Supporting information for

Enhanced enzymatic reactions by solar-to-thermal conversion nanoparticles

Xiaoling Wu,[a,‡] Gang Ou,[b,‡] Cheng Yang,[a] Jun Ge,*[,a] and Hui Wu*[,b]

[a]*Key Lab for Industrial Biocatalysis, Ministry of Education, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China*

[b]*State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China*

‡*These authors contributed equally.*

To whom correspondence should be addressed.

E-mail: junge@mail.tsinghua.edu.cn; huiwu@tsinghua.edu.cn

EXPERIMENTAL SECTION

Preparation of nanoparticles: Ti_8O_{15} nanoparticles were prepared by a fast arc-melting process. TiO_2, Si and SiO_2 nanopowders (weight ratio, 6:1:13) were uniformly mixed and pressed into pellets at 200 MPa for 30 s, and put in the arc furnace. They were melted by the arc at high temperature (> 3000 °C) and cooled to room temperature within one minute.[1] Then, the melt was ground into powders and the SiO_2 matrix was etched by HF, washed with deionized water, centrifuged and dried for characterization. Finally, Ti_8O_{15} nanoparticles without aggregation can be obtained.

Physical characterization: Crystal structure was characterized by an X-ray diffractometer (D/max-2500, Rigaku) with Cu target. The micrograph was taken via a scanning electron microscopy (JSM-7001F, JEOL). The microstructure was characterized by a transmission electron microscopy (JEM-2010, JEOL). Diffuse reflectance spectra were collected on a UV-Vis-NIR spectroscopy (UV-2600, Shimadzu) from 220 nm to 1400 nm. The valence state and defects were probed by an X-ray photoelectron spectrometer (Escalab 250Xi, Thermo Fisher Scientific). The IR photograph was taken by a thermal infrared imager (IR384, RNO)

Enzyme activity assays: The hydrolytic activity of α-amylase (Sigma-Aldrich) was determined using 2-chloro-4-nitrophenylmaltotrioside (Cnp-G3, J&K Tech) as the substrate.[2] Briefly, Cnp-G3 (5 mM) was first dissolved in 2-(N-Morpholino) ethanesulfonic acid hydrate (MES) buffer (55 mM, pH 6.0) containing 50 mM of sodium chloride, 152 mM of sodium azide and 5 mM of calcium acetate. The substrate solution (1.9 mL) was then equilibrated to specific temperatures for at least 5 min,

followed by adding 100 μL of enzyme solution (1.0 mg/mL) to initiate the enzymatic reaction. In the control experiment, 100 μL of MES buffer was added instead of enzyme solution. After reaction for 30 min, the absorbance of the generated 3-chloro-4-hydroxylnitrobenzene (Chn) at 405 nm was measured using a spectrophotometer (UV-2600, Shimadzu).

The hydrolytic activity of cellulase (Sigma-Aldrich) was determined using filter paper as the substrate according to the standard method.[3] In a typical experiment, 50 mg of filter paper was added into the bottle and saturated with 1 mL of citrate buffer (50 mM, pH 4.8). The mixture was equilibrated to specific temperatures, followed by adding 0.5 mL of cellulase solution (0.9 mg/mL in citrate buffer) to initiate the enzymatic reaction. 0.5 mL of sodium phosphate buffer was added instead of the enzyme solution as the control experiment. As the blank sample, 1.0 mL of citrate buffer was mixed with 0.5 mL of cellulase solution without adding the filter paper. The reaction mixture was stirred for 1 h, followed by adding 3 mL of DNS reagent[3] and incubating in boiling water for 5 min. The mixture was then cooled to room temperature by ice water and diluted with 20 mL of deionized water. The absorbance at 540 nm was measured and the amount of glucose produced was calculated using a calibration curve of glucose obtained by using the same procedure.

The hydrolytic activity of *Candida antarctica* lipase B (CALB, Sigma-Aldrich) as determined using 4-nitrophenyl palmitate (p-NPP) as the substrate. Briefly, p-NPP was first dissolved in acetone and then diluted with phosphate buffer (50 mM, pH 7.0) containing 1.25 % (w/v) Triton X-100, giving the final concentration of 0.5 mM. The

reaction was started by adding 100 μL of enzyme solution (50 μg/mL in 50 mM phosphate buffer, pH 7.0) to 1.9 mL of substrate solution and the increase of absorbance was detected at 348 nm by spectrophotometer.

