Supplementary Information

In-situ growth of M-{001}TiO_2/Ti phototelectrode: synergetic dominated {001} facet and ratio-optimally surface junctions for effective oxidation of environment pollutants

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Experimental

Reagents and materials

Acetone, ethyl alcohol and dimethyl phthalate (AR) were purchased from Sinopharm (Shanghai, China). Sodium sulfate, hydrofluoricacid (HF, ≥38 wt %) and ethanol were obtained from Aladdin Co. (Shanghai, China). All reagents were used without further purification. Titanium foil substrate ≥99.99%.

Synthesis of {001}TiO_2/Ti

Ti foils were first mechanically polished with different abrasive papers and washed in distilled water and ethyl alcohol and acetone by ultrasonic. Then, a mixed solution of 38 wt% HF (27μL) and deionized water (30 mL) was transferred to a 100 mL Teflon-lined stainless steel autoclave with a clean Ti flat surface, and kept at 180℃ for different time(2h, 3h, 4h, 5h, 6h). Then, it was washed with deionized water, dried, and annealed at 450℃ for 3 h in an air atmosphere to obtain the {001}TiO_2 / Ti.

Characterization

The morphology of materials were demonstrated through scanning electron microscopy (SEM,Hitachi–S4800) and transmission electron microscopy (TEM, JEM-2100, JEOL). The TEM samples was prepared by scraping the F-{001}TiO_2, M-{001}TiO_2 and H-{001}TiO_2 powders off the photoanodes and a very small amount of powders were put into 2 mL of ethanol for ultrasonic dispersion, respectively. The Brunauer-Emmett-Teller (BET) specific surface areas of samples were tested by N_2 adsorption (Micromeritics ASAP 2460). The crystal phase and structures of materials were investigated by a powder X–ray diffraction (XRD, Rigaku–D/max2550) with Cu Kα irradiation. Raman spectra and UV-visible diffuse reflection spectroscopy (DRS) were recorded on a Raman spectrometer (Renishaw Crop.) using a He/Ne laser with the wavelength of 515 nm and UV-VIS-NIR spectroscopy (Agilent Carry 5000). Photoluminescence (PL, F-7000) spectra were performed on a spectrophotometer using a 300 nm excitation wave-length. The PL lifetime were characterized by a time-resolved fluorescence spectrometer (HORIBA Fluorolog-3-11). The electron paramagnetic resonance signals (EPR, Bruker, EMX plus-10/12) were used to detect the active species.

PEC measurement

The photoelectrochemical (PEC) performance was studied through a CHI 660c electrochemical workstation. All PEC measurements were performed in a typical three-electrode cell system wherein the working electrode, counter electrode and reference electrode are {001}TiO_2/Ti, platinum foil and saturated calomel electrode (SCE),respectively. The amperometric i-t method and electrochemical impedance spectroscopy (EIS) were performed in 0.1 mol L^{-1} Na_2SO_4 electrolyte solution. A 150W LA-410UV-3 lamp (Hayashi, Japan) was severed as the UV-Vis light source with 100 mW cm^{-2}. The distance from the working electrode is 1 cm during the PEC process.

Photoelectrocatalytic experiments

The PEC degradation experiment was carried out in a 100 mL quartz tubular reactor with a circulating cooling system kept at a constant temperature of 25℃. A Xe high-pressure short-arc xenon lamp (PLS-SXE300, Perfect Light Technology Co. Ltd., Beijing, China) was used as UV-Vis light source with the irradiance intensity of 200 mW cm^{-2}. The 90 mL DMP of 5 mg/L with 0.1 mol·L^{-1} Na_2SO_4 solution as supporting electrolyte was degraded at a bias of + 0.4 V (*vs*. SCE) applied by a HDY-II potentiostat. The HPLC (Agilent 1260) was used to measure the concentration of DMP during the degradation. The mobile phase was 40:60 (v/v) acetonitrile/water mixture and the flow rate was 1.0 mL/min. And the wavelength of UV detector was 230nm.

EPR measurement

The {001} TiO_2 powders was dispersed into deionized water by magnetic stirring and irradiated with UV-Vis light for a certain time. Then, Pipetting 50 μl of suspension above mixed with 5, 5-dimethypylpyrroline-1-oxide (DMPO) to create DMPO-•OH adducts, and the electron paramagnetic resonance (EPR) signals were measured (Bruker, EMX plus-10/12, microwave frequency, 9.853 GHz; microwave power, 20 mW; modulation amplitude, 1 G; modulation frequency, 100 kHz)

Table S1. Summary of specific surface area, exposed {001} facets ratio, {001}/{101} junction ratios of photoelectrodes.

