# Band bending and dipole effect at interface of metal-nanoparticles and TiO<sub>2</sub> directly observed by angular-resolved hard X-ray photoemission spectroscopy

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## **Supporting Information**

### **DFT calculations**

The Ti  $2p_{3/2}$  electron binding energies for TiO<sub>2</sub> shown in Fig. 3 were calculated using a DFT method in conjunction with a pseudopotential scheme. To obtain spectra without explicitly including core electrons in the DFT calculations for extended surfaces, as shown in Figure S10, the excitation was separated into four elementary processes: (i) extraction of a Ti atom from the TiO<sub>2</sub> surface, which increases the system energy by  $\Delta E_b$ , (ii) excitation of an electron from the 2p orbital to the LUMO of the Ti atom, which increases the system energy by  $\Delta E_{atom}^*$ , (iii) return of the excited Ti atom to the bulk TiO<sub>2</sub>, which reduces the system energy by  $-\Delta E_b^*$ , and (iv) excitation of an electron in the valence band to the vacuum level, which increases the system energy by  $\Phi^*$ . When incorporating the energy changes for these elementary processes, the Ti  $2p_{3/2}$  binding energy,  $\Delta E_{XPS}$ , can be described as:

$$\Delta E_{\rm XPS} = \Delta E_{\rm b} + \Delta E_{\rm atom}^* - \Delta E_{\rm b}^* + \Phi^*.$$

The sum of the first, second and third terms on the right-hand side of the above equation corresponds to the absorption edge value for the X-ray absorption spectrum (XAS),  $\Delta E_{XAS}$ , as:

$$\Delta E_{\rm XAS} = \Delta E_{\rm b} + \Delta E_{\rm atom}^* - \Delta E_{\rm b}^*.$$

Therefore,  $\Delta E_{\text{XPS}}$  represents the sum of  $\Delta E_{\text{XAS}}$  and the work function for the excited surface,  $\Phi^*$ , as:

$$\Delta E_{\rm XPS} = \Delta E_{\rm XAS} + \Phi^*.$$

A similar method proposed by Mizoguchi *et al.*<sup>1</sup> calculated  $\Delta E_b$ ,  $\Delta E_b^*$  and  $\Phi^*$  using a standard pseudopotential scheme and employing pseudopotentials with core-holes,<sup>2</sup> and also determined  $\Delta E_{atom}^*$  using an all-electron method applied to isolated Ti atoms.

The transferred charge values,  $\Delta Q$ , included in Fig. 3 were obtained from gross charges calculated by a Mulliken population analysis.<sup>3</sup>

As presented in Figs. S7-9, the TiO<sub>2</sub> surface was modeled as a three atomic layer, rutile-type TiO<sub>2</sub> (110) slab with 4 × 2 two-dimensional periodicity, with metal particles or thin layers composed of 1-120 metal atoms placed on top of the TiO<sub>2</sub> surface. Geometrical optimizations were achieved using a quasi-Newton optimizer with a force of 0.05 eV·Å<sup>-1</sup> acting on all atoms. After optimization, a core hole was introduced at a Ti atom in the middle layer of the slab, and the  $\Delta E_{\rm b}$ ,  $\Delta E_{\rm b}$ \* and  $\Phi$ \* values were calculated. Calculations were performed for all 16 Ti atoms in the middle layer of the TiO<sub>2</sub> slab and the resulting  $\Delta E_{\rm XPS}$  values were averaged.

The calculations for  $\Delta E_b$ ,  $\Delta E_b^*$  and  $\Phi^*$  were performed using a DFT code written by our own group,<sup>4</sup> based on linear combinations of pseudo-atomic orbitals (LCPAO) and norm-conserving pseudopotential methods. Valence wavefunctions were expanded using LCPAO basis sets with double zeta plus polarization (DZP) and effective core potentials describing the interactions between valence electrons and inner cores were generated using a Troullier-Martin type scheme.<sup>5</sup> Brillouin zone integrations employed a 2 × 2 Monkhorst-Pack **k**-point mesh.<sup>6</sup> Calculations of  $\Delta E_{atom}^*$  values

used a Herman-Skillman scalar-relativistic all-electron calculation method.<sup>7</sup> All calculations employed a generalized gradient approximation based on a Perdue-Burke-Ernzerhof function.<sup>8</sup>

