Supporting Information Improving SERS Sensitivity of TiO₂ Through Utilizing the Heterogeneity of the Facets Potentials

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Experimental Methods

Synthesis of TiO₂ single crystals. 100 μ L of titanium tetrafluoride solution was added dropwise to 60 mL of 2.0 M hydrochloric acid solution under ice bath conditions. A certain volume of 0.015 M sodium fluoride was added to the above solution under vigorous stirring. The mixture was transferred into a 100 mL Teflon vessel and hydrothermally treated at 160 °C for 12 h. Afterwards, Teflon vessel was taken out and cooled to room temperature. The product was collected by centrifugation and washed 3 times with distilled water and ethanol solution, respectively. The white solid TiO₂ single crystals were then dried in a vacuum oven at 60 °C for 12 h and calcined in a muffle furnace at 550 °C for 2 h. Then, the sample was cooled to room temperature.

Adsorption experiment. 5 mg of TiO_2 single crystals with different crystal face ratios were placed in a round-bottom flask with 20 mL of MB solution (32 mg/ L). The mixture was stirred in a thermostatic oscillator at 25 °C for 5 h. The concentration of MB was determined by UV-vis spectroscopy. The adsorption capacity (Q) of TiO_2 single crystal was calculated as follows:

$$Q = \frac{(C_0 - C_t)V}{W}$$

where C_0 (mg/L) is the initial concentration of MB, C_t (mg/L) is the MB concentration at time t, V (L) is the volume of solution, and W (g) is the mass of the TiO₂ single crystal.

Measurements of SERS Sensitivity. Raman spectra were evaluated by a micro-Raman system (Renishaw in Via-Reflex). Before SERS measurements, 5 mg of TiO₂ single crystals were added to 1 mL of MB solution in a centrifuge tube for 30 min. Then 20 μ L of the mixture were transferred to a glass slide (35 mm×25 mm scale) and dried in dark naturally. Raman spectra were obtained using 532 nm laser (0.5 % power) as the excitation light source with 50×objective. The accumulation time was 10 s.

Recyclability experiment. The substrates were recycled by photo-degradation after SERS characterization of the MB adsorbed on TiO_2 single crystal: 100 µL of water was dropped on the used substrates. Then the substrate was irradiated with a 300 W Xenon lamp equipped with a solar simulator (AM 1.5) for 30 min and then dried in air. The Raman spectra were used to evaluate the degradation degree of MB. This process was continued until no Raman signal of MB could be found. The cycles were repeated for 4 times on each sample to check the reusability of TiO_2 single crystals.

First-principle density functional theory calculation. All calculations were carried out using the density functional theory (DFT) within the generalized-gradient approximation¹ in Materials Studio package (Accelrys Inc.), with the exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE). The spin-polarized DFT + U calculation with the addition of on-site Hubbard U repulsion of 3.3 eV on the Ti 3d orbitals was performed using the CASTEP module to understand the formation of polaron on the surface and sublayer of $\{0 \ 0 \ 1\}$ and $\{1 \ 0 \ 1\}$ facet. MB adsorption calculation was performed in DMOL3 module. Ultrasoft pseudopotentials were used to describe the ionic cores. The wave functions were expanded in a plane wave basis set with a cutoff energy of 300 eV and the gamma k point grid was adopted. The geometries

were optimized using a BFGS method. The atomic structures were relaxed until the forces on all unconstrained atoms were less than 0.05 eV/Å.

Characterizations. Field-emission scanning electron microscopy (FE-SEM) image was collected on S4800 electron microscope operated at an acceleration voltage of 15.0 kV. The X-ray diffraction (XRD) pattern was obtained on a Rigaku D/max 2550 VB/PC apparatus. UV-visible absorbance spectra were achieved for the dry pressed disk samples using a Scan UV-Vis spectrophotometer (Varian, Cary 500) equipped with an integrating sphere assembly, using BaSO₄ as a reflectance sample. X-Ray photoelectron spectroscopy (XPS) was performed on Perkin-Elmer PHI 5000CESC system quipped with Al K α X-ray.

Finite-difference time-domain (FDTD) Simulation: The electric field distribution of TiO_2 single crystals was simulated with the well-established 3D-FDTD method² using the commercial software (FDTD Solutions, Lumerical Inc.). The simulation volume was performed with perfect match layer (PML) conditions along z-direction to simulate a large area pattern. The refractive index of TiO_2 was adopted from the database. The 3D-model was illuminated with a plane-wave total-field scattered-field source (TFSF source) of 532 nm and the electric field was collected by corresponding monitor surrounding the TiO_2 single crystals.