Sample	**S_{BET} (m^2/g)**	**$S_{\{001\}}^*$ (%)**	**{001}/{101} junction ratio $^\#$ (%)**
M-{001}TiO_2	10.982	100	100
H-{001}TiO_2	11.744	15.4	100
F-{001}TiO_2	7.5380	36.8	<100

*: The percentage of exposed {001} facet, which is calculated by the equation: $S\{_{001\}}$ (%) = $S_{\{001\}}/(S_{\{101\}}+S_{\{001\}}) = a^2/[4ab+a^2]\times 100$, where a and b correspond to the average side length of exposed {001} facets and the thickness of exposed truncated tetragonal pyramids units by measuring more than 20 particles in TEM images.

$^\#$:The {001}/{101} junction ratio of M-{001}TiO_2/Ti is regarded as 100%, and others are given by reference to this.

Table S2. The time-resolved PL electron lifetime, carrier density, ac impedance and photocurrent density of photoelectrodes.

Sample	**τ (ns)**	**Carrier density ($\times 10^{19}$ cm^{-3})**	**R_{ct} (Ω)**	**Photocurrent density ($\times 10^{-4}$ A/cm^2)**
M-{001}TiO_2/Ti	3.20	9.98	210	7.4
H-{001}TiO_2/Ti	2.74	8.86	280	3.0
F-{001}TiO_2/Ti	2.44	3.45	310	1.4

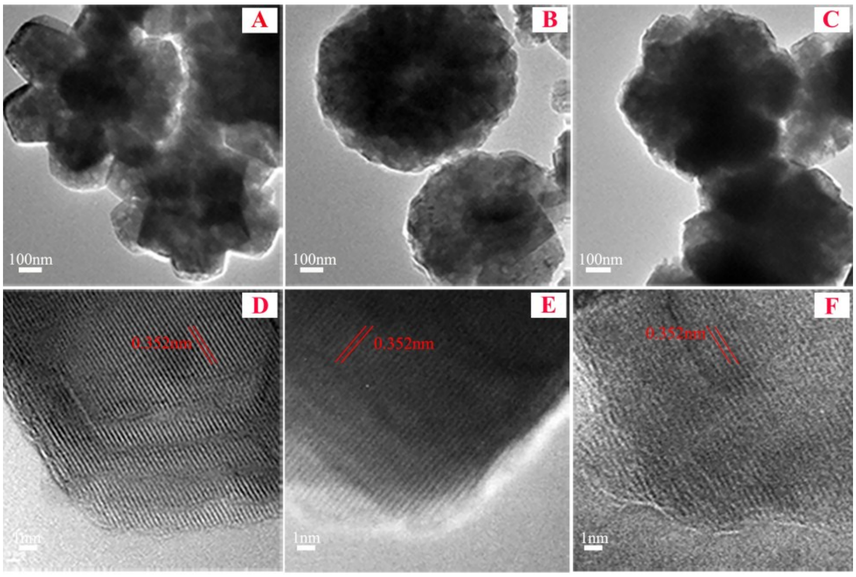

Fig. S1. The TEM images of F-{001}TiO_2/Ti (A), M-{001}TiO_2/Ti (B), H-{001}TiO_2/Ti (C).

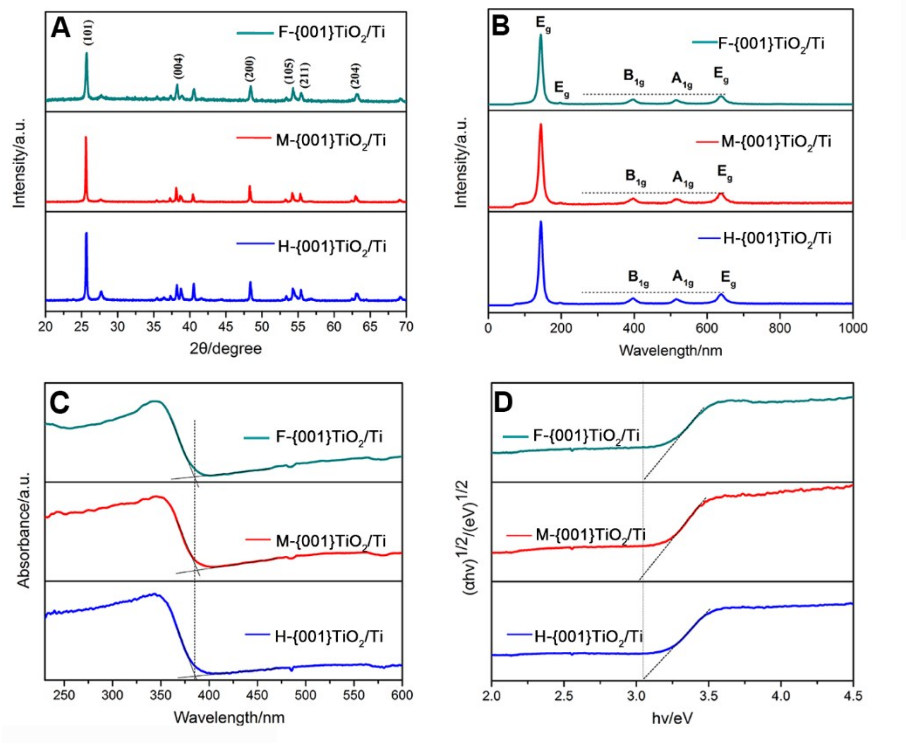

Fig. S2. The XRD (A), Raman (B) spetra, UV-Vis diffuse reflectance absorption (C) spectra and Band gap (D) of photoelectrodes.

