A Microorganism Bred TiO_2/Au/TiO_2 Heterostructure for Whispering Gallery Mode Resonance Assisted Plasmonic Photocatalysis

Xin Yu,[†#] Xin Jin,[‡#] Xuanyu Chen,[†] Aizhu Wang,[*,†] Jianming Zhang,[*,§] Jian Zhang,[¶] Zhenhuan Zhao,[Σ] Mingming Gao,[‖] Luca Razzari,[*,‡] Hong Liu[*,†,Π]

[†]Institute for Advanced Interdisciplinary Research (iAIR), University of Jinan, Jinan 250022, P. R. China

[‡]INRS-EMT, 1650, Boulevard Lionel-Boulet, Varennes, Quebec J3X 1S2, Canada

[§]School of Chemistry and Chemical Engineering, Jiangsu University, Zhejiang 212013, P. R. China

[¶] Institut Charles Gerhardt de Montpellier, UMR 5253, Université de Montpellier, CNRS, ENSCM, 34095, Montpellier Cedex 5, France

[Σ] School of Advanced Materials and Nanotechnology, Xidian University, Xi'an, 710071, P. R. China

[‖]Shandong Provincial Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Qingdao, 266200, P. R. China

[Π]State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, P. R. China

[#]These authors contributed equally to this work.

Materials. All the reagents are analytic grade and commercially available. Titanium oxalate ($K_2TiO(C_2O_4)_2$), diethylene glycol ($(CH_2OH)_2$), Chloroauric acid ($HAuCl_4 \cdot 4H_2O$), and methanol (CH_3OH) were purchased from China National Medicines Corporation Ltd. All the chemicals were used as received without further purification. All chemicals were used as received without further purification. Water was supplied with a Barnstead Nanopure Water System (18.3 MΩ*cm).

Synthesis of P25/Au heterostructure. P25 and chloroauric acid ($HAuCl_4 \cdot 4H_2O$, c = 10 $g \cdot L^{-1}$) were suspended in 20: 80 vol mixture of ethanol: water, and were irradiated with a mercury lamp (300 W) for 30 min. Obtained samples were filtered and washed.

Photoelectrode fabrication. The working electrode was fabricated by the fluorine-doped tin oxide (FTO) glass deposited with production samples. In a typical process of making a working electrode, 50 mg of photocatalyst sample was mixed with 20 mL of terpineol and stirred with a magnetic stirrer for 2 h. The solution was ultrasonicated for 0.5 h to mark a homogeneous ink. Then 200 μL of ink with a pipettor was taken and spread onto FTO glass by dropwise to make an electrode catalyst. Finally, the photoelectrode was dried in air and then was ready for further characterization. A Cu wire was connected to the FTO substrate with the silver colloid paste. Finally, epoxy was solidified to cover the FTO substrate, the silver paste and the Cu wire to avoid short current in the measurement.

Photoelectrochemical measurement. Photoelectrochemical analyses were carried out using a standard three-electrode cell with Ag/AgCl as reference electrode and Pt sheet

as the counter electrode in the KCl solution (1M). The electrolyte was bubbled with N_2 for 2 h to remove O_2. The light source used was identical with that used in the photocatalytic H_2 generation testing.

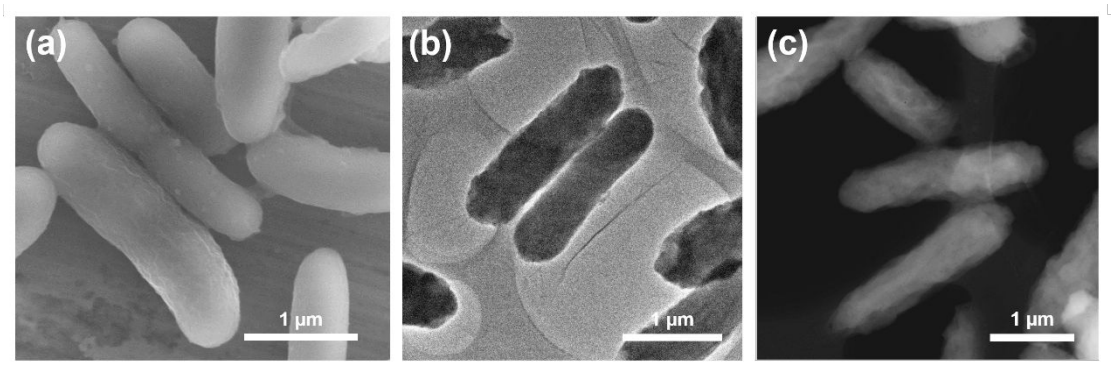

Figure S1 (a-c) SEM, TEM and STEM images of *E. coli*.

