Facet-dependent photocatalytic performance and electronic structure of single-crystalline anatase TiO$_2$ particle revealed by X-ray photoelectron spectromicroscopy

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Estimation of the valence band structure of the interface:

The interface areas for spots II and III were estimated to be approximately 88 nm and 93 nm, respectively. To achieve this, a constraint-based fitting model was employed, formulated as follows:

$$\text{II} - k_1\,\text{I} \approx \text{III} - k_2\,\text{IV}$$

Where I and IV represent the valence band (VB) spectra from the (101) and (001) facets of anatase TiO_2 single crystal, respectively. II and III correspond to the VB spectra from the regions between the (101) and (001) facets, adjacent to I and IV, respectively. The coefficients k_1 and k_2 serve as scaling factors that adjust the influence of the VB spectra I and IV on the interface VB spectra II and III, respectively. As a result, the coefficients were determined to be $k_1 = 0.12$ and $k_2 = 0.07$. Utilizing these coefficients, the overall interface area was calculated as follows:

$$(1 - k_1) \text{ x } 100 \text{ nm} + (1 - k_2) \text{ x } 100 \text{ nm} = 88 \text{ nm} + 93 \text{ nm} = 181 \text{ nm.}$$
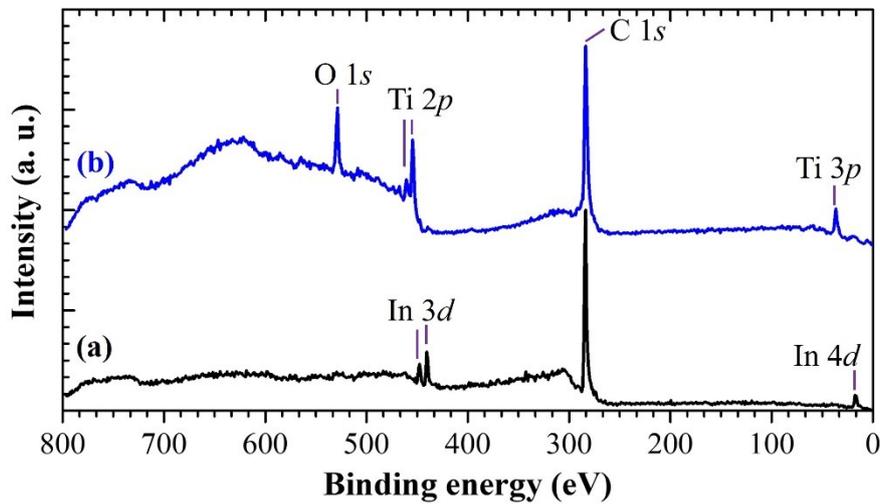
Figure S1. Wide XPS spectra of (a) indium sheet and (b) anatase powder samples held on indium sheet by direct beams without an X-ray condenser (1000 eV for incident X-ray energy).
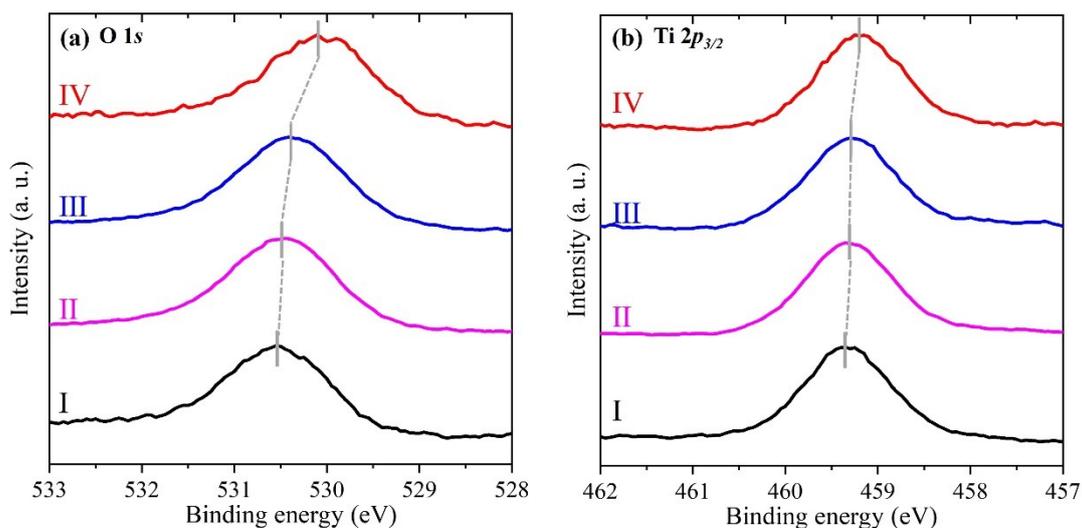
Figure S2. Localized amplification for pinpoint (a) O 1*s* and (b) Ti 2*p* XPS spectra of the single-crystalline anatase TiO_2 particle from consecutive 4 spots (I, II, III, and IV) shown in Fig. 2b.
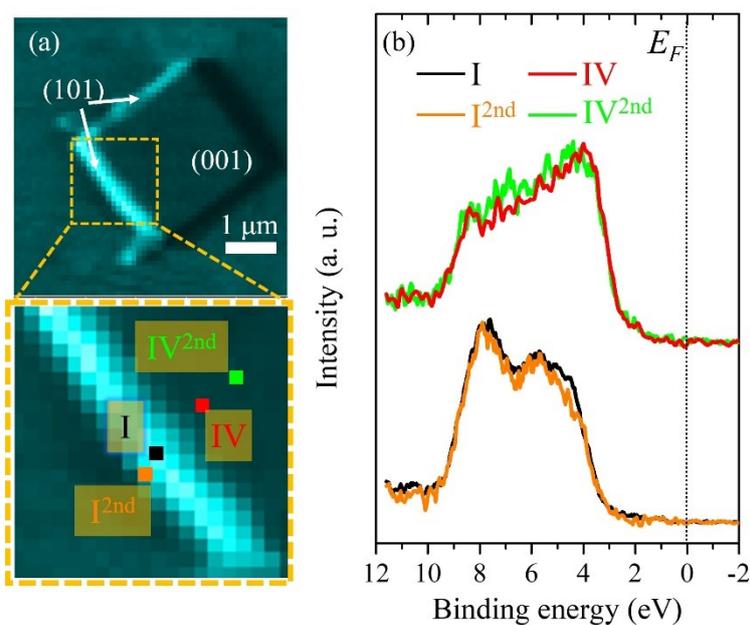
Figure S3. (a) O 1*s* photoelectron intensity mapping image and its enlarged area of the orange square of anatase TiO_2 single-crystalline particle and (b) Valence band XPS spectra of anatase TiO_2 particle for 2 spots from (101) (I and I[2nd]) and (001) (IV and IV [2nd]) facets shown in Fig. S3a, respectively.
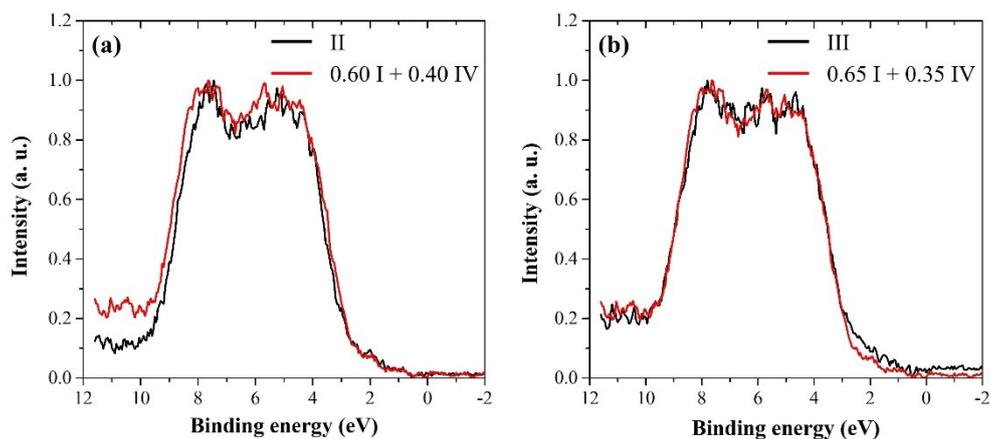
Figure S4. Reproducibility of the VB spectra at positions II (a) and III (b) by the sum of the VB spectra at positions I and IV shown in Fig. 3S. The ratios obtained here are based on the simulation of their peak intensities.
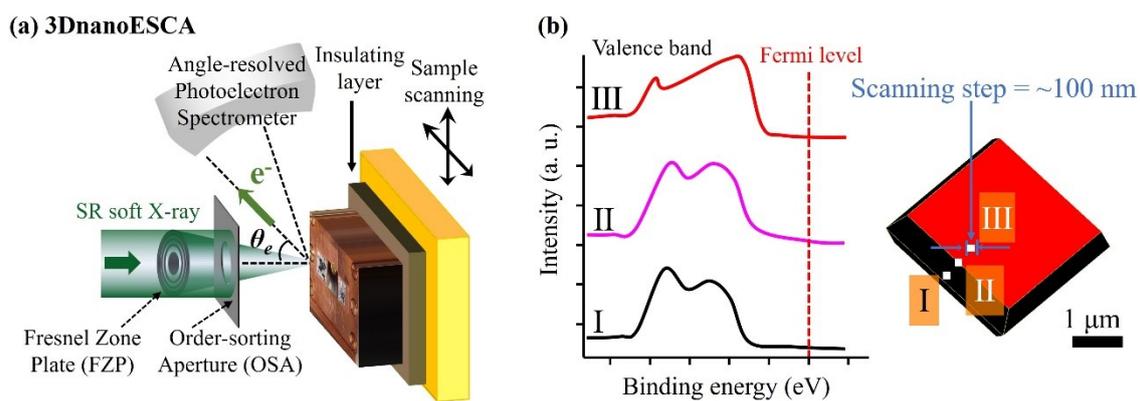
Figure S5. Schematic images for (a) 3DnanoESCA system and (b) facet-dependent valence band analysis of particle by microscopic XPS using 3DnanoESCA.