

Regulate Upconversion Effect to Promote Removal of Biofilms on Titanium Surface via Photoelectrons

Kai Wang,^a Yufei Tang,^b Keyi Yao,^a Shuqi Feng,^b Bingfeng Wu,^b Lin Xiang,^{*b}
Xuemei Zhou^{*a}

^a School of Chemical Engineering, Sichuan University, Chengdu 610065, China.
Email: xuemeizhou@scu.edu.cn.

^b State Key Laboratory of Oral Diseases & National Center for Stomatology &
National Clinical Research Center for Oral Diseases, West China Hospital of
Stomatology, Sichuan University, Chengdu 610041, Sichuan, China. E-mail:
dentistxiang@126.com.

Contents

1. Experimental conditions to prepare different samples (**Table S1**)
2. Atomic percentage of samples according to XPS spectra (**Table S2**)
3. SEM image of side view of TiO₂ (**Fig. S1**)
4. SEM images of Au₃/TiO₂ (**Fig. S2**)
5. Size distribution of Au NPs and RE NPs (**Fig. S3**)
6. EDS mapping of Au₁-RE₁(Yb₂₀-Er₂)/TiO₂ (**Fig. S4**)
7. XPS spectra of Au₁-RE₁(Yb₂₀-Er₂)/TiO₂ (**Fig. S5**)
8. The degradation curve of RhB (**Fig. S6**)
9. Absorbance of RhB aqueous solution measured over time, catalyzed by Fe²⁺ and H₂O₂ (**Fig. S7**)
10. The capability of Au₁-RE₁(Yb₂₀-Er₂)/TiO₂ to generate ¹O₂, ·OH, and ·O₂⁻ (**Fig. S8**)
11. Antibacterial effect under near infrared light after penetration (**Fig. S9**)
12. Illustration on the mechanism of bacterial death (**Fig. S10**)
13. Release of Au and Y ions from Au₁-RE₁(Yb₂₀-Er₂)/TiO₂ (**Fig. S11**)

Table S1. Experimental conditions to prepare different samples.

| Samples | Au sputtering time (min) | RE deposition time (h) | Concentration of Yb ³⁺ (%) | Concentration of Er ³⁺ (%) |
|--|--------------------------|------------------------|---------------------------------------|---------------------------------------|
| TiO ₂ | 0 | 0 | 0 | 0 |
| Au _α -RE ₁ (Yb ₂₀ -Er ₂)/TiO ₂ | α=0, 1, 3 | 1 | 20 | 2 |
| Au ₁ -RE _β (Yb ₂₀ -Er ₂)/TiO ₂ | 1 | β=0, 1, 3 | 20 | 2 |
| Au ₁ -RE ₁ (Yb _γ -Er ₂)/TiO ₂ | 1 | 1 | γ=0, 20, 40 | 2 |
| Au ₁ -RE ₁ (Yb ₂₀ -Er _δ)/TiO ₂ | 1 | 1 | 20 | δ=0, 2, 4 |

Table S2. Atomic percentage (at. %) of different samples according to high-resolution XPS spectra of different elements.

| Samples/Elements | C | O | F | Na | Ti | Au | Y |
|--|------|------|-------------|------------|------|-------------|------------|
| Au ₁ -RE ₁ (Yb ₂₀ -Er ₂)/TiO ₂ | 31.4 | 21.4 | 28.5 | 4.1 | 4.3 | 6.3 | 4.1 |
| Au ₃ -RE ₁ (Yb ₂₀ -Er ₂)/TiO ₂ | 28.4 | 20.5 | 21.9 | 3.6 | 6.3 | 12.4 | 6.9 |
| RE ₁ (Yb ₂₀ -Er ₂)/TiO ₂ | 25.5 | 40.8 | 12.1 | 3.3 | 16.4 | 0 | 1.9 |
| Au ₁ -RE ₃ (Yb ₂₀ -Er ₂)/TiO ₂ | 27.6 | 14.3 | 33.7 | 5.5 | 4.0 | 9.0 | 7.4 |
| Au ₁ /TiO ₂ | 29.5 | 33.5 | 0 | 0 | 16.6 | 20.4 | 0 |