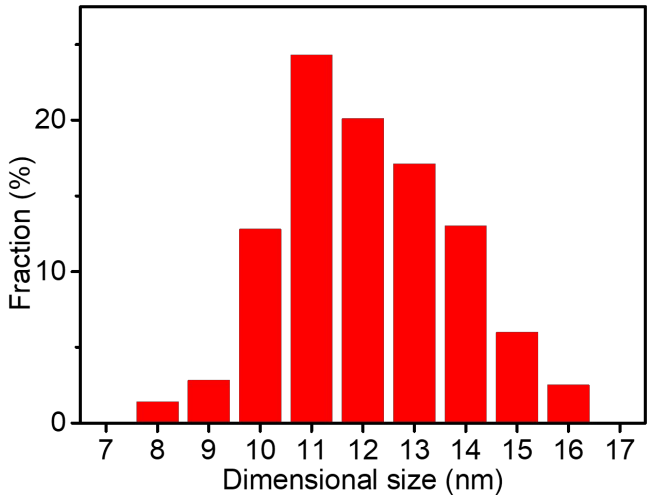

Figure S2 Size distribution of Au nanoparticles.

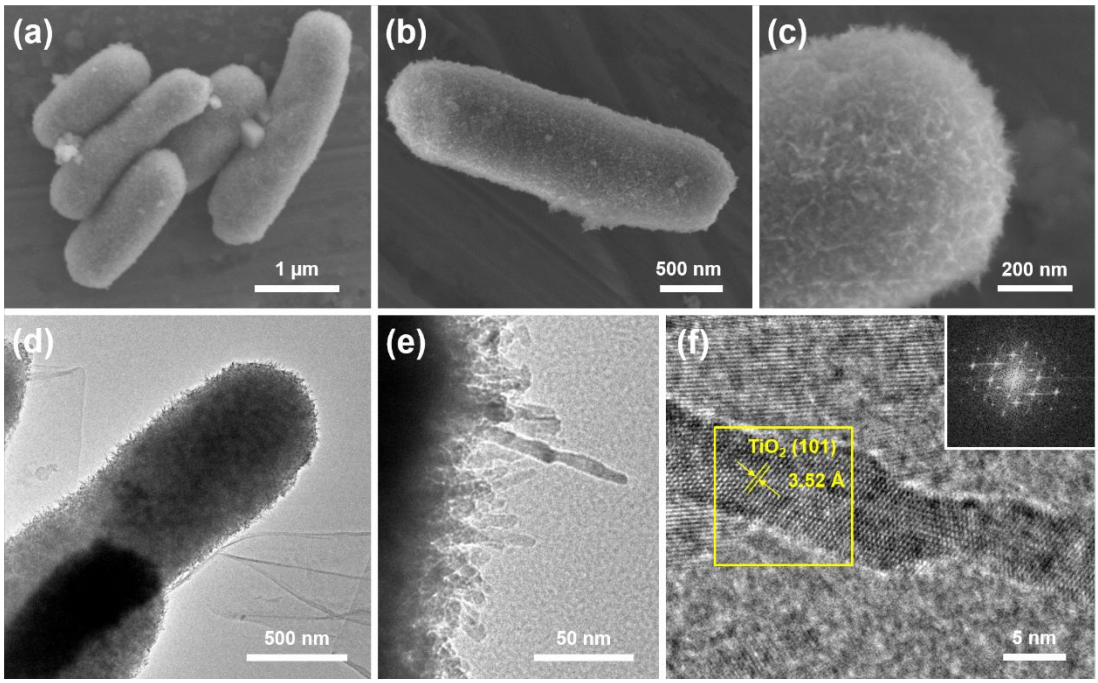

Figure S3 SEM (a-c) and TEM (d-f) images of *E. coli*-like TiO_2. Inset (f) shows the Fast Fourier transform (FFT) pattern take from the yellow square in (f), corresponding to the (101) faces of anatase TiO_2.