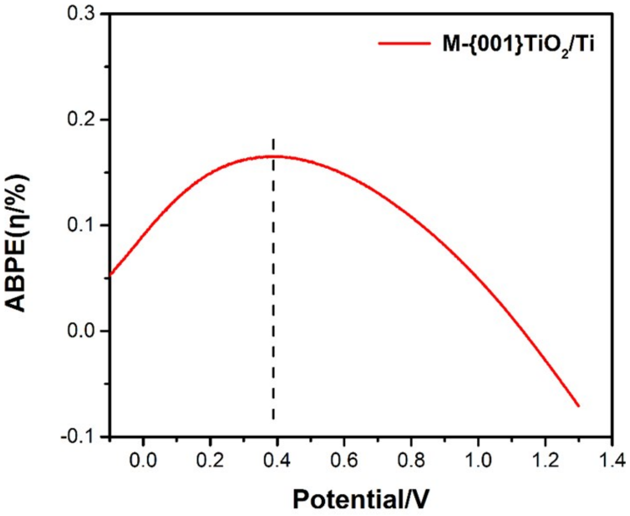

Fig.S3. The Applied bias photo-to-current efficiency (ABPE) of M-{001}TiO_2/Ti.

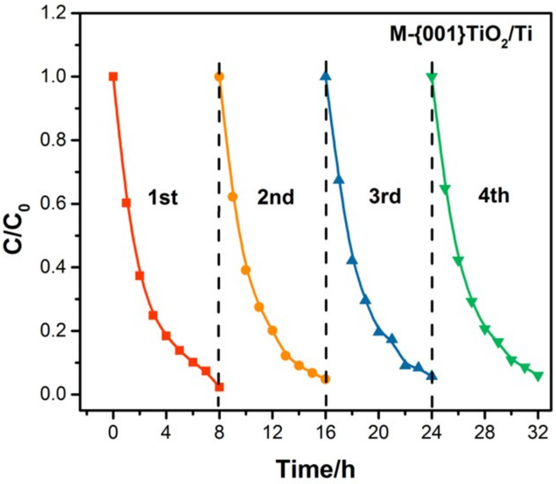

Fig. S4. Cycle experiments for PEC degradation of DMP on M-{001}TiO_2/Ti.

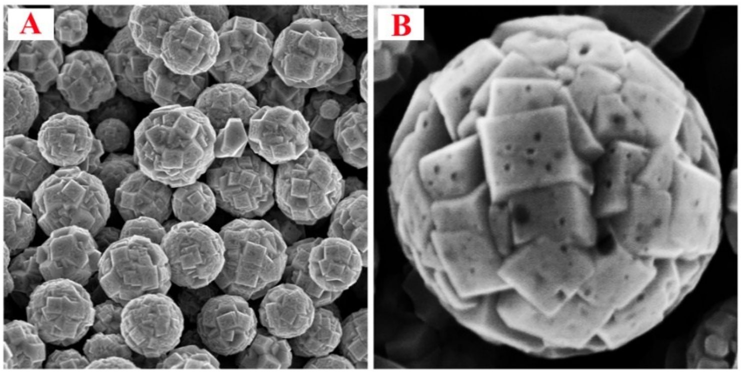

Fig. S5. The SEM images of M-{001}TiO_2/Ti after cycling degradation of DMP.

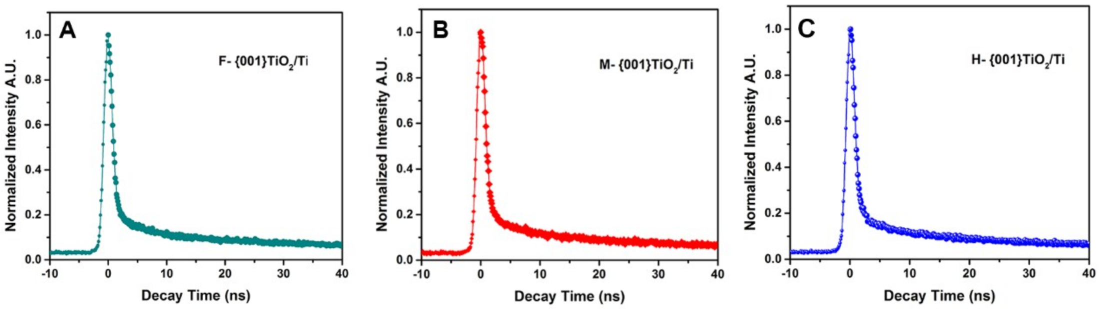

Fig. S6. The The transient fluorescence of F-{001}TiO_2/Ti (A), M-{001}TiO_2/Ti (B), H-{001}TiO_2/Ti (C).