Enzyme stability assays: The solutions containing 5 mg/mL enzymes and 0.5 mg/mL Ti_8O_{15} nanoparticles were irradiated at one solar with an equilibrium temperature of 50 °C. Samples were taken out at interval of 0.5 h and diluted with corresponding buffer solutions, followed by standard enzyme activity assays.

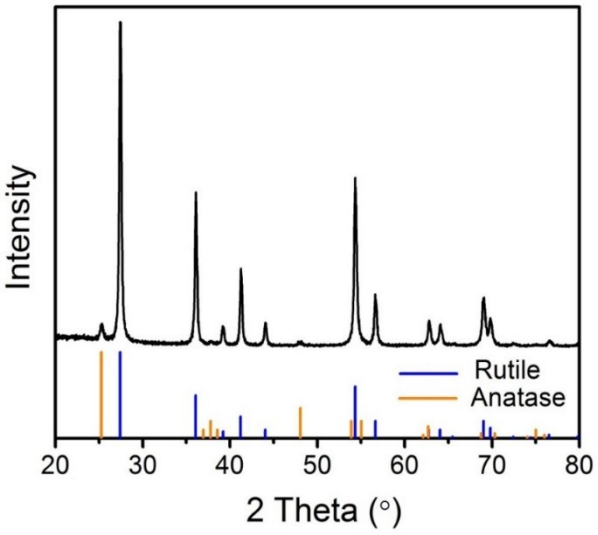

Figure S1. XRD plot of the pristine TiO_2 (Aladdin). The major phase is rutile and the minor phase is anatase in TiO_2.

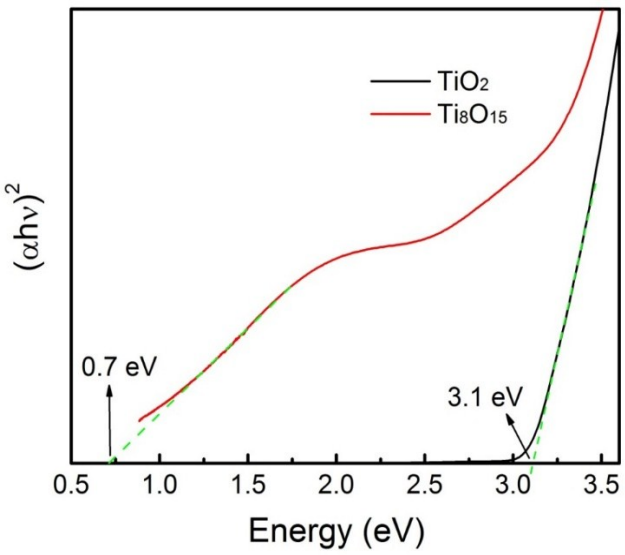

Figure S2. Tauc plots of TiO_2 and Ti_8O_{15} powders. The bandgap narrowed from 3.1 eV to 0.7 eV after the TiO_2 was deoxidized to Ti_8O_{15}.