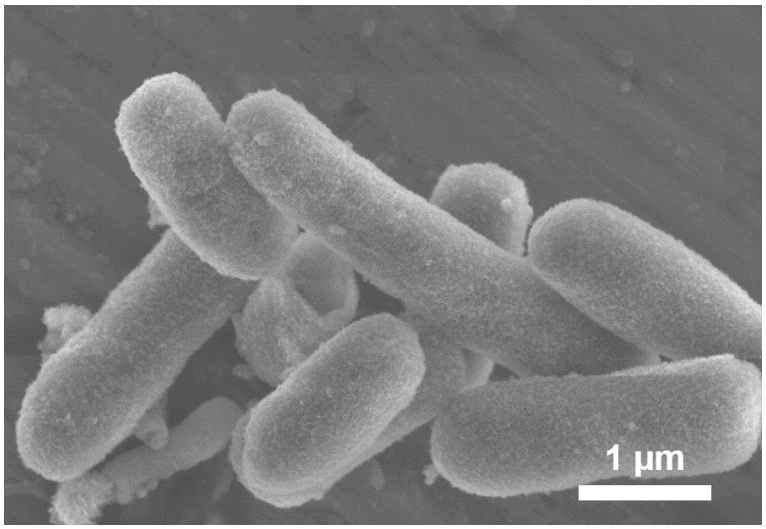

Figure S4 SEM image of *E. coli*-like TiO_2.

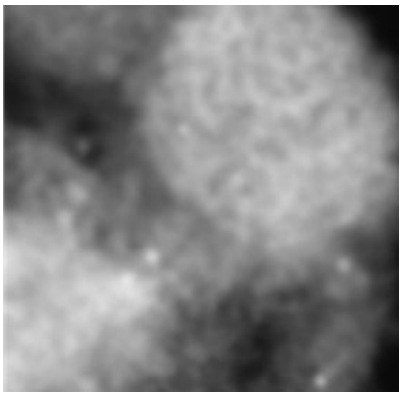

Figure S5 SETM image of *E*-TiO_2/Au/TiO_2

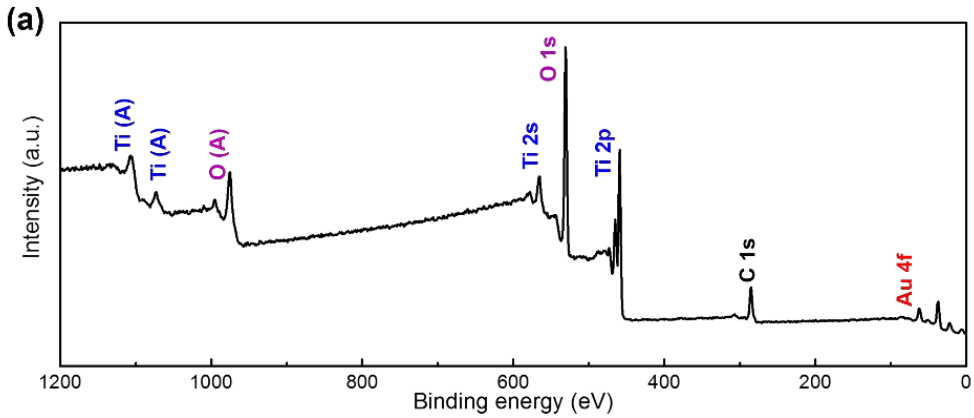

Figure S6 Survey spectrum for *E*-TiO_2/Au/TiO_2.

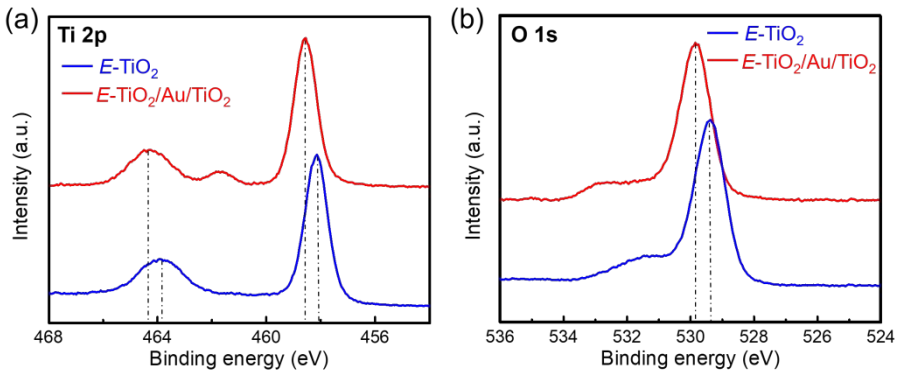

Figure S7 XPS characterization of (a) Ti 2p and (b) O 1s for *E*-TiO_2/Au/TiO_2 and pure *E*-TiO_2.

