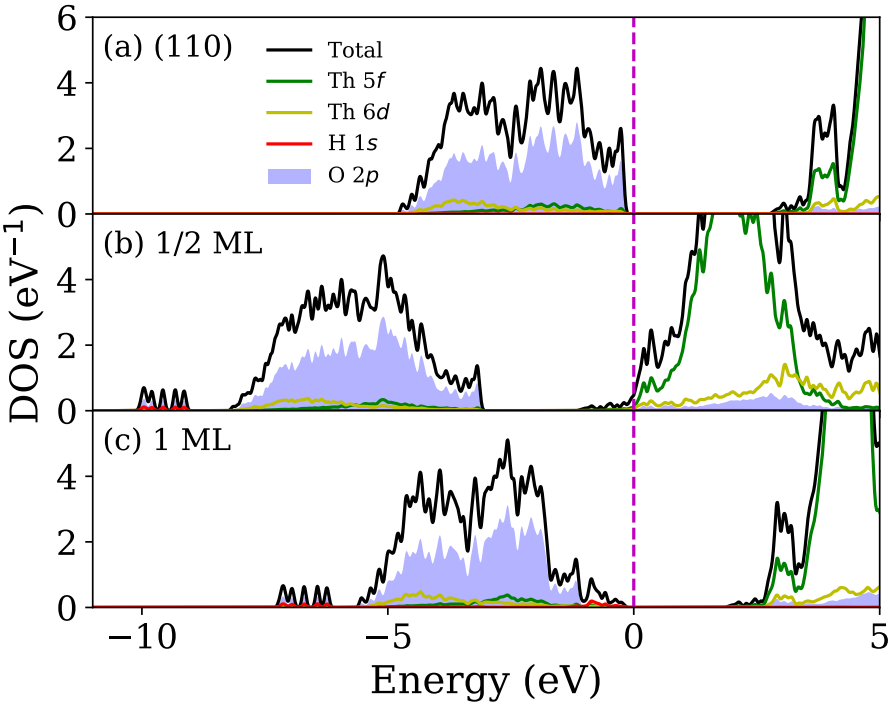

Figure 7 The total and partial DOS of (a) clean, (b) 1/2 ML, and (c) 1 ML hydrogen-adsorbed ThO_2 (100) surface. The Fermi level is denoted by the vertical dashed line.

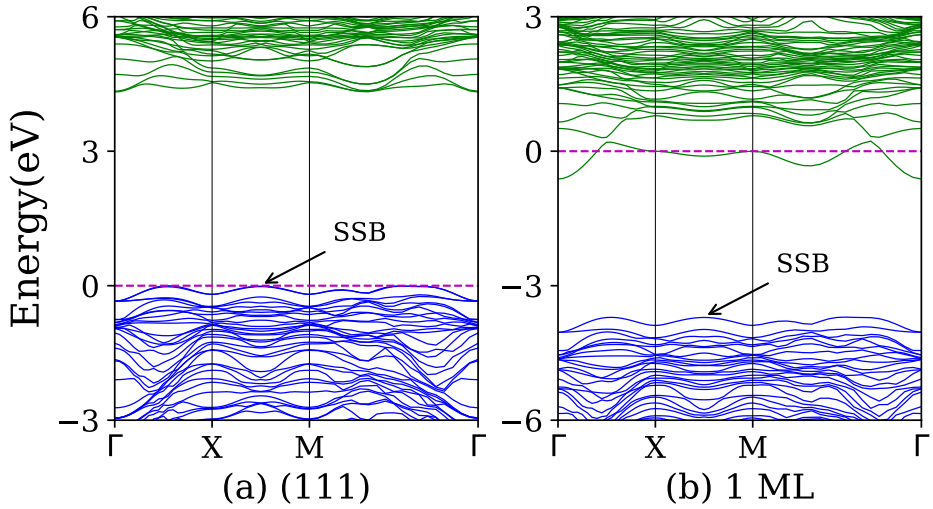

Figure 8 The band structures of (a) clean and (b) 1 ML hydrogen-adsorbed ThO_2 (111) surface. The Fermi level is denoted by the horizontal dashed line and surface-state bands are labelled by arrows.