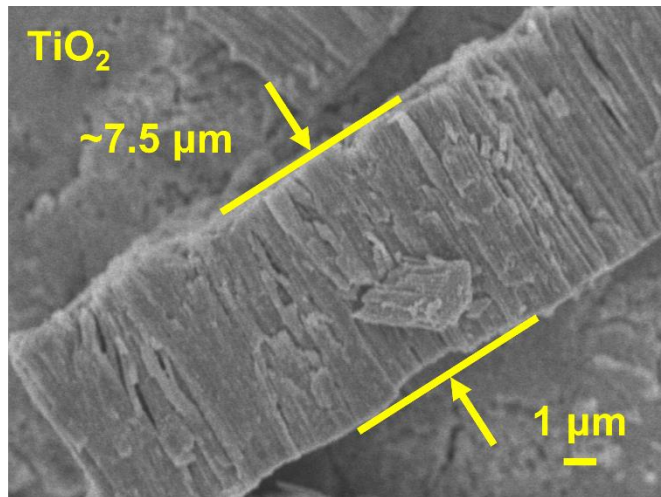


Fig. S1. SEM image of side view of TiO₂.

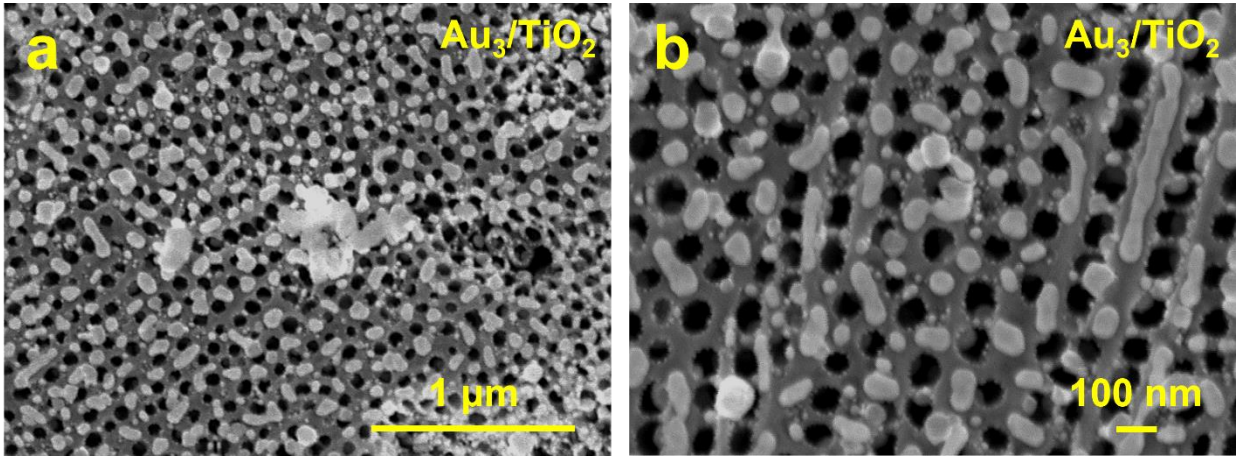


Fig. S2. SEM images of Au₃/TiO₂ in (a) overview and (b) close observation.