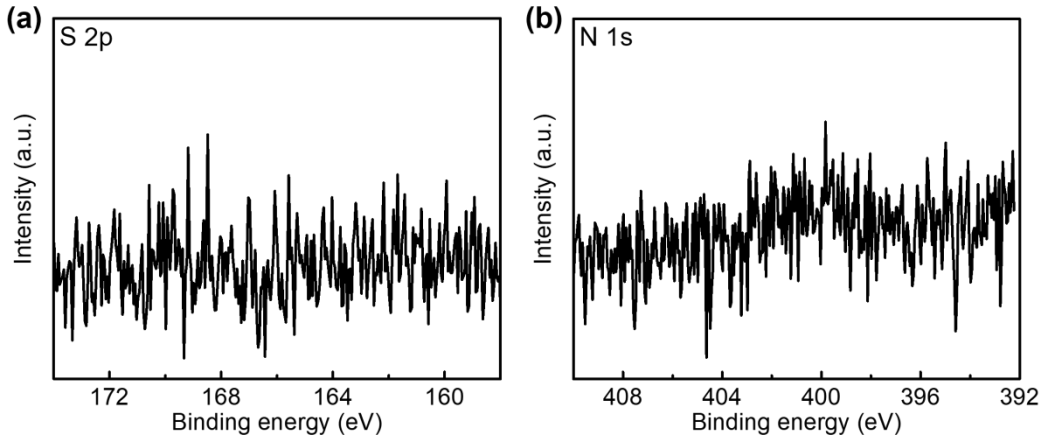

Figure S8 XPS spectrum of S 2p and N 1s for *E*-TiO_2/Au/TiO_2-Ar.

The content of N and S elements in bacteria is very low. In our work, the *E. coli*/Au/TiO_2 composite was calcined under air atmosphere to remove *E. coli* and obtain an *E*-TiO_2/Au/TiO_2 heterostructure. C, N and S element may be oxidized during the calcination process and volatilize into the air. To illustrate, we calcined the *E. coli*/Au/TiO_2 in the Ar atmosphere (*E*-TiO_2/Au/TiO_2-Ar). It can be seen from the XPS spectrum of S 2p and N 1s for *E*-TiO_2/Au/TiO_2-Ar that annealing under Ar protective gas, the S and N elements contained in the material are also very low.

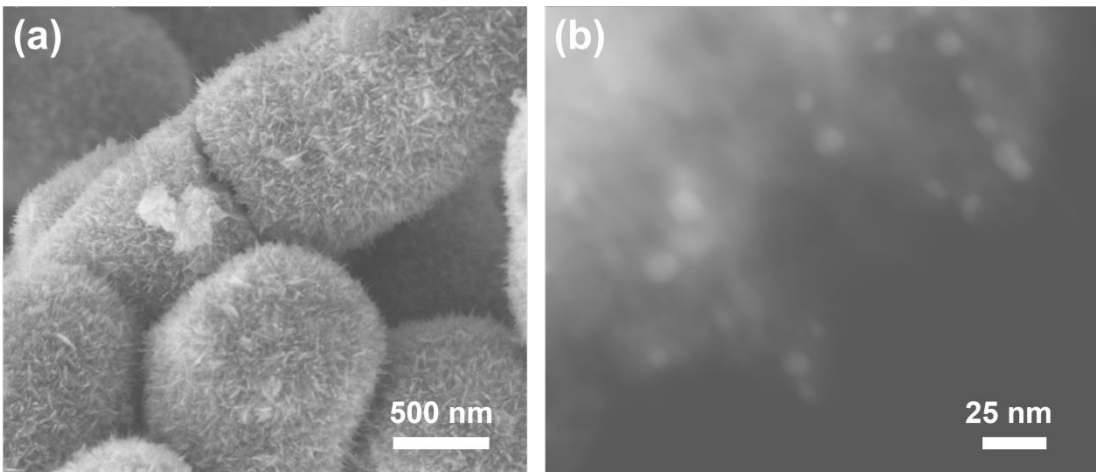

Figure S9 SEM and HRTEM images of *E*-TiO_2/Au.