Enhancement factor (EF) measurement. 20 μ L of the mixture of TiO₂ single crystal and 10⁻⁵ M MB was dropped on the glass slide and dried at room temperature. As a comparison, 20 μ L of 10⁻² M MB aqueous solution was dropped on a glass slide. Raman spectra were obtained using 532 nm laser (0.5 % power) as the excitation light source with 50×objective, and the accumulation time was 10 s.

Calculation of SERS enhancement factor (EF)

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{bulk}/N_{bulk}}$$
(1)
$$N_{SERS} = CVN_A \frac{A_{Raman}}{A_{Sub}}$$
(2)

$$N_{bulk} = N_A \frac{\rho h A_{Raman}}{M}$$
(3)

I_{SERS} and I_{bulk} are the intensities of the selected Raman peak (1626 cm⁻¹) in the SERS and non-SERS spectra, and N_{SERS} and N_{bulk} are the average number of molecules in scattering area for SERS and non-SERS measurement. A_{sub} is the area of the substrate. The data for MB (10⁻² M, aqueous solution) on bare glass was used as non-SERS-active reference. Specifically, the intensity was obtained by taking average from measurements of 30 spots, and the number of analyte molecules was estimated by Supplementary equation (2) on the assumption that the analyte molecules were distributed uniformly on the substrates. C is the molar concentration of the analyte solution, V is the volume of the droplet, NA is Avogadro constant. ARaman is the laser spot area (1 µm in diameter) of Raman scanning. Twenty microliters of the droplet on the substrate was spread into a circle of about 5 mm in diameter after solvent evaporation, from which the effective area of the substrate, A_{Sub}, can be obtained. The confocal depth (h) of the laser beam is 21 µm, and on the basis of molecular weight (M) and density (p) of bulk MB (1 g cm⁻³), N_{bulk} is calculated by Supplementary equation (3). $I_{SERS} = 47380$ and $I_{bulk} = 376$, substituting these values into equation (1), EF was calculated about 8.1×10^5 .

 $S_{001} = 2a^2$

Equation S1:

$$S_{101} = 8(\frac{1}{2}CE \times b - \frac{1}{2}CD \times a)$$

$$S_{001} \% = \frac{S_{001}}{S_{001} + S_{101}}$$

$$= \frac{2a^2}{2a^2 + 8(\frac{1}{2}CE \times b - \frac{1}{2}CD \times a)}$$

$$= \frac{a^2}{a^2 + 4(\frac{1}{2} \times \frac{\frac{1}{2}b}{\cos\theta} \times b - \frac{1}{2} \times \frac{\frac{1}{2}a}{\cos\theta} \times a)}$$

$$= \frac{a^2}{a^2 + \frac{b^2 - a^2}{\cos\theta}}$$

$$=\frac{\cos\theta}{\cos\theta+\frac{b^2}{a^2}-1}$$

Equation S2:

$$C^{-2} = \left(\frac{2}{e\varepsilon\varepsilon_0 N_d}\right) [E - E_{fb} - Kt/e]$$

Carrier concentration is calculated through the slope of the Mott-Schottky plot, where e is the electron charge, ε is the dielectric constant of anatase, ε_0 is the permittivity of vacuum, N_d is the dopant density, and C is the capacitance derived from the electrochemical impedance obtained at each potential (V) with 3000 Hz frequency.



Figure S1. SEM image of anatase TiO_2 (S₀₀₁20%) single crystals.



Figure S2. (a) The growth of anatase TiO₂ along {0 0 1} and {1 0 1} directions according to the Wulff construction; (b) Anatase single crystal with two flat and square {0 0 1} facets featuring 100% unsaturated Ti5c and O2c, and the eight isosceles trapezoidal {1 0 1} facets composed of 50% Ti5c; (c) Slab models of anatase TiO₂ {0 0 1} (left) and {1 0 1} facets.



Figure S3. SEM image of anatase TiO_2 single crystal before the calcination.



Figure S4. (a) XRD pattern, (b) UV-Vis absorption and (c) survey XPS spectra of TiO₂ single crystals.



Figure S5. SEM images of (a) TiO_2 (S₀₀₁12%) single crystals, (b) TiO_2 (S₀₀₁35%) single crystals and (c) TiO_2 (S₀₀₁45%) single crystals.

To further explore the effect of $\{0\ 0\ 1\}$ facet ratio, TiO₂ (S₀₀₁15%) single crystal was also prepared, which is between TiO₂ (S₀₀₁12%) single crystal and TiO₂ (S₀₀₁20%) single crystal as a transition (The corresponding SEM image was shown in Figure S6a). As presented in Figure R6b, the SERS activity obtained from as-prepared TiO₂ (S₀₀₁15%) single crystals is better than the TiO₂ (S₀₀₁12%) but worse than the TiO₂ (S₀₀₁20%) sample, which further demonstrated TiO₂ single crystals with 20% percentage of $\{0\ 0\ 1\}$ facets have the highest SERS activity among all TiO₂ single crystals.