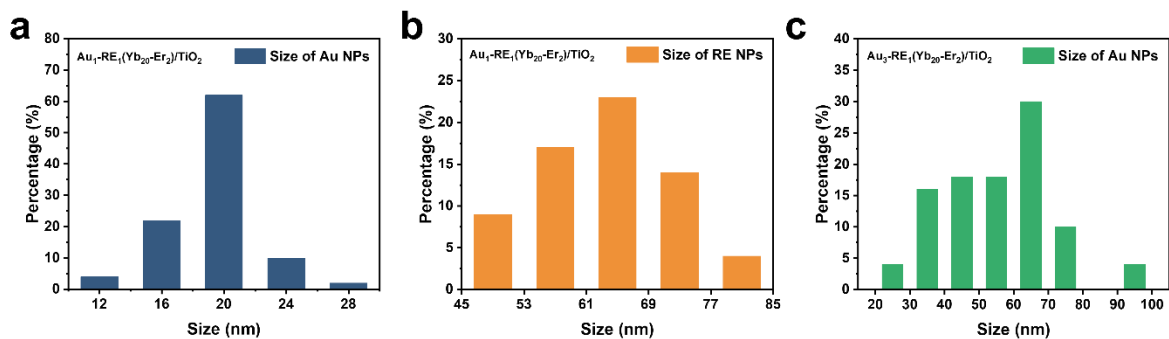


Fig. S3. Analysis on the size distribution of (a) Au NPs (20 ± 3 nm) and (b) RE NPs (64 ± 9 nm) for $\text{Au}_1\text{-RE}_1(\text{Yb}_{20}\text{-Er}_2)/\text{TiO}_2$. (c) Analysis on the size distribution of Au NPs for $\text{Au}_3\text{-RE}_1(\text{Yb}_{20}\text{-Er}_2)/\text{TiO}_2$ (55 ± 16 nm).

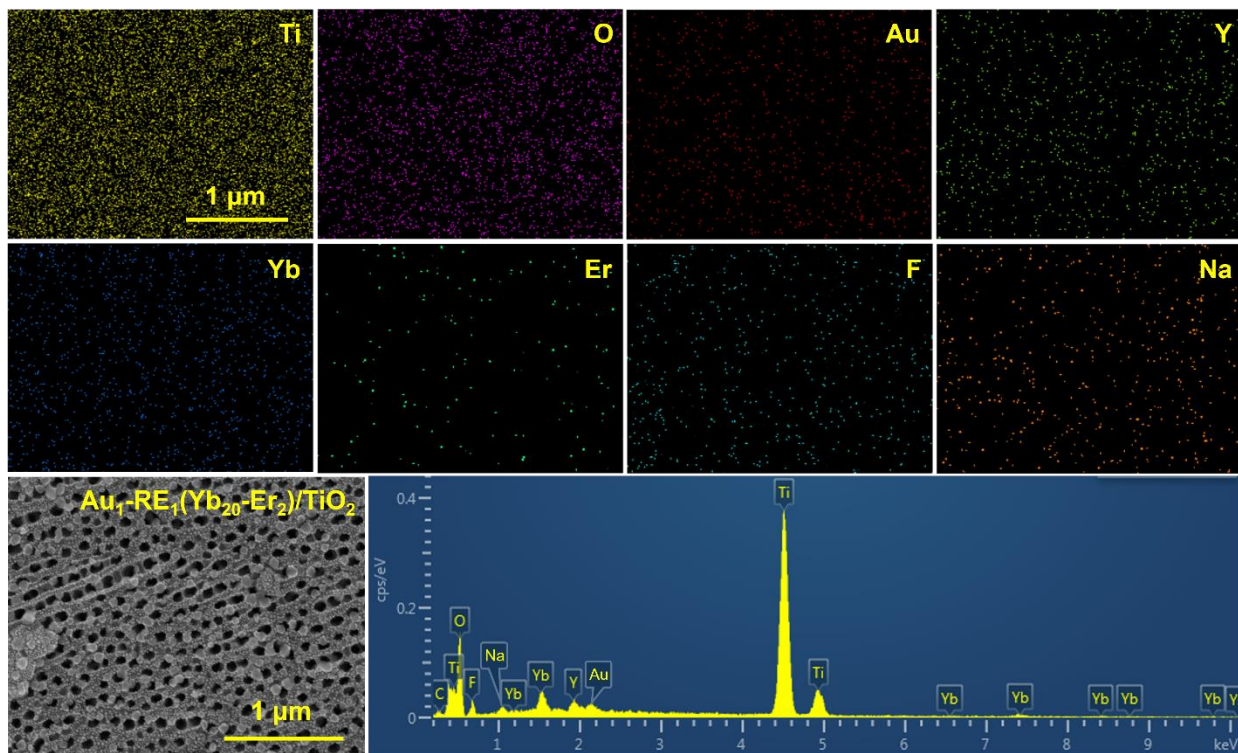


Fig. S4. EDS mapping of $\text{Au}_1\text{-RE}_1(\text{Yb}_{20}\text{-Er}_2)/\text{TiO}_2$.

