

Defect States-Induced Efficient Hot Electron Transfer in Au Nanoparticles/Reduced TiO₂ Mesocrystal Photocatalyst

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Section 1. Experimental Details

1.1. Synthesis Method

Preparation of TiO₂ mesocrystal (TMC). TMC was prepared from a precursor solution of TiF₄, H₂O, NH₄NO₃ and NH₄F (molar ratio = 1:117:6.6:4). The above precursor was placed on a silicon wafer to form a thin layer with thickness no more than 1 mm. Then, the precursor solution was calcined in the air using a heating rate of 10 °C min⁻¹ at 500 °C for 2h. At last, the obtained powders were calcined at 500 °C in the oxygen atmosphere for 8 h to completely remove the surface residue.

Preparation of reduced TiO₂ mesocrystal (RTMC). RTMC was prepared by reducing TMC using NaBH₄. In detail, 60 mg of as-prepared TMC was mixed with 20 mg of NaBH₄ and the mixture was ground for 10 min thoroughly. Then the mixture was calcined at 350 °C in the Ar atmosphere for 20 min. After naturally cooling down to the room temperature, the obtained powders were washed with Milli-Q ultrapure water several times to remove unreacted NaBH₄, and dried at 60 °C. Finally, RTMC with blue color was obtained.

Preparation of Au nanoparticles (NPs). 1.5 mL of HAuCl₄ solution (1 wt %) was dissolved in 99 mL of Milli-Q ultrapure water in a three-neck round-bottom flask which was equipped with a reflux condensing tube and heated to 100 °C. Under vigorous stirring, 1.2 mL of sodium citrate (1 wt %) was added, and the reaction

mixture was maintained at the boiling temperature for further 30 min before cooling down to room temperature. Finally, the colloidal solution of Au NPs was obtained.

Preparation of Au/TMC and Au/RTMC. 20mg of TMC was mixed with 40 mL of Au colloidal solution and sonicated for 2 min. The solvent of this suspension was evaporated by a rotary evaporator and then the obtained powders were calcined in air using a heating rate of 10 °C min⁻¹ at 500 °C for 0.5 h. The powders were again dispersed in water, sonicated in an ultrasonic bath, and centrifuged at 9500 rpm to remove the weakly attached Au NPs. Finally dried at 60 °C, Au/TMC was obtained. Au/RTMC was prepared by following the same method as Au/TMC, except for replacing TMC with RTMC.

1.2. Characterization

The samples were characterized using X-ray diffraction (XRD, Rigaku, Smartlab; operated at 40 kV and 200 mA, Cu K α source), scanning electron microscopy (SEM, JEOL, JSM-6330FT), high resolution transmission electron microscopy (HRTEM, JEOL, JEM 3000F; operated at 300 kV), The XPS measurements were carried out on a PHI X-tool 8ULVAC-PHI instrument. The steady-state absorption spectra were conducted on a UV-vis-NIR spectrophotometer (Jasco, V-570) at room temperature. The Photoelectron yield spectroscopy (PYS) was carried out at excitation photon energies in the range of 4.0 to 9.0 eV with D₂ lamp using a Bunkou-keiki BIP-KV202GD in vacuum.

1.3. Photocatalytic Activity Tests

For typical photocatalytic runs, 2 mg of as-prepared sample was dispersed into a mixture of 2 mL of methylene blue (MB) aqueous solution (1.0×10^{-5} M) and 0.5 mL of tert-butyl alcohol (TBA) in a quartz cuvette with circulating cooling water to keep the reaction temperature constant. Prior to illumination, the mixed suspension was magnetically stirred in the dark for 30 min to obtain the adsorption-desorption equilibrium. Subsequently, the suspension with continuous stirring was irradiated under a Xe lamp (Asahi Spectra, HAL-320; 350 mW cm⁻²) equipped with a 420 nm cutoff filter at room temperature. After the visible illumination was stopped, the