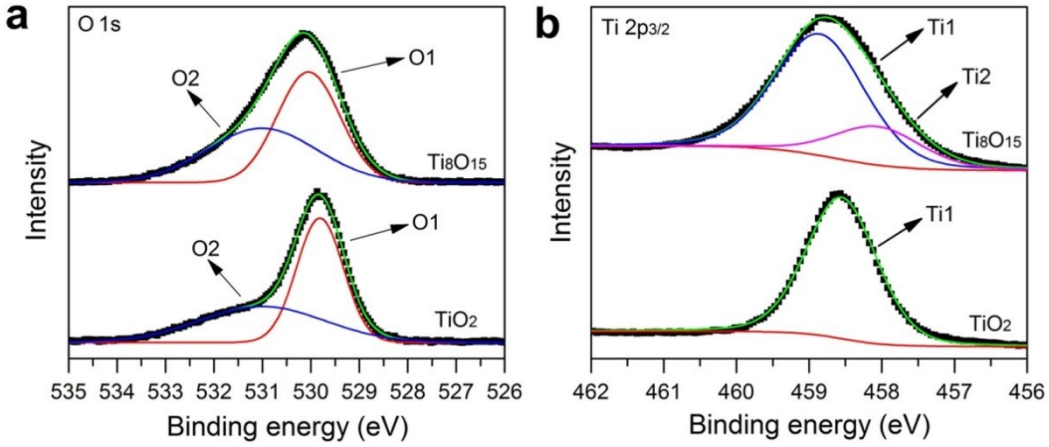

Figure S3. XPS spectroscopy of TiO_2 and Ti_8O_{15} nanoparticles. **a,** O1 and O2 are corresponding to the lattice oxygen and oxygen defects in titanium oxide, respectively, indicating oxygen defects in Ti_8O_{15} nanoparticles are highly increased compared with the pristine TiO_2 nanoparticles. **b,** Ti1 and Ti2 are corresponding to the Ti^{4+} and Ti^{3+} in titanium oxide, respectively. The appearance of Ti^{3+} peak in Ti_8O_{15} is due to the reduction of TiO_2.

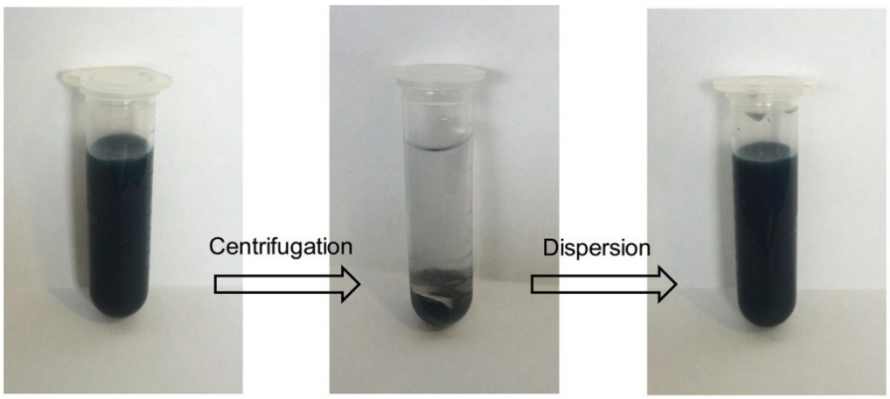

Figure S4. Photograph of solutions with Ti_8O_{15} nanoparticles (0.5 mg/mL) before and after centrifugation. The Ti_8O_{15} nanoparticles can be centrifuged from the reaction solution at 10000 rpm for 3 min and reused due to the excellent thermal stability.

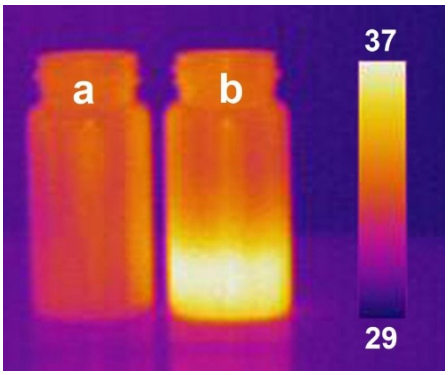

Figure S5. IR photograph of solutions irradiated at one solar for 5 minutes. **a,** Pure water. **b,** Solution with Ti_8O_{15} nanoparticles (0.5 mg/mL). Compared with pure water, the temperature of the solution with Ti_8O_{15} nanoparticles increased significantly.