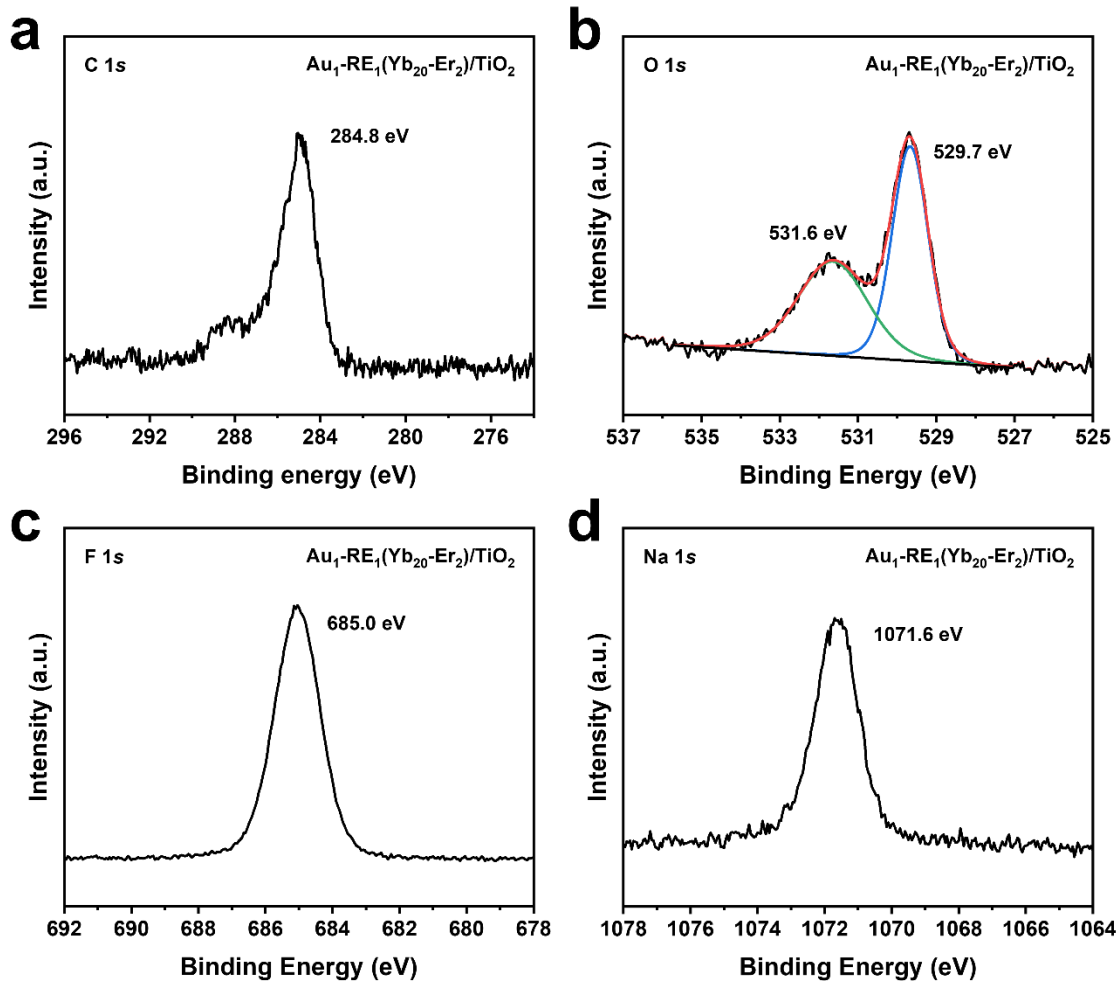


Fig. S5. XPS spectra of (a) C 1s, (b) O 1s, (c) F 1s, and (d) Na1s. $\text{Au}_1\text{-RE}_1(\text{Yb}_{20}\text{-Er}_2)/\text{TiO}_2$.