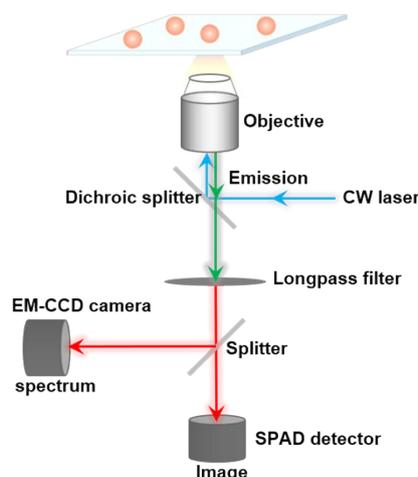
sample was centrifuged at 9500 rpm to remove the particles. The concentration of unreacted MB molecules was analyzed by a UV–vis spectrophotometer (Shimadzu, UV-3100) at the characteristic wavelength. After the last photodegradation run, the precipitates after centrifugation were recovered, washed and dried, and reused four times to test the photocatalytic stability of as-prepared samples.

1.4. Sample Preparation for Single-particle Photoluminescence (PL) Experiments.

Samples were dispersed on the cover glasses in prior to the single-particle PL measurements. In detail, the cover glasses were firstly cleaned by sonication in a 20% detergent solution for 7 h, followed by repeated washing with warm water 5 times. The colloidal solution of Au NPs was centrifuged and then washed by water several times. Au NPs, Au/TMC and Au/RTMC were dispersed in water to form a well-dispersed aqueous suspensions. Subsequently, the above suspensions were spin-coated on the cleaned cover glass. The cover glass was annealed at 80 °C for 1 h to immobilize the particles on the surface.

1.5. Single-Particle PL Measurements by Confocal Microscopy.

Single-particle PL images and spectra were recorded by using an objective scanning confocal microscope system (PicoQuant, MicroTime 200) coupled with an Olympus IX71 inverted fluorescence microscope (Scheme S1).



Scheme S1. Experimental setup of confocal microscopy for single-particle PL measurement.

The samples were excited through an oil-immersion objective lens (Olympus, UplanSApochromat, 100 \times , 1.4 NA) a circular-polarized 488 nm continuous wave (CW) laser controlled by a PDL-800B driver (PicoQuant). Typical excitation powers for the PL measurements were 300 μ W at the sample. The emission from the sample was collected by the same objective and detected by a single-photon avalanche photodiode (SPAD, Micro Photon Devices, PDM 50CT) through a dichroic beam splitter (Chroma, 488rdc) and long pass filter (Chroma, HQ513CP). For the spectroscopy, only the emission that passed through a slit entered the imaging spectrograph (Acton Research, SP-2356) that was equipped with an electron-multiplying charge-coupled device (EMCCD) camera (Princeton Instruments, ProEM). The spectra were typically integrated for 10 s. The spectrum detected by the EMCCD camera was stored and analyzed by using a personal computer. The PL spectra were not fully displayed because the above pass filter (>513 nm) was inserted to completely remove the excitation light. All the experimental data were obtained at room temperature.

1.6. Finite-difference Time-domain (FDTD) Calculations.

The enhancement of electric field at the interface of Au/TiO₂ was calculated by using a software package, FDTD Solutions 8.19 (Lumerical Solutions, Inc.). During simulations, an electromagnetic pulse in the wavelength range from 400 to 700 nm was launched into a box containing a target nanostructure. The override mesh cell size used was $1 \times 1 \times 1$ nm³. The model can be described as a gold nanosphere of 50 nm in diameter supported on a TiO₂ nanosheet of 20 nm in thickness. The optical constants of Au and TiO₂ were adopted from tabulated values bulk gold measured by Johnson and Christy¹ and Hand book of Optical Constants of Solids,² respectively. The refractive index of the medium (water) was set to be 1.33.