E-TiO_2/Au still maintaining the bacteria shape. The difference from *E*-TiO_2/Au/TiO_2 is that Au nanoparticles are distributed on the surface of TiO_2 (Figure S8b). What's more, the diameter of the Au nanoparticles in *E*-TiO_2/Au is also distributed 10-15 nm.

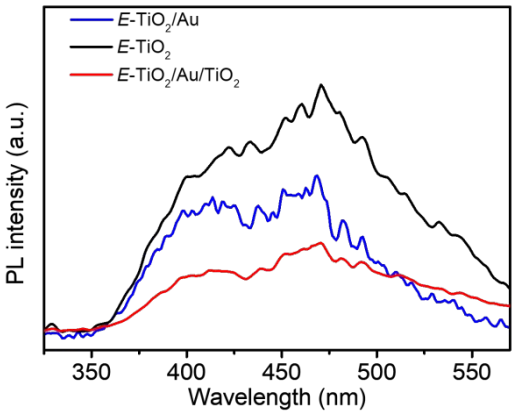

Figure S10 PL emission of *E*-TiO_2/Au/TiO_2, *E*-TiO_2/Au and pure *E*-TiO_2.

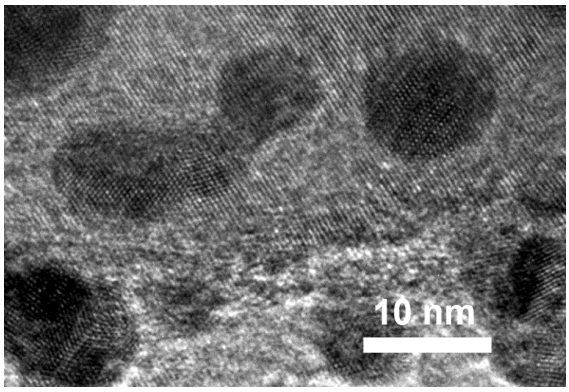

Figure S11 TEM image of P25/Au.

From the TEM image of the P25/Au, it can be seen the Au nanoparticles are distribution from 9-14 mn. Furthermore, through ICP-MS measurement, the loading amount of Au in the P25/Au is 0.4 wt% which is the same with that in the *E*-TiO_2/Au/TiO_2 sample.

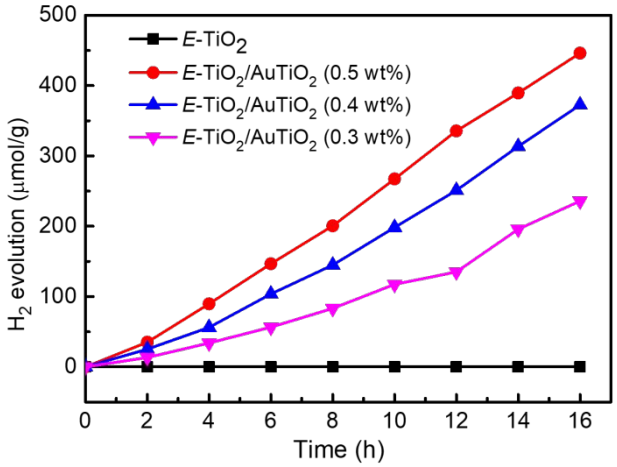

Figure S12 H_2 evolution of *E*-TiO_2/Au/TiO_2 with different Au amount.

Through ICP-MS measurement, the loading amount of Au in the final *E*-TiO_2/Au/TiO_2 composite is 0.4 wt%. Furthermore, by adding different amounts of gold solution in the process of bacterial reduction, we have prepared *E*-TiO_2/Au/TiO_2 composite with different amounts of Au. And the photocatalytic H_2 evolution activity has been tested. The *E*-TiO_2/Au/TiO_2-0.4 wt% composite has the highest H_2 evolution rate (In this paper, *E*-TiO_2/Au/TiO_2 is used instead of *E*-TiO_2/Au/TiO_2-0.4 wt% unless otherwise specified).