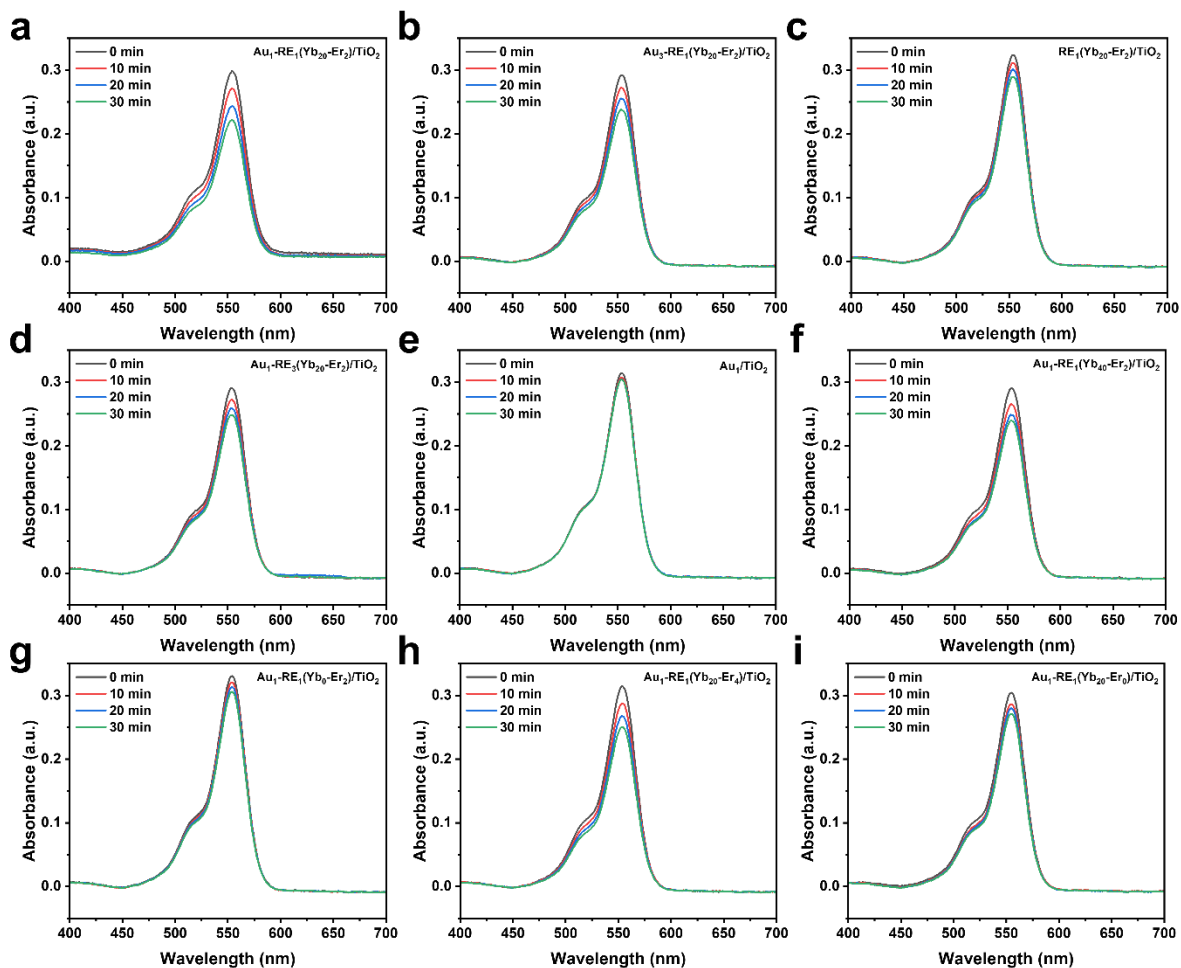


Fig. S6. The degradation curve of RhB for different samples under NIR irradiation: (a) $\text{Au}_1\text{-RE}_1(\text{Yb}_{20}\text{-Er}_2)/\text{TiO}_2$ (b-c) different Au loading, (d-e) different RE deposition amount, (f-g) different concentration of Yb^{3+} , (h-i) different concentration of Er^{3+} .