Section 2. Supplementary Data

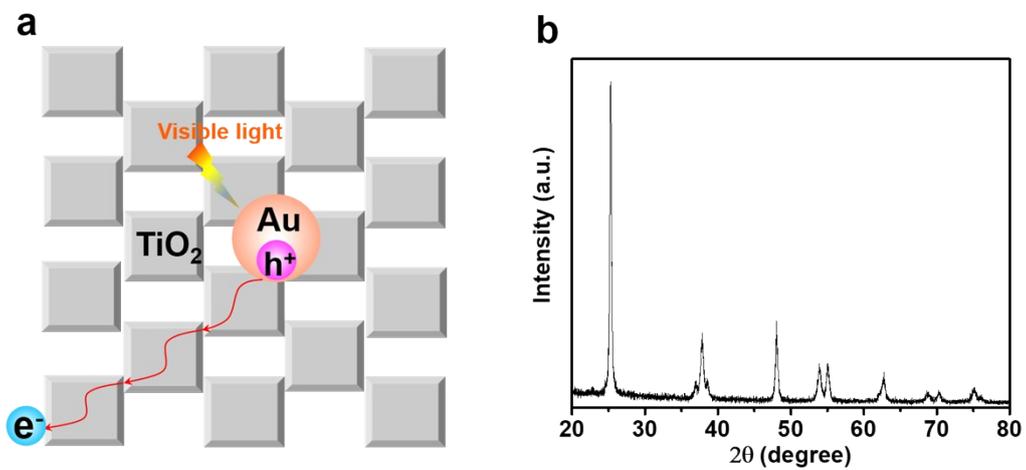


Figure S1. Schematic diagram of the migration of the hot electrons assisted by TMC (a). XRD pattern of TMC (b).

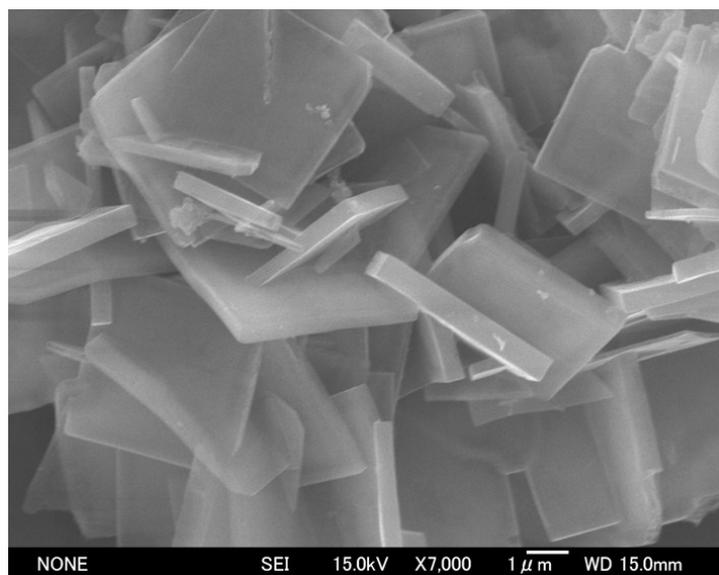


Figure S2. SEM image of RTMC.

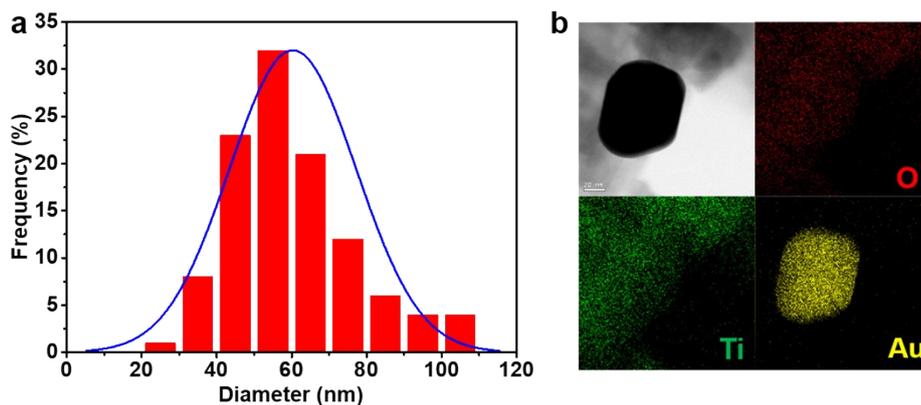


Figure S3. Size distribution of Au NPs in Au/RTMC (a). STEM image and corresponding EDS elemental mapping of Au/RTMC (b).

