Electronic Supplementary Information

Solar-driven plasmonic heterostructure Ti/TiO_{2-x} with gradient doping for sustainable plasmon-enhanced catalysis

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Supplemental Figures (color)



Fig. S1. Atomic force microscopy (AFM) surface topology image of heterostructure Ti/TiO_{2-x}.



Fig. S2. X-ray diffraction (XRD) patterns of the as-prepared Ti foil and the heterostructure Ti/TiO_{2-x}. Reference (Rutile TiO₂, ICSD 9161).



Fig. S3. Dark-field optical images for the Ti foil and Ti/TiO_{2-x}. (**a-c**) Images of the Ti foil with surface structures after etching; **a**, Image took in bright field (scale bar: 5 mm); **b**, Dark-field image in low resolution (scale bar: 500 μ m); **c**, Dark-field image in high resolution (scale bar: 25 μ m). (**d-f**) Images of the Ti/TiO_{2-x}. **d**, Image took in bright field (scale bar: 5 mm); **e**, Dark-field image in low resolution (scale bar: 500 μ m); **f**, Dark-field image in high resolution (scale bar: 25 μ m).



Fig. S4. Absorption spectra of the Ti/TiO_{2-x} with varied thermal oxidation time at 500 °C. The spectra in response to the photons of different wavelengths shows a redshift for higher thermal oxidation time.

Numerical calculations

A model of the heterostructure containing top dielectric nanoparticles and bottom metal substrate parts was approximated. The three-dimensional model was constructed using COMOSL Multiphysics. The simulated model consists a nanoparticle of TiO_2 and a Ti metal substrate which are separated by a nanogap. The gap will be filled with air, gradient increasing of TiO_2 film closer to the real experimental environment. Finite-element numerical calculations in frequency domains were performed to investigate the field intensity enhancement mechanism and further relevance of the field enhancement with optical light absorption enhancement. Convergence tests were firstly performed.



Fig. S5. Model with a nanogap between Ti metal substrate and TiO_2 nanoparticle. **a**, A 3dimensional model for the heterostructure under study. **b**, Cross-section of the model. The incident excitation field at the upper port propagates toward the negative Z direction with TE polarization in the y-direction. The radius of nanosphere TiO_2 particle was fixed to be 10 nm. The nanoparticle is placed above the Ti substrate with a nanogap of 1 nm. Such a gap can be filled with air or a transition dielectric layer.

The calculations were composed of two steps: the first step computes electric field for the substrate solely. Two port conditions were used to solve the full field, with a TE polarized uniform plane

wave incident at the upper port. In the first step, the side boundaries were set to Floquet periodic conditions, extending the geometry infinitely in the xy-plane. The second step solves total electric field with the presence of nanoparticle on the substrate by using the achieved full field solution from the first step as the background field. Perfectly matched layers (PML) with thickness of 100 nm were then used to surround the geometry (Fig. S5). The normalized field intensity enhancement was then calculated as a ratio of the electric field with the nanoparticle to the incident field, $|E|/|E_0|$, at various wavelengths.

The maximum field enhancement was calculated along a horizonal line in the middle gap between the nanoparticle and the substrate. The optical light absorption enhancement was determined from the ratio of the absorbed light in the substrate with and without the nanoparticle, by using the following formula ¹:

 $f_{abs} = \omega \cdot Im(\varepsilon) \iiint |E|^2 dv$ (1), where E(x, y, z) is the calculated electric field and v is the volume of the corresponding geometry.

The model was solved through parametric sweep of wavelength with interval distance of 10nm. The optical constants for the materials, TiO_2 and Ti, were taken from references ²⁻³, respectively. The maximum mesh size was set to 20 nm for the air domain, 3 nm for the nanoparticle domain and 10nm for the substrate. Maximum mesh size of 0.2 nm was used at the surface of the nanoparticle and at the gap. The gap between the nanoparticle and the substrate is filled with dielectric constant of Air and various thickness of TiO_2 thin film, respectively.