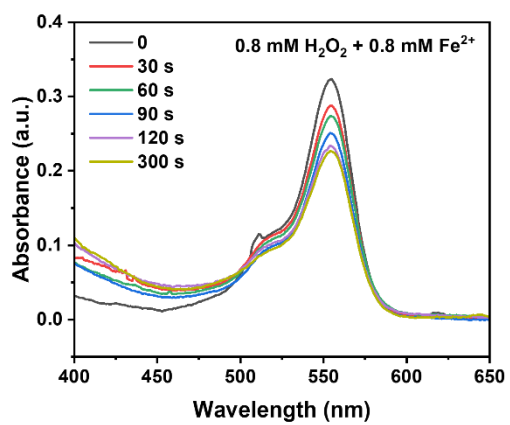


Fig. S7. Absorbance of RhB aqueous solution measured over time, catalyzed by Fe²⁺ (0.8 mM) and H₂O₂ (0.8 mM).

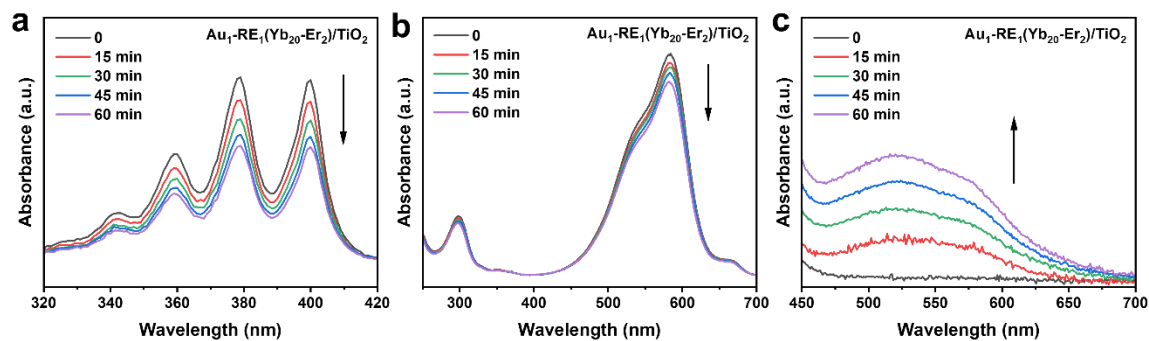


Fig. S8. UV-vis absorbance spectra of (a) ADBA and (b) MV for $Au_1-RE_1(Yb_{20}-Er_2)/TiO_2$ under NIR irradiation. (c) Absorbance of NBT solution with $Au_1-RE_1(Yb_{20}-Er_2)/TiO_2$ under NIR irradiation.

