Supporting Information

Pressure-induced Photoconductivity Enhancement of Black-

TiO_2

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1. Experiment details

Epitaxial film fabrication

Firstly, SrTiO₃ (001) substrate was pre-annealed at under vacuum condition (5×10^{-5} Pa) for 30 min at 950 °C to achieve sharp step-and-terrace surfaces. The Sr₃Al₂O₆ layer was grown first on top of the SrTiO₃ (001) substrate followed by the growth of amorphous TiO_{2-x} film by pulsed laser deposition using a 248 nm KrF excimer laser. The Sr₃Al₂O₆ layer was grown at a substrate temperature 750 °C under vacuum condition for 10 min, using 1.5 J cm⁻² laser fluence and a repetition rate of 2 Hz. Amorphous TiO_{2-x} film was grown at 100 °C under vacuum condition for 20 min by using 1.5 J cm⁻² laser fluence and a repetition for 20 min by

Release of freestanding membranes

Firstly, the amorphous TiO_{2-x} film surface was adhered onto the polydimethylsiloxane (PDMS) surface. Then, the structure was immersed into room-temperature filtered deionized water to dissolve the $Sr_3Al_2O_6$ layer. Finally, we transferred the amorphous TiO_{2-x} thin film on the PDMS onto the diamond surface using a transfer stage.

In situ high-pressure characterizations

The high-pressure characterizations of black-TiO₂ and white-TiO₂ nanocrystals were provided by symmetrical diamond anvil cell (DAC). Type II-a diamonds with a culet size of 400 μ m were chosen to measure the Raman spectroscopy, while type I-a diamonds were used to measure resistance and photocurrent. A stainless-steel gasket was indented to 50 μ m in thickness followed by laser-drilling the central part to form a 200 μ m diameter hole to serve as the sample chamber. The pressure was determined by the ruby fluorescence method.¹

In situ Raman spectroscopy

In situ Raman spectra were collected in the range of 100-1000 cm⁻¹ by Renishaw Raman

microscope. A laser excitation wavelength of 532 nm was utilized. Neon was used as the pressure-transmitting medium.

In situ electrical transport measurement

The resistance of balck-TiO₂ and white-TiO₂ nanocrystals were determined using a Keithley 4200A semiconductor characterization system. NaCl powders were used as the pressure-transmitting medium. The resistivity (ρ) was determined by the ρ = RS/L, where R was resistance measured by the 4-point probes method and S and L are the cross-sectional area and distance of the sample between the two electrodes, respectively. The black-TiO₂ and white-TiO₂ nanocrystals sample were pressed into a 100 × 40 µm²× 10 µm sheet and used to test the electrical transport measurement.

In situ high-pressure photocurrent measurements

The black-TiO₂ and white-TiO₂ nanocrystals sample were pressed into a 150×60 μ m²× 10 μ m sheet and used to test the photocurrent. The photocurrent was collected by the Keithley 4200A semiconductor characterization system by applying a bias voltage of 0.1 V, and a 360 nm laser was chosen as the light source. The photoconductivity (σ) was calculated by the following equation²:

$$\sigma = \frac{I \times l}{U \times S}$$

where U is bias voltage, I is photocurrent, and S and l are the cross-sectional area and distance of the sample between the two electrodes, respectively. The incident monochromatic light-to-electron conversion efficiency (IPCE) is an important parameter for evaluating the photoelectric conversion efficiency of semiconductor materials, and its calculation formula is shown in the following equation^{3, 4}:

$$IPCE = \frac{|j_p - j_d| \times 1240}{P_{in} \times \lambda}$$

where j_p refers to the photocurrent density, j_d refers to the dark current density, λ refers to the wavelength of the incident monochromatic light, and P_{in} refers to the optical power density received by the photoelectrode. The monochromatic light used is a 360 nm light source with a power density of 25 mW/cm².

First-principles calculations

All calculations were done in the framework of density functional theory (DFT)^{5, 6} using the projector augmented wave (PAW)^{7, 8} pseudopotential method, as implemented in the VASP package.^{9, 10} The electron exchange-correlation functional was treated in generalized gradient approximation as proposed by Perdew-Burke-Ernzerhof (PBE). The valance electrons were considered as $3s^23p^63d^34s^1$ for Ti, and $2s^22p^4$ for O. The kinetic energy cutoff for the plane-wave basis set expansion was set to 600 eV in all cases to avoid Pulay stress. The Brillouin zone is sampled by a Γ -centered Monkhorst mesh with 0.2 Å⁻¹ as the spacing between *k*-points. The energy convergence of 1.0×10^{-6} eV was used for the electronic energy minimization steps. The convergence tolerance for all atomic positions calculations was set to be 1.0×10^{-2} eV/Å.