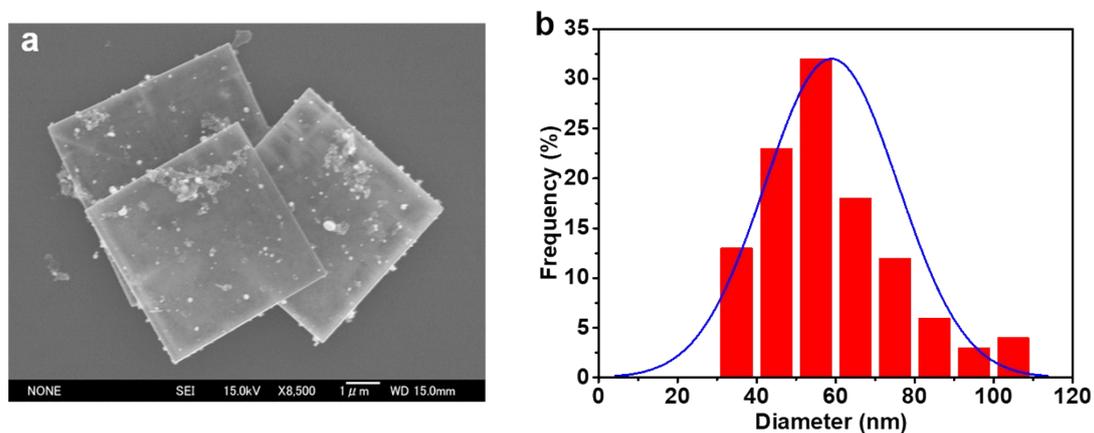


Figure S4. SEM image of Au/TMC (a). Size distribution of Au NPs in Au/TMC (b).

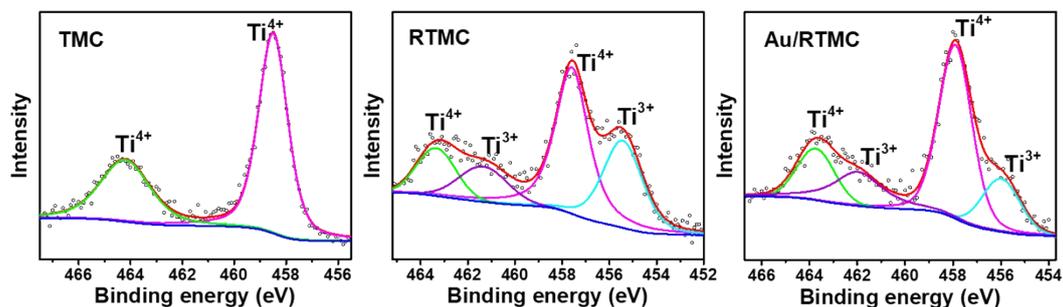


Figure S5. Ti 2p XPS spectra of TMC, RTMC, and Au/RTMC.

Compare to the XPS of TMC, the XPS peak of Ti^{4+} in RTMC shifts to a lower binding energy because partial electrons trapped at O vacancies can transfer to the Ti^{4+} sites, leading to the increase of electron density at Ti^{4+} sites.^{3,4}

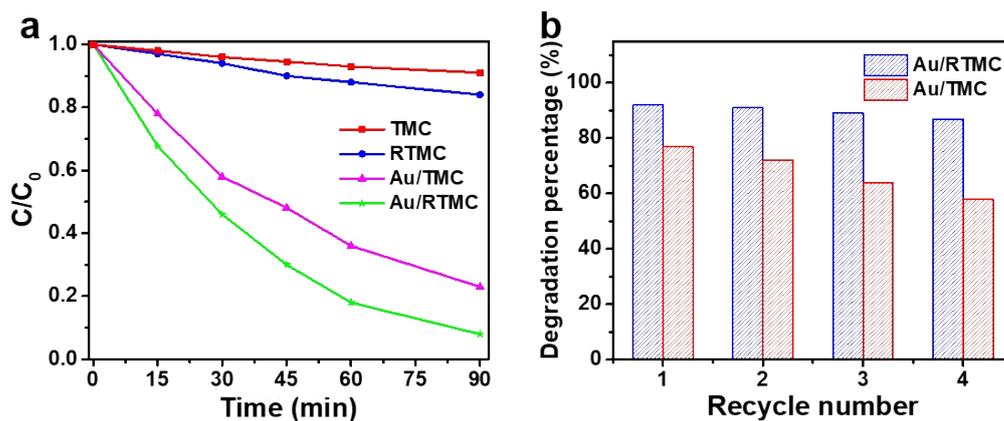


Figure S6. Photocatalytic degradation curves of MB using as prepared-samples under visible-light irradiation ($\lambda > 420$ nm) (a). Recycling test results using Au/TMC and Au/RTMC as the photocatalysts (b). Reaction time for each run: 90 min.