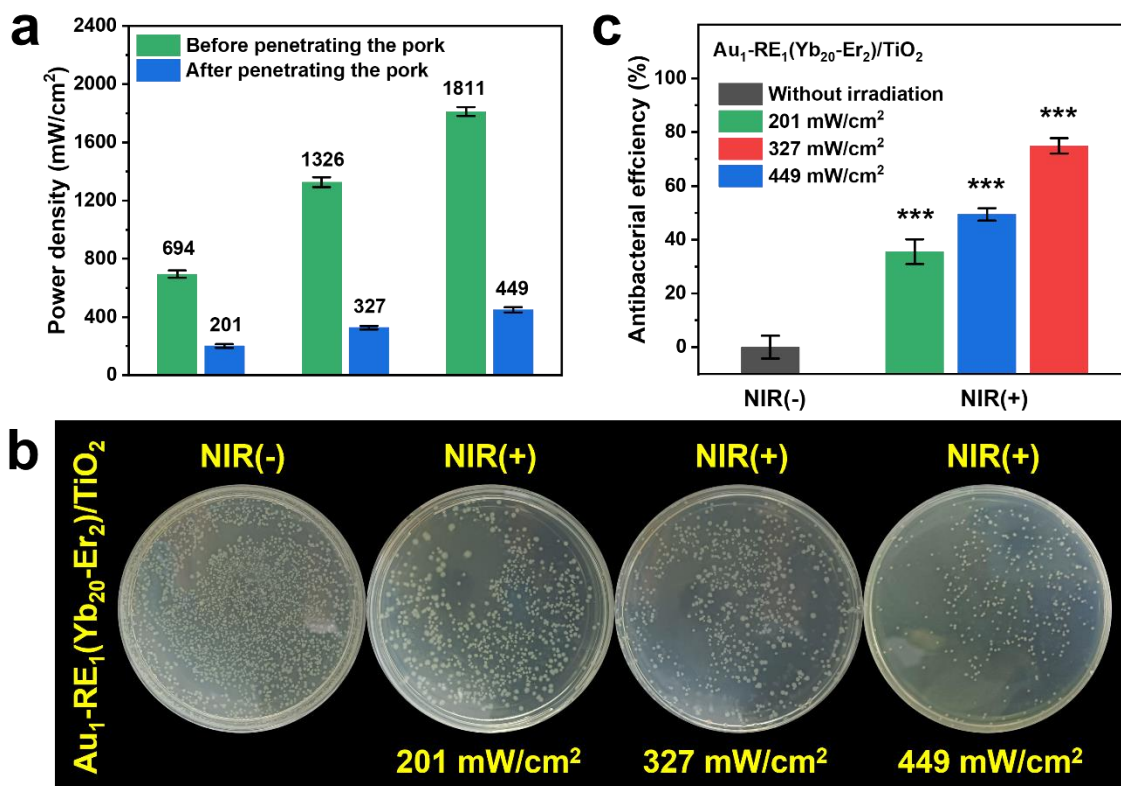


Fig. S9. (a) Penetration ability of the 980 nm laser in 3 mm thick pork. (b) and (c) Antibacterial effect of NIR with different power density after penetrating 3 mm thick pork. The statistics were presented as means \pm S. D., $n=3$, * $p<0.05$, ** $p<0.01$, *** $p<0.001$, and ns (not significant).