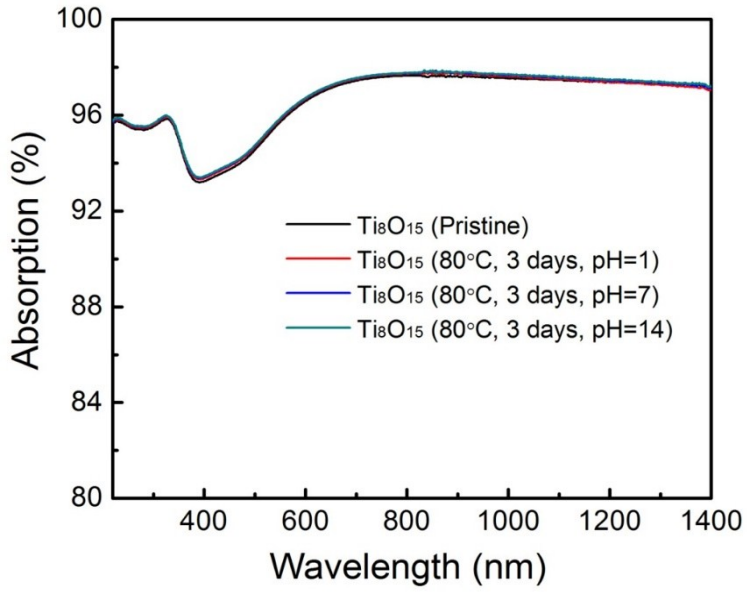

Figure S6. UV-Vis-NIR diffuse reflectance spectra of Ti_8O_{15} powders before and after ageing. The Ti_8O_{15} powders keep the same good optical absorption after ageing at 80 °C for 3 days in solution with different pH value, indicating the superior thermal and chemical stability.

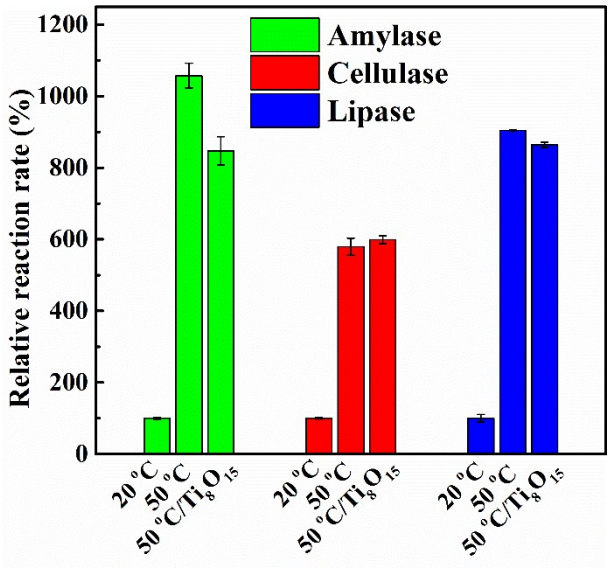

Figure S7. The relative reactions rates were determined at 50 °C without solar irradiation and without the addition of Ti_8O_{15} and at 50 °C+Ti_8O_{15} (0.5 mg/mL) irradiated at one solar, respectively. (The reaction rate at 20 °C without solar irradiation and without the addition of Ti_8O_{15} was set as 100%).