(1) In the case that the gap is filled with air



Fig. S6. Spatial field-enhancement when the gap is filled with air. **a**, A cross-sectional view of the spatial field-enhancement ($|\mathbf{E}|/|\mathbf{E}_0|$) distribution in the y-z plane, at 280 nm when a nanoparticle of TiO₂ placed over a Ti substrate with 1 nm gap. **b**, Top view of the spatial field variation in the gap. **c**, Corresponding electric field enhancement $|\mathbf{E}|/|\mathbf{E}_0|$ profile along a horizontal line in the middle of the gap. **d**, Wavelength-dependent spectral plots of the maximum of electric field enhancement in the gap (**Left**), and corresponding wavelength-dependent spectral profile of optical light absorption enhancement (**Right**).

The spatial electric field distribution $(|E|/|E_0|)$ clearly shows highly enhanced field intensity in the gap due to the excitation of surface plasmon polarization in the bottom Ti metal substrate by the top TiO₂ dielectric particle. The local minimum in the electric field profile (Fig. S7c) locates just

in the middle of the gap below the nanoparticle due to the excitation field resulting in the shifting of electrons in the metal substrate. Remarkably, the wavelength of the maximum point of field enhancement is closely in line with the wavelength of the trough in ultraviolet light range. The optical light absorption is much more enhanced in visible light range comparing to ultraviolet light range, even though the field intensity enhancement is slightly decreasing. We attribute the reason to the longer mean free path lengths and deeper penetration depths of photons in visible light range, when interacting in the gap between the top nanoparticle and the Ti metal substrate. (2) In the case that the gap is filled with gradient thickness of TiO_2 thin film



Fig. S7. Enhancement of electric field and light absorption when the gap is filled with 1 nm of TiO_2 thin film. Cross-sectional views of the spatial field-enhancement ($|E|/|E_0|$) distribution in the y-z plane, respectively, at 290 nm (**a**) and at 430 nm (**b**). The gap between the nanoparticle of TiO_2 and the Ti substrate was filled with 1 nm TiO_2 dielectric film. **c**, Wavelength-dependent spectral plots of the maximum of electric field enhancement in the gap (**Left**), and wavelength-dependent spectral profile of optical light absorption enhancement (**Right**).

The electric field is highly enhanced and confined in the gap at the wavelength points of 290 nm and 430 nm. The spatial field shows a stronger electric field distribution through the dielectric film of TiO_2 at 430 nm. As expected, the trough of absorption enhancement locates at 300 nm, while a higher light absorption peak is obtained in the visible light range due to the field enhancement resulting in the photons with longer wavelength more confined.



Fig. S8. Enhancement of electric field and light absorption when the gap is filled with 3 nm and 5 nm of TiO₂ thin film, respectively. **a**, Wavelength-dependent spectral plots of the maximum of electric field enhancement in the gap (**Left**), and wavelength-dependent spectral profile of optical light absorption enhancement (**Right**). The gap between the nanoparticle of TiO₂ and the Ti substrate was filled with **3** nm TiO₂ dielectric film. **b**, Wavelength-dependent spectral plots of the maximum of electric field enhancement in the gap (**Left**), and wavelength-dependent spectral plots of the maximum of electric field enhancement in the gap (**Left**), and wavelength-dependent spectral plots of the maximum of electric field enhancement in the gap (**Left**), and wavelength-dependent spectral plots of the maximum of electric field enhancement (**Right**). The gap between the nanoparticle of TiO₂ and the Ti substrate was filled with **5** nm TiO₂ dielectric film. In the plot (b, left), all the data of $|E|/|E_0|$ are greater than 0 in the y-axis.

With increasing the thickness of TiO_2 dielectric film to 3nm and 5nm, respectively, the intensity of field enhancement is decreasing with a slight red shifting. The maximum points of field enhancement are still in line with the valley of light absorption enhancement. In the visible light range, more light is absorbed due to the field enhancement.