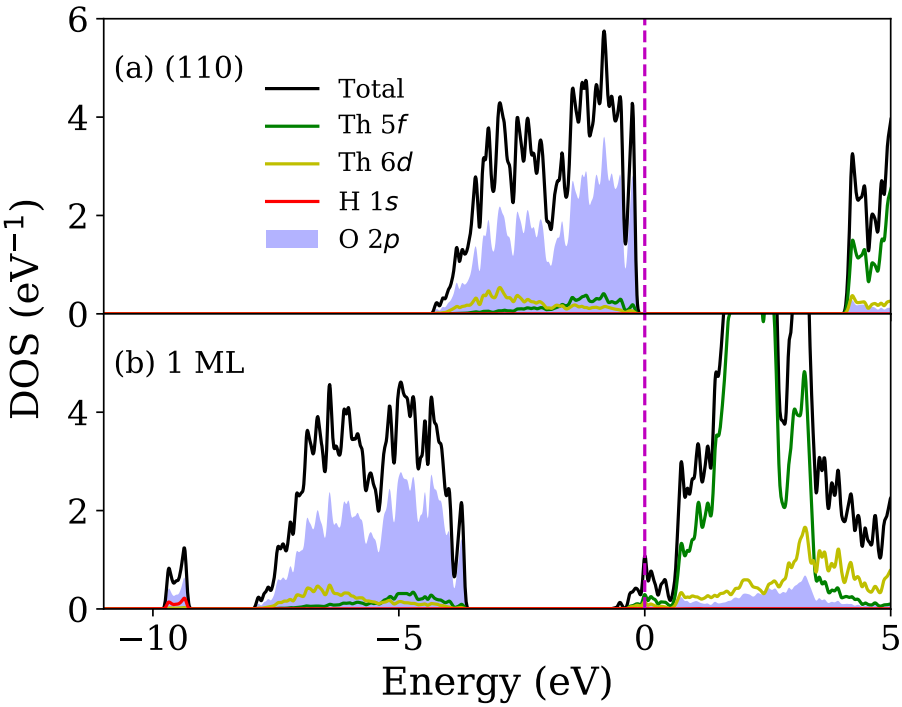

Figure 9 The total and partial DOS of (a) clean and (b) 1 ML hydrogen-adsorbed ThO_2 (111) surface. The Fermi level is denoted by the vertical dashed line.