#### Surface roughness effect for the angular-resolved HAXPES measurements

The ATO and FTO specimens exhibited surface roughness values of less than 10 and approximately 30 nm, respectively. Figure S11 shows the effects of surface roughness on the angular-resolved HAXPES measurements. A smaller band bending of 0.07 eV was observed for the Pt/TiO<sub>2</sub>/FTO sample compared to a value of 0.09 eV for Pt/TiO<sub>2</sub>/ATO, and this difference is attributed to the variation in surface roughness. Based on this minimal difference, the effect of surface roughness on the angular-resolved HAXPES measurements was considered to be negligible.

#### References

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Figure S1. Transmission electron microscopy (TEM) images of (a)  $TiO_2$ , (b)  $Pt/TiO_2$ , (c)  $Au/TiO_2$ , and (d)  $Rh/TiO_2$ .



Figure S2. Photocatalytic and photochemical hydrogen production using metal/semiconductor films under Xe lamp irradiation. Photocatalytic hydrogen evolution from 10% aqueous methanol solution using TiO<sub>2</sub>, Au/TiO<sub>2</sub>,Pt/TiO<sub>2</sub> and Rh/TiO<sub>2</sub> without bias



Figure S3. Ti  $2p_{3/2}$  spectra acquired from (a) TiO<sub>2</sub>, (b) Pt/TiO<sub>2</sub>, (c) Au/TiO<sub>2</sub>, and (d) Rh/TiO<sub>2</sub> by angular-resolved HAXPES (red lines: at take-off angle of 10°, blue lines:  $28 \sim 56^{\circ}$  and black lines:  $65^{\circ}$ ).



Figure S4. Change in Ti  $2p_{3/2}$  HAXPES spectrum of TiO<sub>2</sub> film with light intensity (black line: photon flux of 2.3 × 10<sup>11</sup> photons, red line: photon flux of 1.15 × 10<sup>11</sup> photons).



Figure S5. Shifts in top peak position relative to the positions in the angular spectrum for series of Ta  $3d_{5/2}$  spectra obtained on N-Ta<sub>2</sub>O<sub>5</sub>, Au/N-Ta<sub>2</sub>O<sub>5</sub>, Pt/N-Ta<sub>2</sub>O<sub>5</sub>, and Rh/N-Ta<sub>2</sub>O<sub>5</sub>.



Figure S6. Shift in peak position relative to that for  $Rh/TiO_2$  and 10nmRh-film/TiO<sub>2</sub> films in angular spectra.



Figure S7. (a) Calculated binding energy values for Ti  $2p_{3/2}$  peaks for Pt particles or thin films on TiO<sub>2</sub> as determined by DFT, and (b) model structures for Pt(n)/TiO<sub>2</sub> (n = 1 to 12 particles, n = 20, 60 or 120 thin films).



Figure S8. (a) Calculated binding energy values for Ti  $2p_{3/2}$  peaks for Au particles or thin films on TiO<sub>2</sub> as determined by DFT, and (b) model structures for Au(n)/TiO<sub>2</sub> (n = 1 to 12 particles, n = 20, 60 or 120 thin films).



Figure S9. (a) Calculated binding energy values for Ti  $2p_{3/2}$  peaks for Rh particles or thin films on TiO<sub>2</sub> as determined by DFT, and (b) model structures for Rh(n)/TiO<sub>2</sub> (n = 1 to 12 particles, n = 20, 60 and 120 thin films).



Figure S10. Schematic diagram of XPS excitation process separated into four elementary steps. Gray squares indicate TiO<sub>2</sub> surface system and gray circles indicate Ti atoms.



Figure S11. Ti  $2p_{3/2}$  photoelectron peak positions as functions of the take-off-angles of photoelectrons for Pt/TiO<sub>2</sub> (red circles: ATO), Pt/TiO<sub>2</sub> (red squares: FTO), TiO<sub>2</sub> (black circles: ATO) and TiO<sub>2</sub> (black squares: FTO).