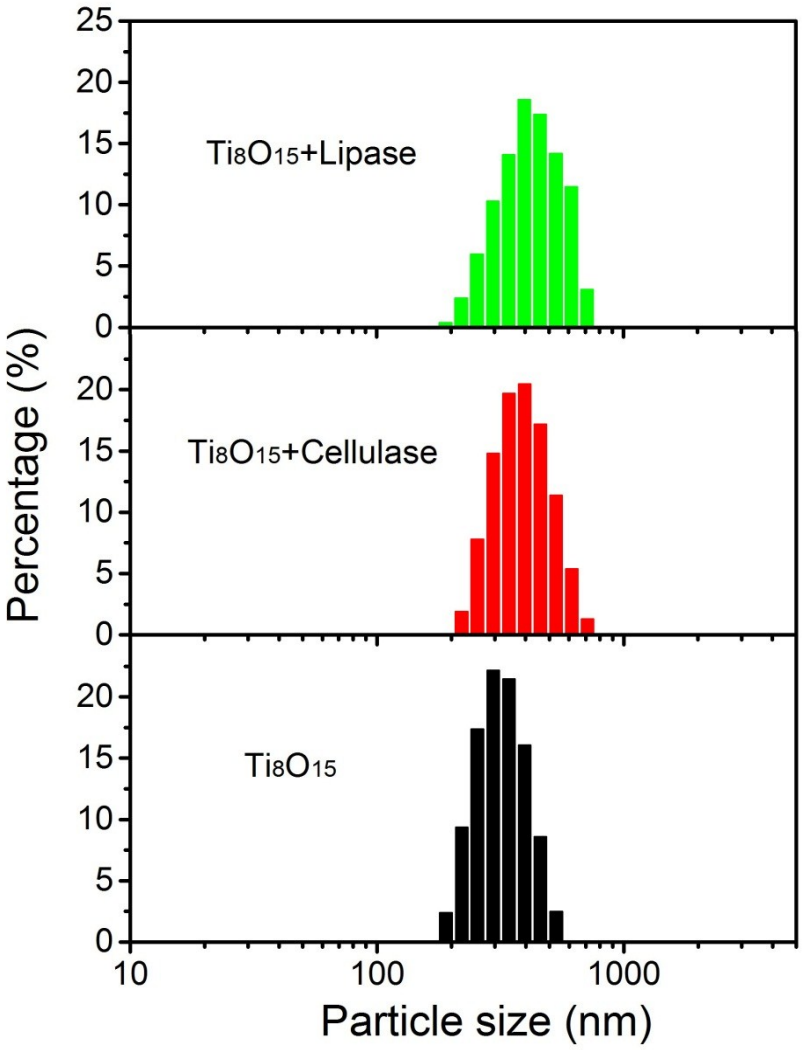

Figure S8. DLS characterization of Ti_8O_{15} nanoparticles in the presence of cellulase and lipase. The particle size of Ti_8O_{15} nanoparticles showed a slight increase after mixing with enzymes, indicating the addition of enzyme almost has no effect on the particle size of Ti_8O_{15} nanoparticles.

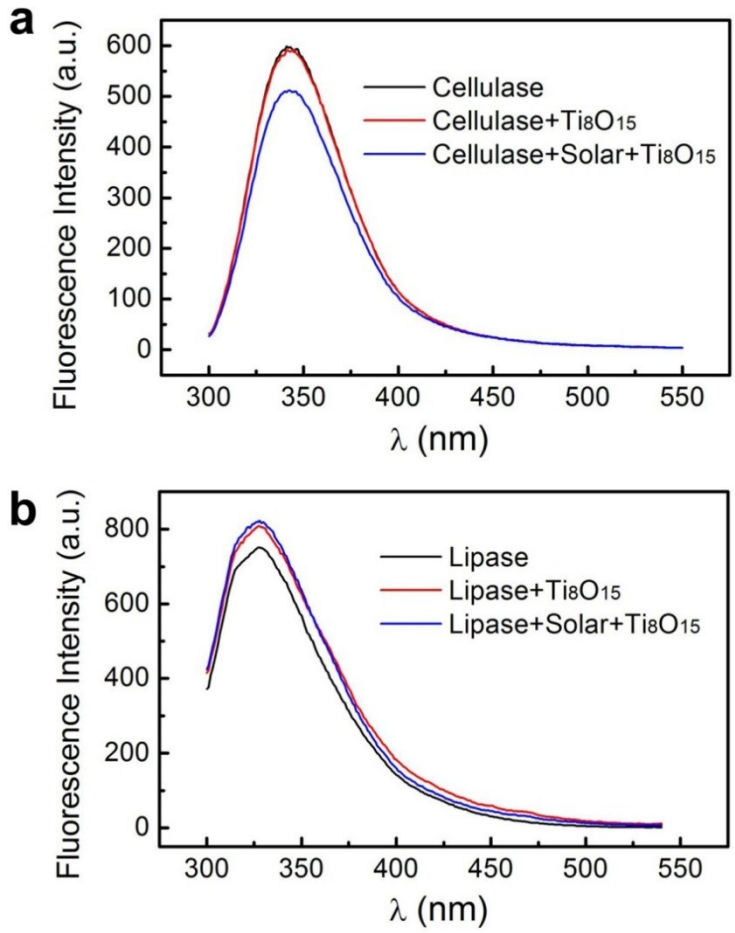

Figure S9. Fluorescence spectra of cellulase and lipase in the presence of Ti_8O_{15} nanoparticles and treated after solar irradiation. The fluorescence spectra of enzymes in buffer solution at different conditions (20 °C without solar irradiation; 20 °C+Ti_8O_{15} (0.5 mg/mL) without solar irradiation; 50 °C+Ti_8O_{15} (0.5 mg/mL) irradiated at one solar, respectively) revealed almost the same intensity, indicating the negligible effect of Ti_8O_{15} nanoparticles and solar irradiation on the tertiary structures of proteins.

References

1. G. Ou, D. Li, W. Pan, Q. Zhang, B. Xu, L. Gu, C. Nan and H. Wu, *Adv Mater*, 2015, 27, 2589-2594.

2. L.-B. Wang, Y.-C. Wang, R. He, A. Zhuang, X. Wang, J. Zeng and J. G. Hou, *J Am Chem Soc,* 2013, **135**, 1272-1275.

3. T. Ghose, *Pure Appl Chem*, 1987, **59**, 257-268.