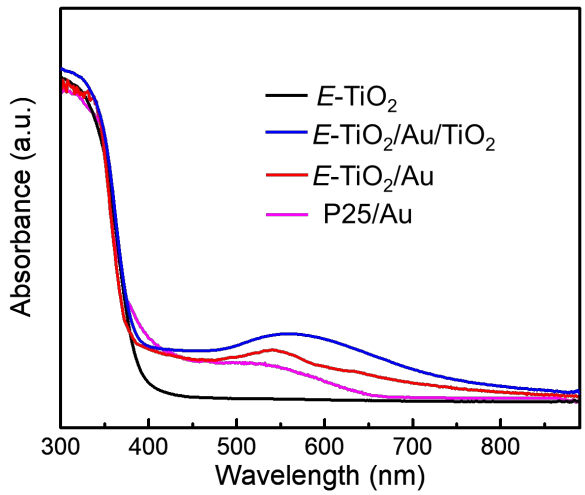

Figure S13 UV-vis absorption of *E*-TiO_2/Au/TiO_2, *E*-TiO_2, *E*-TiO_2/Au and P25/Au.

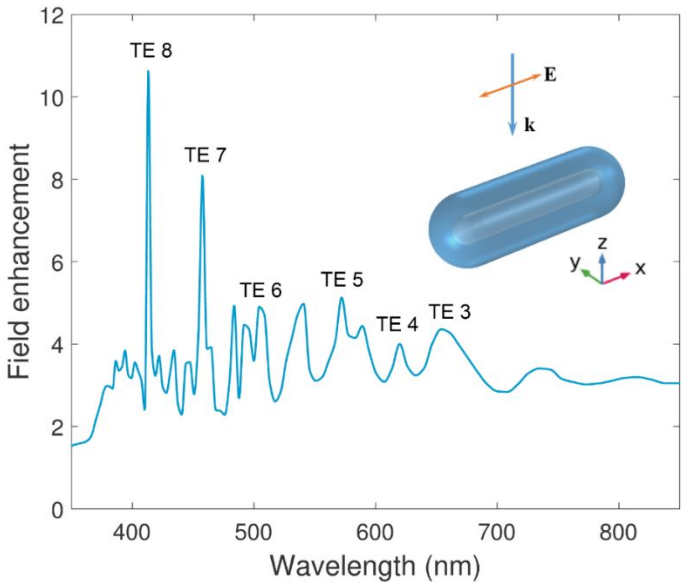

Figure S14 The field enhancement of a capsule model of the TiO_2 replaced bacteria. The capsule is illuminated by a plane wave that is polarized along the long axis of the capsule.

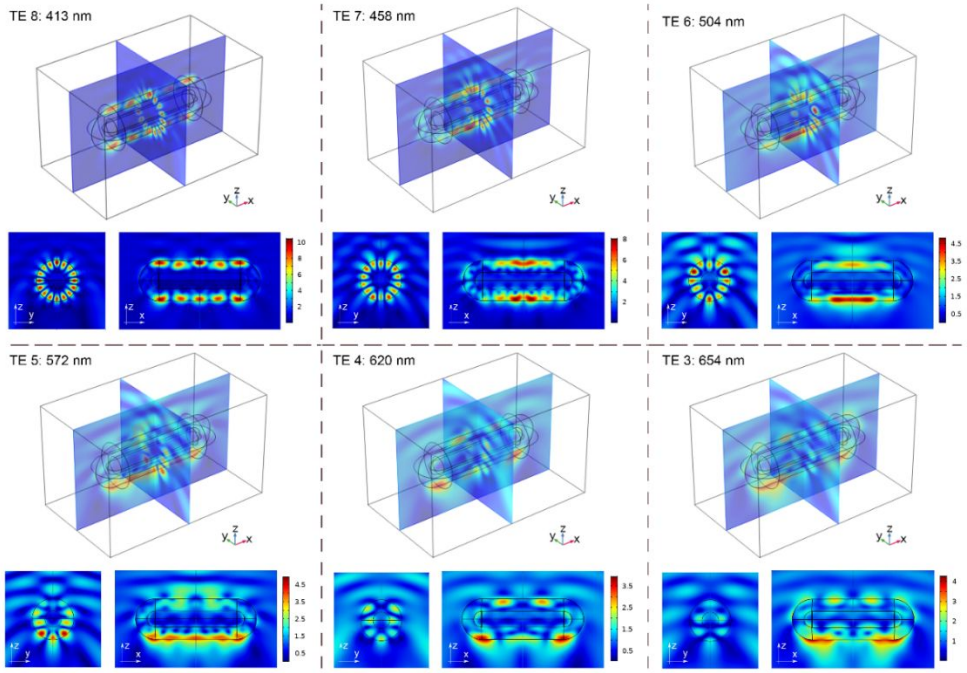

Figure S15 Field enhancement distributions of the TE WGMs labeled in Figure S14.