Fig. S9. Enhancement of electric field and light absorption when the gap is filled with 7 nm and 10 nm of TiO₂ thin film, respectively. **a**, Wavelength-dependent spectral plots of the maximum of electric field enhancement in the gap (**Left**), and wavelength-dependent spectral profile of optical light absorption enhancement (**Right**). The gap between the nanoparticle of TiO₂ and the Ti substrate was filled with 7 nm TiO₂ thin film. **b**, Wavelength-dependent spectral plots of the maximum of electric field enhancement in the gap (**Left**), and wavelength-dependent spectral plots of the maximum of electric field enhancement in the gap (**Left**), and wavelength-dependent spectral plots of the maximum of electric field enhancement in the gap (**Left**), and wavelength-dependent spectral plots of the maximum of electric field enhancement (**Right**). The gap between the nanoparticle of TiO₂ and the Ti substrate was filled with **10** nm TiO₂ thin film.

With continually increasing the thickness of dielectric film to 7 nm and 10 nm, the intensity of field enhancement is literally reducing with a red shifting of the maximum of field enhancement. The resonant light absorption enhancement band is observed at around 430 nm corresponding to a field enhancement band. It is noted that the trough in the absorption enhancement spectra are both still in the field enhancement bands.



Fig. S10. Enhancement of electric field and light absorption when the gap is filled with 20 nm of TiO_2 thin film. Cross-sectional views of the spatial field-enhancement ($|E|/|E_0|$) distribution in the y-z plane, respectively, at 340 nm (**a**) and at 440 nm (**b**). The gap between the nanoparticle of TiO_2 and TiO_2 substrate was filled with 20 nm TiO_2 thin film. **c**, Wavelength-dependent spectral plots of the maximum of electric field enhancement in the gap (**Left**), and wavelength-dependent spectral profile of optical light absorption enhancement (**Right**).

When increasing the thickness of TiO_2 dielectric film to 20 nm, the electric filed is still enhanced and confined in the gap with a reduced intensity. Due to the high thickness of dielectric film, more electric field distribution is confined in the interface between the film and the metal substrate, resulting in a higher field enhancement band in the spectra at 440 nm and a resonant absorption band in the absorption enhancement spectra. The spatial field distributions clearly show excitation of two modes of SPPs at 340 nm and LSPRs at 440 nm, respectively. The absorption band is highly enhanced in the visible light range, while the trough in absorption enhancement spectra is still in line with an enhanced electric field band. The coincidence of the enhanced field distribution and optical light enhancement further confirms the modes of SPPs and LSPRs existing in the heterostructure. The results show that it is highly beneficial to have a thin film of surface dielectric with surface nanoparticles to maximize the plasmonic enhancement effect of near-field and resonant light trapping in the structure, plasmon-enhanced generation of charge carriers is highly expected in a wider wavelength spectrum, including the maximum and minimum points of the experimental absorption spectra.



Fig. S11. Photoelectrochemical measurements by employing the heterostructure Ti/TiO_{2-x} as a photoanode. **a**, Mott-Schottky plots of the Ti/TiO_{2-x} in dark and under light conditions at frequency of 1 kHz, respectively. **b-c**, Linear sweep voltammetry of the Ti/TiO_{2-x} photoanode in dark and under light, respectively, at 1 mv/s under illumination of simulated AM 1.5G full-spectrum solar light: **b**, measured in 0.5 M Na₂SO₄ aqueous electrolyte at an incident power density of 100 mW cm⁻²; **c**, obtained in 1M KOH aqueous electrolyte under the different incident power densities.



Fig. S12. IPCE spectra for the first specimen heterostructure Ti/TiO_{2-x} . **a**, IPCE spectra for the first specimen heterostructure Ti/TiO_{2-x} . The inset is a magnified profile of the IPCE with the same unit (×100 %) in the wavelength range of 450 - 500 nm, which shows a rough profile of trough around the 470 nm. **b**, Enhancement peaks by fitting the IPCE spectra to a Gaussian function in the wavelength range of 250 - 400 nm. The peak band (blue line) centered at around 340 nm is attributed to the enhancement by the excitation of plasmon resonances, while the other two enhancement peaks are due to the direct energy conversion in the TiO_{2-x} excited by high energy photons in the range of 280 nm - 325 nm.