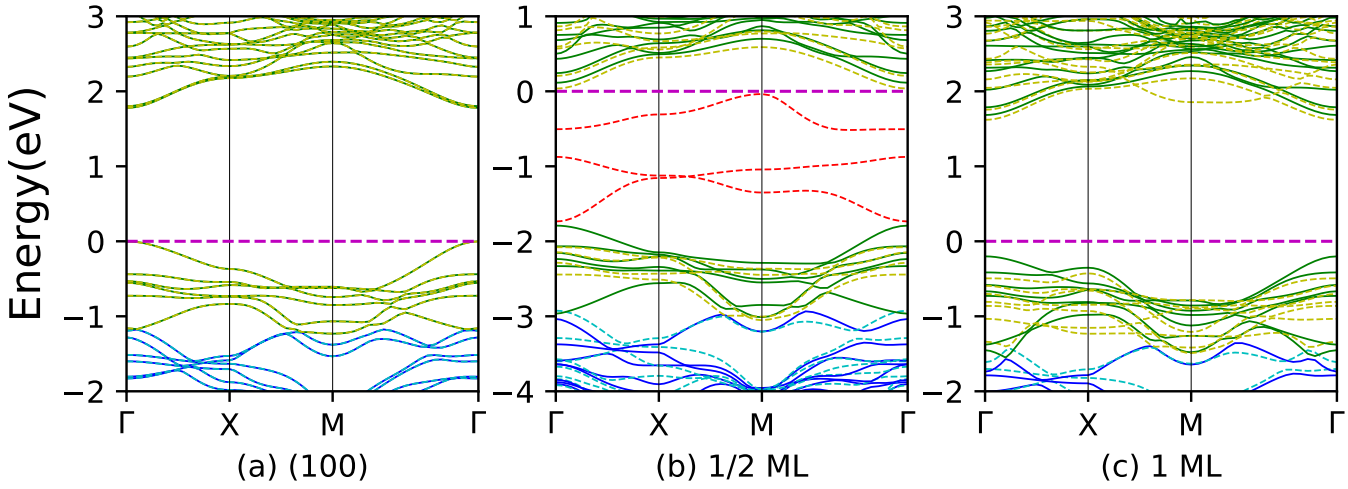

Figure 10 The band structures of (a) clean, (b) 1/2 ML, and (c) 1 ML hydrogen-adsorbed UO_2 (100) surface. The Fermi level is denoted by the horizontal dashed line.

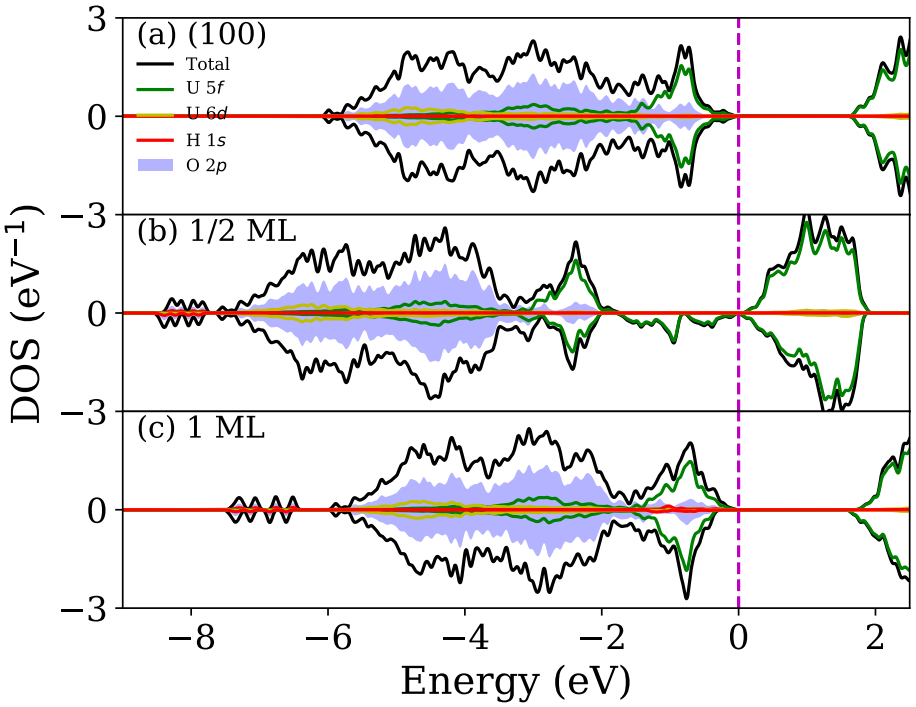

Figure 11 The total and partial DOS of (a) clean, (b) 1/2 ML, and (c) 1 ML hydrogen-adsorbed UO_2 (100) surface. The Fermi level is denoted by the vertical dashed line.

