Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Information

A pH/H_2O_2 dual triggered nanoplateform for enhanced photodynamic antibacterial efficiency

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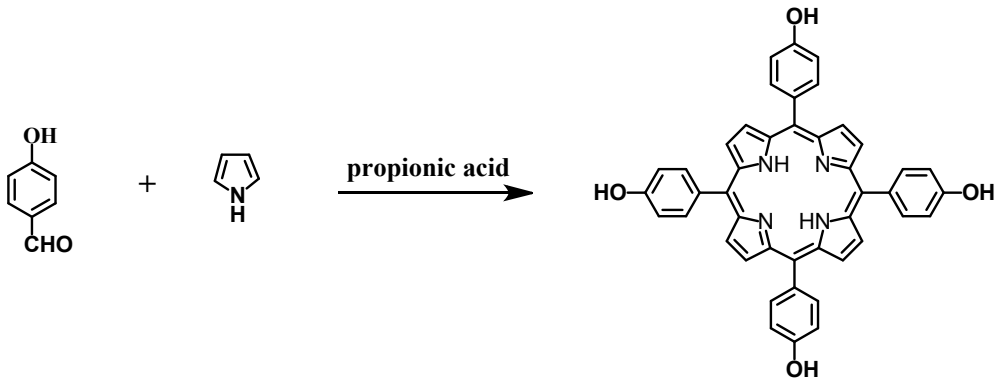
Characterization

^{1}H NMR spectra were recorded at 400 MHz, using BRUKER AV400 spectrophotometer. The fluorescence spectra were recorded on an F-4500 fluorescence spectrophotometer at room temperature. The UV-Vis spectra of the sam ples were measured over different irradiation time intervals by using a Thermo Scientific Evolution 220 spectrophotometer. The hydrodynamic diameter was measured by Litesizer 500. Transmission electron microscopy (TEM) images were obtained with an electron microscope (JEM-2100F, 200 kV). MTT assays were conducted with a Spark™ Multimode Microplate Reader.

Sample Synthesis.

1.1 **Synthesis and characterization of 5, 10, 15, 20-Tetrakis (4-hydroxyphenyl) porphyrin (THPP).**

Synthetic routes employed for the preparation of 5, 10, 15, 20-Tetrakis (4-hydroxyphenyl) porphyrin THPP was synthesized and purified according to the method reported in the literature[1]. Finally, we can obtain the purple solid product with 10% yield and verified by ^{1}H NMR. ^{1}H NMR (400 MHz, DMSO) δ 9.96 (s, 4H), 8.87 (s, 9H), 8.00 (d, J = 8.4 Hz, 9H), 7.21 (d, J = 8.4 Hz, 10H), -2.89 (s, 2H).



Scheme S1. Synthetic routes employed for the preparation of THPP.

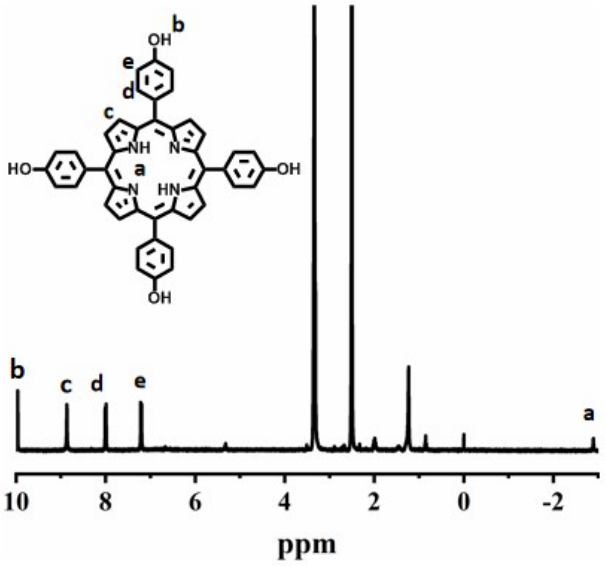
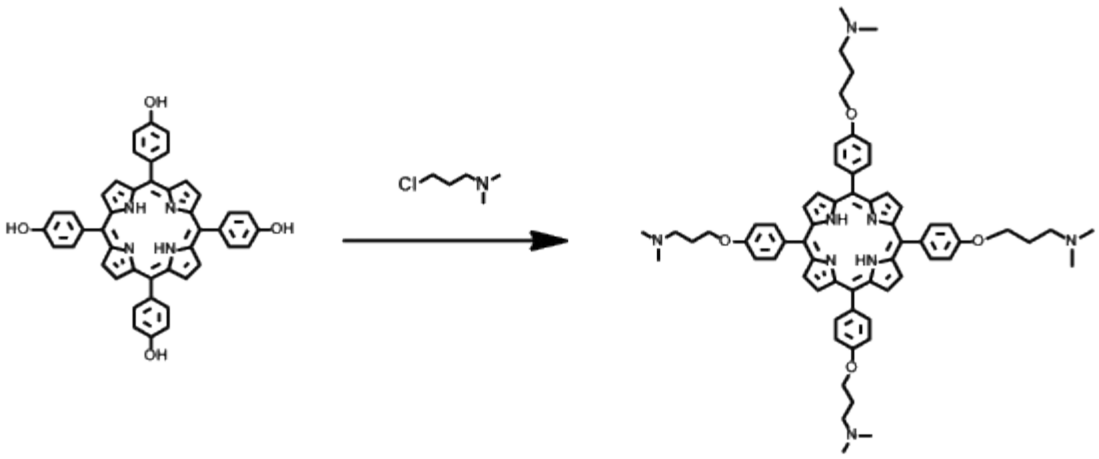


Figure S1. ^{1}H NMR spectrum of THPP in *d*-DMSO.