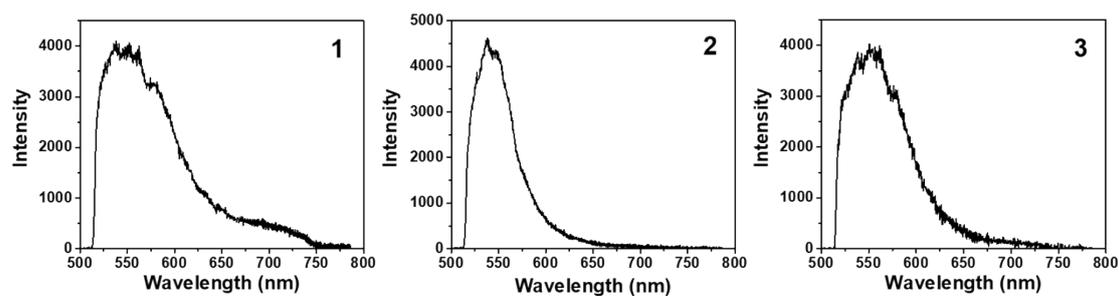


Figure S7. Single-particle PL spectra of Au NPs corresponding to numbered points in Figure 3a.

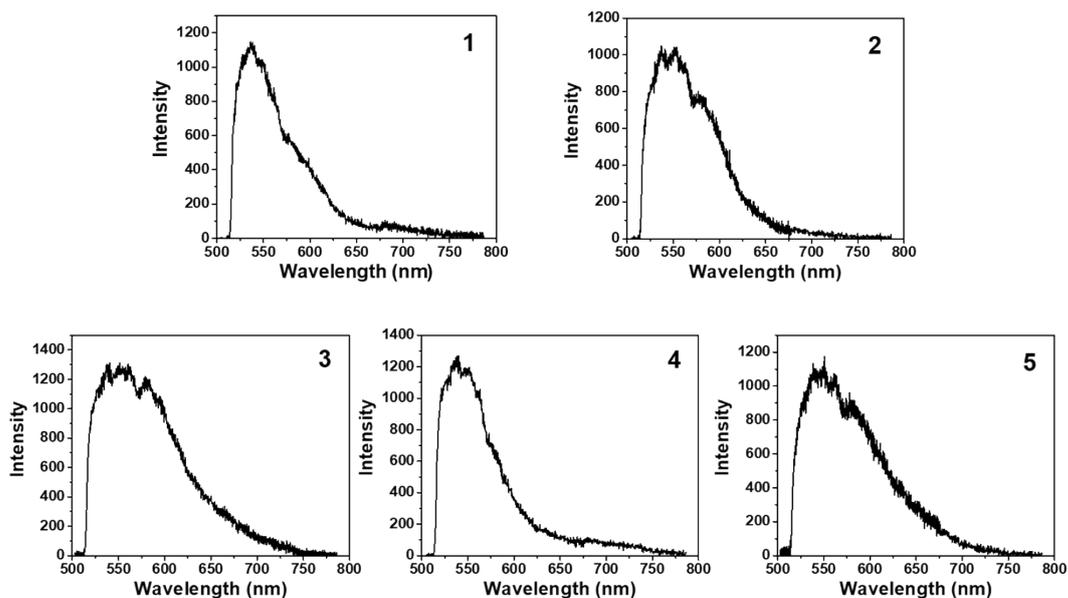


Figure S8. Single-particle PL spectra of Au NPs in Au/TMC corresponding to numbered points in Figure 3b.