Figure S6. (a) SEM image of TiO₂ (S₀₀₁15%). (b) SERS spectra of MB (10⁻⁵ M) adsorbed on TiO₂ (S₀₀₁20%), TiO₂ (S₀₀₁15%) and TiO₂ (S₀₀₁12%) single crystals.



Figure S7. (a) SERS spectra of MB (10⁻⁵ M) adsorbed on TiO₂ (S₀₀₁45%) single crystals and P25. The simulated electric field of (b) TiO₂ (S₀₀₁45%) single crystals, (c) TiO₂ (S₀₀₁12%) single crystals, (d) TiO₂ (S₀₀₁20%) single crystals and (e) TiO₂ (S₀₀₁35%) single crystals.



Figure S8. SERS spectra of (a) CV (10^{-5} M), (b) 2, 4-DCP(10^{-4}) and (c) PATP (10^{-5} M) on the TiO₂ ($S_{001}20\%$) single crystal before and after calcination.



Figure S9. (a) The SERS spectra recorded from 10 random positions on TiO_2 (S₀₀₁20%) single crystals. (b) The corresponding relative standard deviation (RSD) for 1625 cm⁻¹ band based on 10 random positions.



Figure S10. SERS spectra of MB (10^{-5} M) on TiO₂ (S₀₀₁20%) single crystal after exposure to laboratory atmosphere for different times.



Figure S11. (a) Raman monitoring of MB adsorbed on TiO₂ single crystal under the irradiation of simulated solar light; (b) SERS spectra of 10⁻⁵ M MB on TiO₂ single crystal before and after photocatalytic self-cleaning for 4 cycles.



Figure S12. Adsorption isotherms of MB on the TiO_2 (S₀₀₁20%) single crystal before and after calcination.



Figure S13. Adsorption isotherms (a) and maxima adsorption capacity (b) of MB on different crystals.



Figure S14. The calculated work function of the (a) $\{0 \ 0 \ 1\}$ surface, (b) edge site / <1 0 0> surface and (c) $\{1 \ 0 \ 1\}$ surface.

Band alignment The band alignment in Figure 4c was determined by the calculated DOS results as presented in Figure 4b. Although the band gap of facets is obtained by the theoretical calculations, DFT is formally exact for estimating the band gap center (BGC), noted by $E_{BGC.}^3$ And then, the valence band maximum (VBM) and the conduction band minimum (CBM) can be calculated by the following equation:

$$E_{VBM} = E_{BGC} - 1/2Eg$$
(3)

$$E_{CBM} = E_{BGC} + 1/2E_g \tag{4}$$

where E_g represents the energy gap originated from experimental result, i.e., 3.18eV and 3.22 eV for the {0 0 1} and {1 0 1} surfaces of TiO₂, respectively.⁴ Considering the experimental E_g of the edge sites is not measured, the average value of the {0 0 1}

and {1 0 1} surfaces is used as this experimental value. In addition, the work function W, which is defined as the minimum energy for extracting an electron from the surface of a material to the vacuum level, also affects the band alignment in determining the conduction band and valence band positions. The calculated work function results is shown in Figure S7. As a result, the E_{BGC} relative the vacuum level is defined as $E'_{BGC}=E_{BGC}$ -W. Then, the CBM and VBM relative the vacuum level can be aligned.



Figure S15. The photoluminescence (PL) emission spectrum of TiO₂ single crystal.

Two peaks located at ca. 451 and 470 nm are from the band-edge free excitons, and the other two peaks at ca. 483 and 493 nm are associated with bound excitons. Additionally, the highest photoluminescence intensity was shown in TiO_2 (S₀₀₁45%) single crystals, while TiO_2 (S₀₀₁20%) single crystals show the weakest intensity among all samples, which is in accordance with their SERS activity. It can be further concluded that rich-vacancies defect with the high percentage of {0 0 1} facets would contribute to poor SERS activity.



Figure S16. Mott-Schottky plots of different TiO₂ samples.

The EE concentrations of TiO₂ (S₀₀₁20%) before and after slight etching are calculated as 4.02×10^{18} and 5.11×10^{18} cm⁻³ using Equation S2.



Figure S17. SERS spectra of MB (10⁻⁵ M) adsorbed on TiO₂ (S₀₀₁20%) single crystals under 532 nm and 785 nm laser.



Figure S18. UV-Vis absorption spectra of TiO_2 single crystal and PNTP (10⁻³ M) complex before and after UV irradiation.



Figure S19. Photocatalytic reduction of PNTP on (a) TiO_2 ($S_{001}20\%$) and (b) TiO_2 ($S_{001}45\%$) single crystal; (c) The reaction kinetics on TiO_2 ($S_{001}20\%$) and (b) TiO_2 ($S_{001}45\%$).

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