Fig. S13. Absorbance spectra and EDX of the Ti foil. a, UV-Vis absorbance spectra of the Ti foil, before and after the coating 2-nm Nickel (Ni) with and without the vacuum annealing at 400 °C.
b, EDX of the Ti foil. EDX analysis was carried out after the Ti foil with annealed Ni thin film. One peak at the energy point of 0.851 KeV is assigned to be from the L shell of Ni.

Thin film of Ni was chosen as the protection material due to its excellent physiochemical properties. Ni metal has been long and widely preferred as a protecting materials and/or a catalyst for efficient and stable catalytic reactions, not only because of its low-cost and Earth-abundance, but also its great corrosion resistance and high catalytic activity. ^{4, 5}

In the Figure S13a, the UV-Vis absorbance spectra show a slight difference between the Ti foils after 2nm-Ni coating with and without the vacuum annealing at 400 °C. We attribute the reason to the nano-thickness of Ni film. Before the annealing, the 2nm-Ni metal film could absorb photons in a specific wavelength range ^{6, 7}, superimposing on the absorption spectrum of Ti foil. But after the annealing process, the 2nm-Ni film could transform into dispersed nanocrystal particles on the surface ^{8, 9}. Depending on the distribution of size and shape, the particles could exhibit a broader absorption spectrum at a small intensity ^{10, 11}. As shown in the Figure S13a, the absorbance of Ni after the annealing process has little effect on the optical absorbance of heterostructure Ti/Ti_{2-x}.



Fig. S14. Absorbance spectra and EDX of the second specimen heterostructure Ti/TiO_{2-x} . **a**, UV-Vis absorbance spectra of the second specimen heterostructure Ti/TiO_{2-x} before the coating 2-nm Ni, after the coating 2-nm Ni with and without the annealing at 400 °C. **b**, EDX of the second specimen Ti/TiO_{2-x} . EDX analysis was carried out after the Ti/TiO_{2-x} with the annealed Ni thin film. One peak at the energy point of 0.851 KeV is assigned to be from the L shell of Ni.



Fig. S15. Current density spectra on a second specimen heterostructure Ti/TiO_{2-x} . Current density versus the wavelength for the second specimen heterostructure Ti/TiO_{2-x} measured under dark and the monochromatic light, respectively. The inset is a magnified profile in the y-axis range closing to zero, which shows an obvious resonant trough profile. The negative enhancement peak is correlated with the surface plasmon resonances.



Fig. S16. Stability test for the third representative specimen Ti/TiO_{2-x} . **a**, Current density as a function of time on the third representative specimen Ti/TiO_{2-x} , under constant AM1.5G solar light illumination with a power density of 100 mW/cm² and a potential of 0.21 V (versus Ag/AgCl) for durable 25 hours. The current shows a tendency to increase over time accompanied by brief rising spikes, which we attribute to the surface corrosion caused directly by photons. **b**, UV-Vis absorbance spectra for the Ti foil and the third specimen Ti/TiO_{2-x}, respectively, took before and after the stability test of 25 hours. After the 25-hour durable test, a significant attenuation of the absorbance intensity is shown.



Fig. S17. Electronical properties of bulk Ti after oxygen doping. After geometry optimization of the bulk Ti, Oxygen elements are doped in the surface, following a convergent geometric optimization. **a**, (Left) Optimized crystal structure of α -Ti and (Right) corresponding total density of states (TDOS). **b**, (Left) Crystal Ti structure with light doping at the surface, four surface edge Ti atoms were replaced by oxygen atoms, and (Right) corresponding partial density of states (PDOS) and TDOS. **c**, (Left) Crystal Ti structure with heavy doping at the surface, four surface

edge Ti atoms were replaced by oxygen atoms and two interstitial oxygen atoms in lattice underneath the surface, and (Right) corresponding PDOS and TDOS.