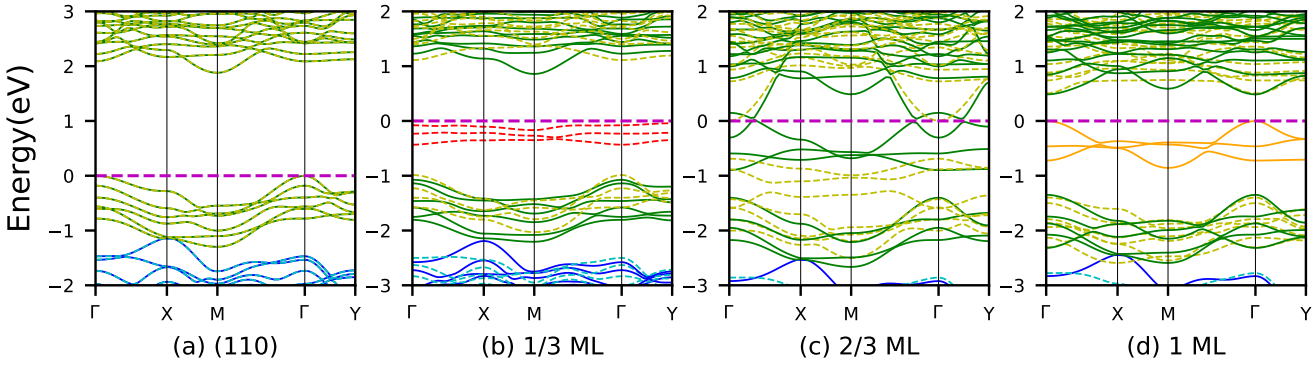

Figure 12 The band structures of (a) clean, (b) 1/3 ML, (c) 2/3 ML, (d) 1 ML hydrogen-adsorbed UO_2 (110) surface. The Fermi level is denoted by the horizontal dashed line.

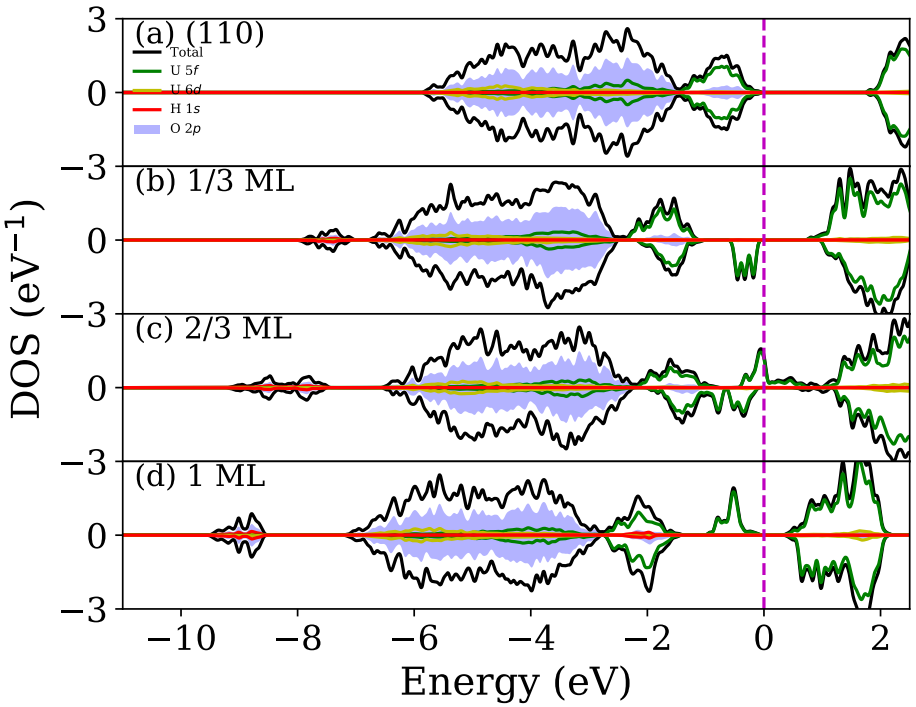

Figure 13 The total and partial DOS of (a) clean, (b) 1/3 ML, (c) 2/3 ML, and (d) 1 ML hydrogen-adsorbed UO_2 (110) surface. The Fermi level is denoted by the vertical dashed line.