Packing Factor Model

Crystal packing factor (PF) is a widely used crystal-structural parameter, which is computed by dividing the sum of spherical ion or atom volumes by the unit-cell volume,^{11, 12}

$$PF = Z \sum_{i}^{V_i} \frac{V_i}{V_{cell}}$$

where Z is the number of primitive unit cells; V_i is the ionic volume of each atom in the unit cell, calculated from the Shannon radius; V_{cell} is the volume of the unit cell.

The PF model was applied to assess charge separation, transport abilities, and photocatalytic activities in materials with similar compositions or structures. An open structure (lower PF value) allows for greater atomic vibration, resulting in a higher transient polarizing field. A more polarizable structure leads to a larger exciton Bohr radius and thus a longer carrier lifetime.¹² Additionally, a structure with a lower PF is generally more deformable, which reduces the polaron hopping barrier, thereby enhancing mobility.¹¹ This combination of increased carrier lifetime and mobility contributes to higher electrical conductivity. For instance, in TiO₂, electron transport in the anatase phase surpasses that in rutile, which the PF model explains by anatase's lower PF value (64.6%) compared to rutile (70.5%). Specific PF values for various TiO₂ phases are listed in Table S1.

2. Supplementary Figures and Tables



Fig. S1. The Raman spectra measurements of the white-TiO $_{\rm 2}$ and black-TiO $_{\rm 2}$ nanocrystals



Fig. S2. The XRD patterns of the white- TiO_2 and black- TiO_2 nanocrystals.



Fig. S3. (a)The Absorption spectra and (b) the bandgap of the white- TiO_2 and black- TiO_2 nanocrystals. The bandgap was determined by the Tauc plot method.



Fig. S4. Raman spectra of black-TiO₂ nanocrystals under pressure (a) 0.0-17.6 GPa and (b) 18.1-40.5 GPa.



Fig. S5. (a) Pressure-dependent Raman spectra of white- TiO_2 nanocrystals. (b) Raman mode frequency evolution of white- TiO_2 nanocrystals under pressure.



Fig. S6. Raman spectra of white- TiO_2 nanocrystals under pressure (a) 0.0-17.6 GPa and (b) 18.1-40.5 GPa.



Fig. S7. Photocurrent of the black-TiO₂ nanocrystals under pressure during compression (a) 0.0-17.7 GPa; (b) 17.7-39.8 GPa.



Fig. S8. Photocurrent of the white- TiO_2 nanocrystals under pressure during compression (a)0.0-18.0 GPa; (b) 18.0-39.7 GPa.



Fig. S9. IPCE spectra of the black-TiO₂ and white-TiO₂ nanocrystals collected at 0.1 V as a function of pressure.



Fig. S10. Photocurrent-time curve of black-TiO₂ at 17.7 GPa.



Fig. S11. The evolution of photoconductivity of (a) black-TiO₂ and (b) white-TiO₂ nanocrystals as a function of pressure.



Fig. S12. Pressure-dependent resistivity of the white- TiO_2 .



Fig. S13. The absorption spectra of amorphous TiO_{2-x} film under pressure during (a) 0.0-17.7 GPa and (b) 17.7-40.2 GPa.



Fig. S14. Compressibility along different lattice axes by DFT calculations for (a) rutile phase and (b) baddeleyite phase under pressure. Calculated unit cell volume for (c) rutile phase and (d) baddeleyite phase as a function of pressure.



Fig. S15. The calculated bandgap of the rutile and baddeleyite phase TiO_2 with (without) defect states.

Phase	Crystal system	Space group	Density (g/cm ³)	PF (%)
anatase	tetragonal	I4 ₁ /amd	3.895	64.6
rutile	tetragonal	P4 ₂ /mnm	4.248	70.5
TiO ₂ -II	orthorhombic	Pbcn	4.329	71.6
baddeleyite	monoclinic	$P2_1/c$	5.092	78.1

Table S1. The structure and PF values of different phases of TiO₂.^{13, 14}

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