DFT calculations. All geometry optimizations and electronic density of states of original and doped Ti were performed using DFT with plane-wave basis sets and ultra-soft pseudopotentials ¹²⁻¹³. The generalized gradient approximation by PW91¹⁴ was employed to describe the exchange-correlation interaction with correction. The cutoff energy of the plane wave basis set was set to 450 eV. The surface structures of Ti were built by cleaving the optimized bulk material of a α -Ti crystal. The criteria for doping was to replace one Ti atom at the top of surface with one oxygen atom and introduce interstitial oxygen atom in the crystalline lattice underneath the surface. The K-point grid was set as 10 x 10 x 4 in the irreducible Brillouin zone with Monkhorst-Pack-scheme. The convergence tolerances of total energy, maximum force, maximum displacement and stress were set to 2x10⁻⁶ eV/atom, 0.01 eV/A, 5x10⁻⁴ A, and 0.02 GPa, respectively.



Fig. S18. Schematic illustration of the charge carriers in $\text{Ti}/\text{TiO}_{2-x}$ when immersed in aqueous solution. **a**, Sandwich composition of a bulk Ti foil with oxygen elements doped in the surface. Gradient distribution of oxygen elements develops a thin dielectric film of TiO_2 on the top, a transition region of TiO_{2-x} (0 < x < 2) in the middle and the underlying Ti metal on the bottom. **b**, Slight energy band bending in the surface region of $\text{Ti}/\text{TiO}_{2-x}$ in dark when interfacing with an electrolyte. **c**, Under the solar light irradiance, the Fermi level balance introduces additional band bending. The separated charge carriers are distributed across a wide range of potentials.

References

- R. A. Pala, J. White, E. Barnard, J. Liu, M. L. Brongersma, *Adv. Mater.* 2009, 21, 3504-3509.
- T. Siefke, S. Kroker, K. Pfeiffer, O. Puffky, K. Dietrich, D. Franta, I. Ohlídal, A. Szeghalmi, E.-B. Kley, A. Tünnermann, *Adv. Opt. Mater.* 2016, 4, 1780-1786.
- W. S. M. Werner, K. Glantschnig, C. Ambrosch-Draxl, J. Phys. Chem. Ref. Data, 2009, 38, 1013-1092.
- M. J. Kenney, M. Gong, Y. Li, J. Z. Wu, J. Feng, M. Lanza and H. Dai, *Science* 2013, 342, 836-840.
- 5. I. Roger, M. A. Shipman and M. D. Symes, *Nat. Rev. Chem.* 2017, 1, 0003.
- M. J. Kenney, M. Gong, Y. Li, J. Z. Wu, J. Feng, M. Lanza and H. Dai, *Science* 2013, 342, 836-840.
- N. Ahmad, J. Stokes, N. A. Fox, M. Teng and M. J. Cryan, *Nano Energy* 2012, 1, 777-782.
- 8. V. Starý and K. Šefčik, *Vacuum* 1981, **31**, 345-349.
- D. Q. McNerny, B. Viswanath, D. Copic, F. R. Laye, C. Prohoda, A. C. Brieland-Shoultz, E. S. Polsen, N. T. Dee, V. S. Veerasamy and A. J. Hart, *Sci. Rep.* 2014, 4, 5049.
- 10. D. Li and S. Komarneni, J. Am. Ceram. Soc. 2006, 89, 1510-1517.
- 11 M. Ganjali, M. Ganjali, P. Vahdatkhah and S. M. B. Marashi, *Procedia Materials Science* 2015, **11**, 359-363.
- J. Graciani, L. J. Álvarez, J. A. Rodriguez, J. F. Sanz, J. Phys. Chem. C 2008, 112, 2624-2631.
- 13. R. Long, N. J. English, Y. Dai, J. Phys. Chem. C 2009, 113, 17464-17470.
- J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B* 1992, 46, 6671-6687.