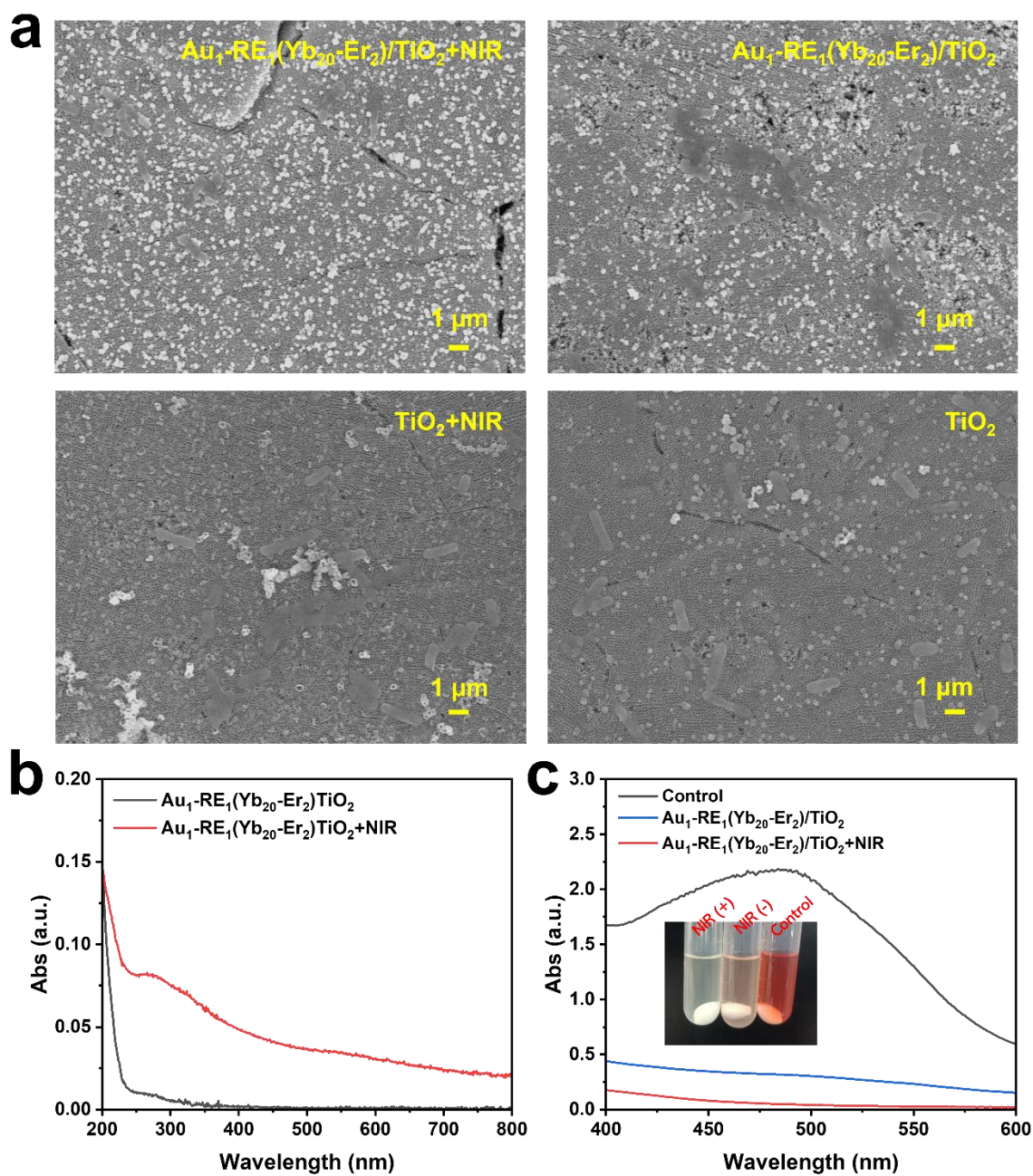


Fig. S10. (a) SEM images of *E. coli* of $\text{Au}_1\text{-RE}_1(\text{Yb}_{20}\text{-Er}_2)/\text{TiO}_2$ and TiO_2 under NIR irradiation or dark. (b) The release of nucleic acid and protein from *E. coli* of $\text{Au}_1\text{-RE}_1(\text{Yb}_{20}\text{-Er}_2)/\text{TiO}_2$ group under NIR irradiation or dark. (c) The absorption curves of *E. coli* of control and $\text{Au}_1\text{-RE}_1(\text{Yb}_{20}\text{-Er}_2)/\text{TiO}_2$ mixed with INT solution under NIR irradiation or dark.

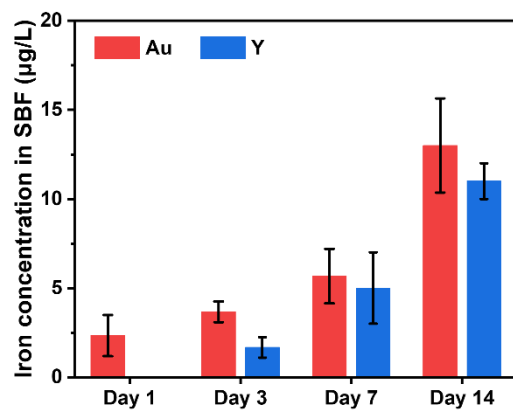


Fig. S11. Release of Au and Y ions from $\text{Au}_1\text{-RE}_1(\text{Yb}_{20}\text{-Er}_2)/\text{TiO}_2$ in SBF solution, detected on day 1, 3, 7, and 14.