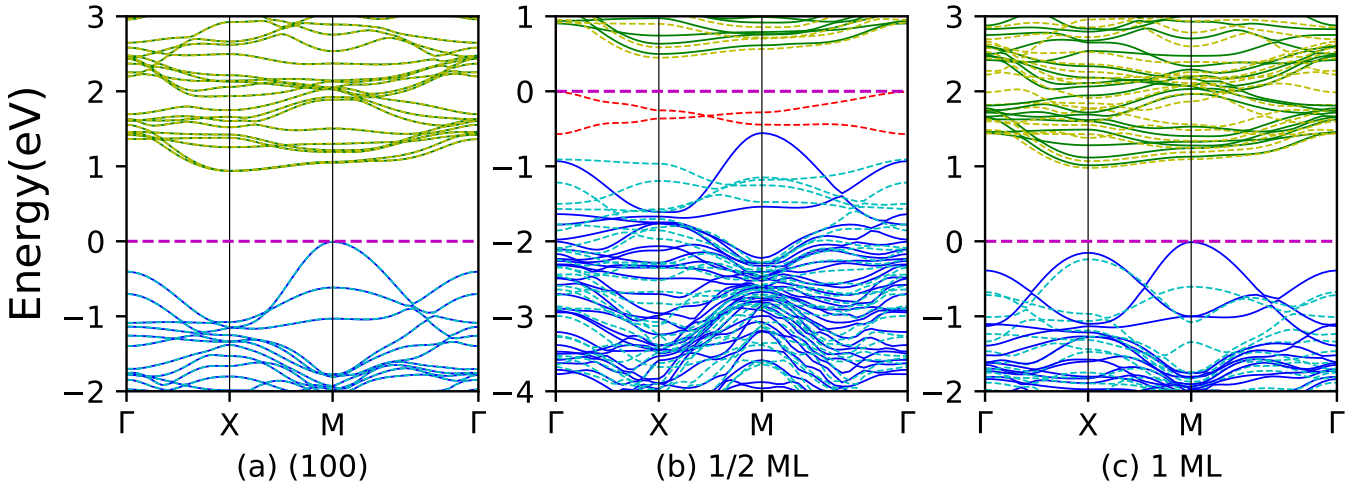

Figure 14 The band structures of (a) clean, (b) 1/2 ML, and (c) 1 ML hydrogen-adsorbed PuO_2 (100) surface. The Fermi level is denoted by the horizontal dashed line.

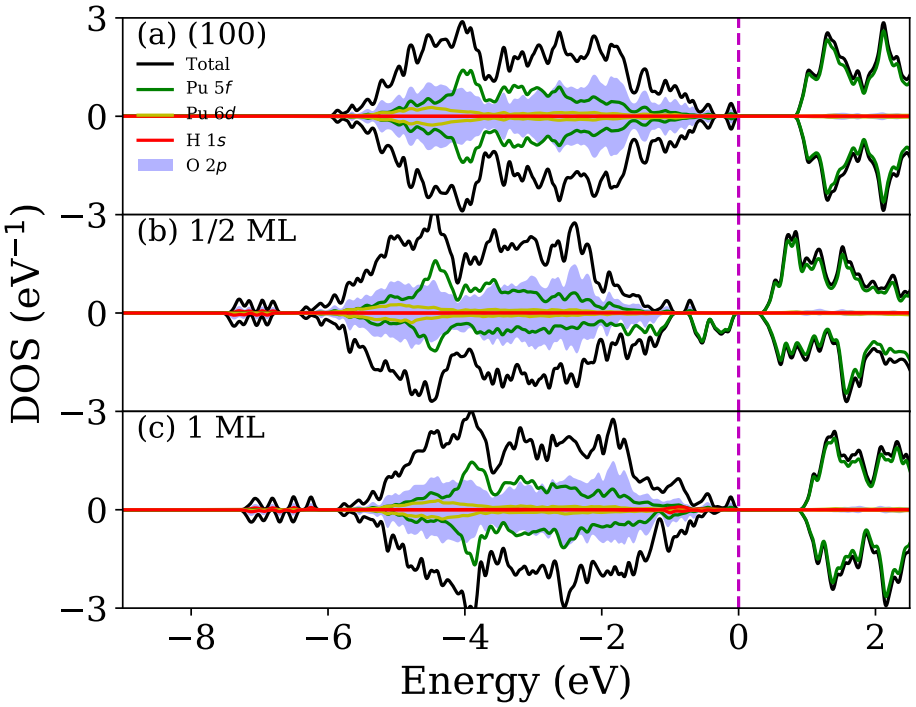

Figure 15 The total and partial DOS of (a) clean, (b) 1/2 ML, and (c) 1 ML hydrogen-adsorbed PuO_2 (100) surface. The Fermi level is denoted by the vertical dashed line.