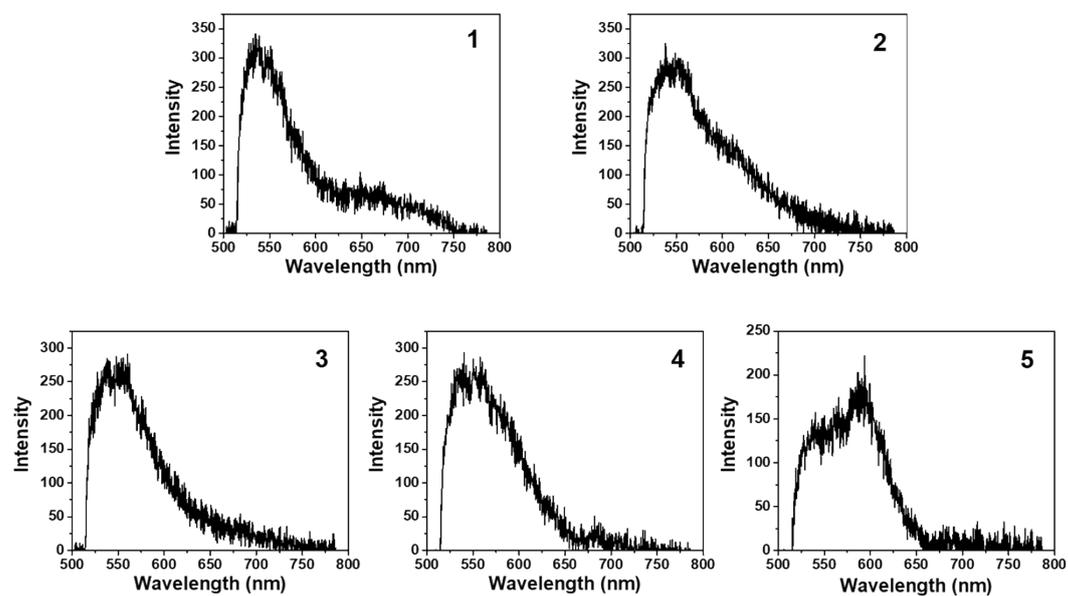


Figure S9. Single-particle PL spectra of Au NPs in Au/RTMC corresponding to numbered points in Figure 3(c).

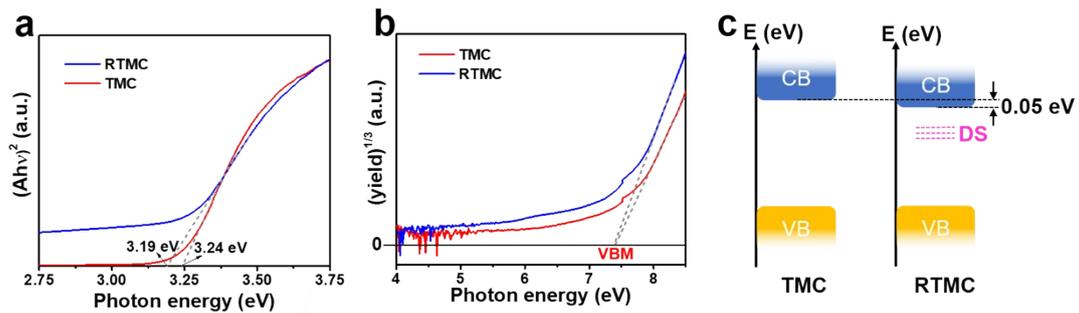


Figure S10. Tauc plot for band gap determination (a). Photoelectron yield spectroscopy (PYS) (b). Band structure diagram (c). DS, defect states.

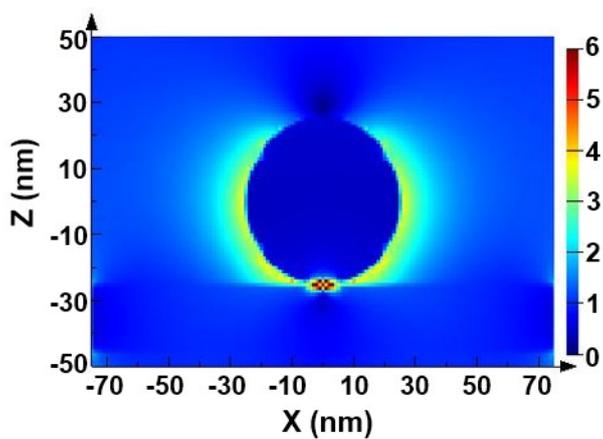


Figure S11. Electric field intensity enhancement contours of the Au/TiO₂ hybrid system under the parallel polarized excitation.

References:

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