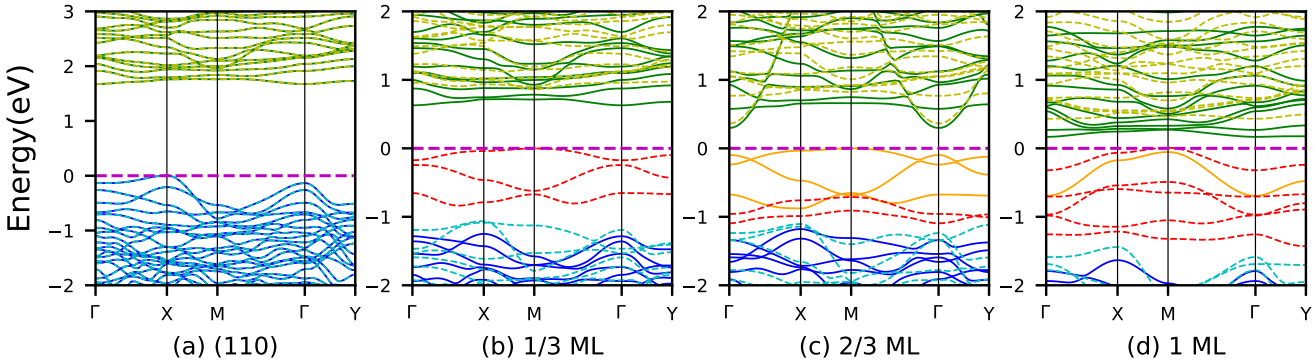

Figure 16 The band structures of (a) clean, (b) 1/3 ML, (c) 2/3 ML, (d) 1 ML hydrogen-adsorbed PuO_2 (110) surface. The Fermi level is denoted by the horizontal dashed line.

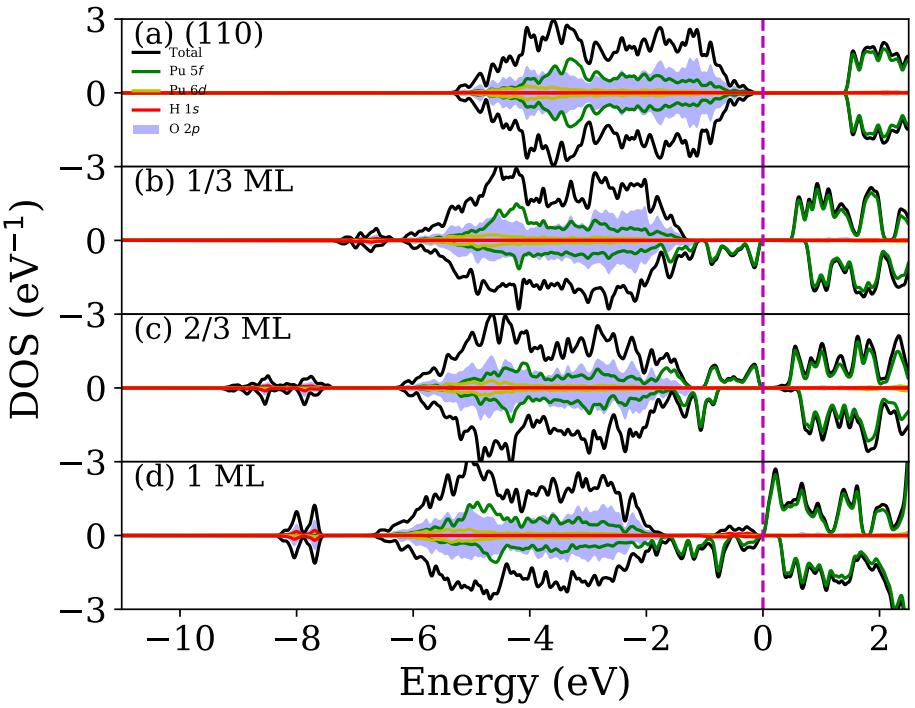

Figure 17 The total and partial DOS of (a) clean, (b) 1/3 ML, (c) 2/3 ML, and (d) 1 ML hydrogen-adsorbed PuO_2 (110) surface. The Fermi level is denoted by the vertical dashed line.