1.2 **Synthesis and characterization of 5, 10, 15, 20-tetra-{4-[3-(N, Ndimethyl-ammonio)propoxy]phenyl} porphyrin (TAPP) .**

The synthesis of TAPP was referenced to the previous work of our group[1]. The final product was a purple-black solid with 31% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 8H), 8.11 (d, J = 8.5 Hz, 8H), 7.29 (d, J = 4.8 Hz, 7H), 4.32 (t, J = 6.3 Hz, 8H), 2.72 – 2.52 (m, 8H), 2.42 – 2.22 (m, 24H), 2.01 (s, 8H), -2.77 (s, 2H).



Scheme S2. Synthetic routes employed for the preparation of TAPP.

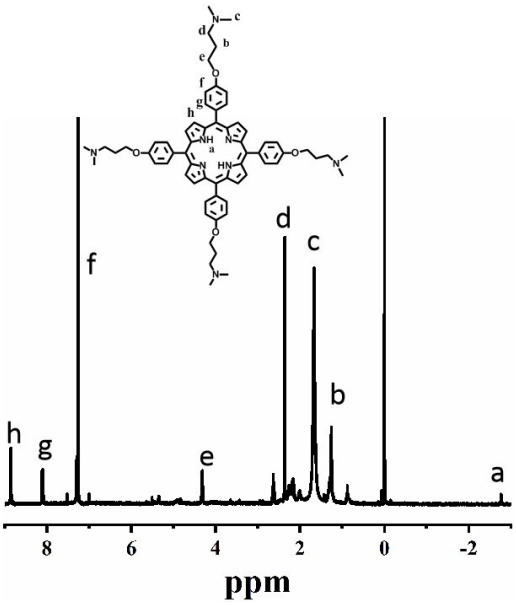


Figure S2. ^{1}H NMR spectrum of TAPP in $CDCl_3$.

1.3 **Synthesis and characterization of amphiphilic block copolymer, POEGMA-*b*-PBMA.**

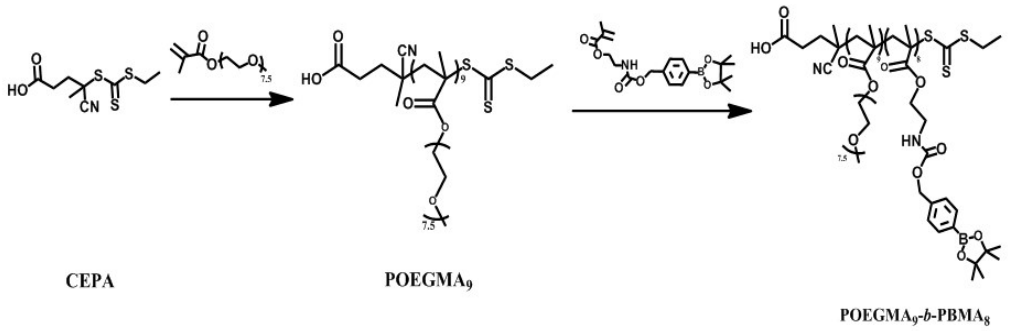
The synthesis routine was referenced to the work of our group[2].

Synthesis of POEGMA (**Scheme S3**). The typical preparation process of POEGMA is as followings. OEGMA (1.0 g, 2.1 mmol), CEPA (27 mg, 0.103 mmol), AIBN (5.6 mg, 34.1 μmol) and 2 mL of THF were added into a dry glass tube equipped with a magnetic stirring bar. The

mixture was degassed by sparging with nitrogen through at least three freeze-pump-thaw cycles, and the polymerization tube then was sealed under vacuum. The degassed solute on was immersed into an oil bath at 70°C. After stirred for 12 h, the polymerization was quenched by plunging the reaction flask into liquid nitrogen, opened, and diluted with THF. The mixture was then precipitated into an excess amount of diethyl ether three times, and then the product was dried in vacuum oven at room temperature, and the final product was characterized by ^{1}H NMR as shown in **Figure S3**.

Synthesis of Amphiphilic Block Copolymer, POEGMA-*b*-PBMA (**Scheme S3**). The block copolymer was prepared via the subsequent RAFT polymerization of PBMA monomer using POEGMA as macro-RAFT agent (**Figure S3**). Typically, POEGMA (200 mg, 42.11 μmol), PBMA (150 mg, 188.0 μmol), AIBN (1.82 mg，11.1 μmol) and 2 mL THF were added into a dry polymerization tube with a magnetic stirring bar. The mixture was degassed through at least three freeze-pump-thaw cycles, and the polymerization tube then was sealed under vacuum. After being thermostated and stirred at oil bath at 70 ℃ for 24 h，the polymerization was quenched by plunging the reaction flask into liquid nitrogen. The mixture was then precipitated into an excess amount of diethyl ether three times, and then the product was dried in vacuum oven at room temperature. The final product was characterized by as shown in

Figure S3.



Scheme S3. Synthetic routes employed for the preparation of POEGMA-*b*-PBMA.

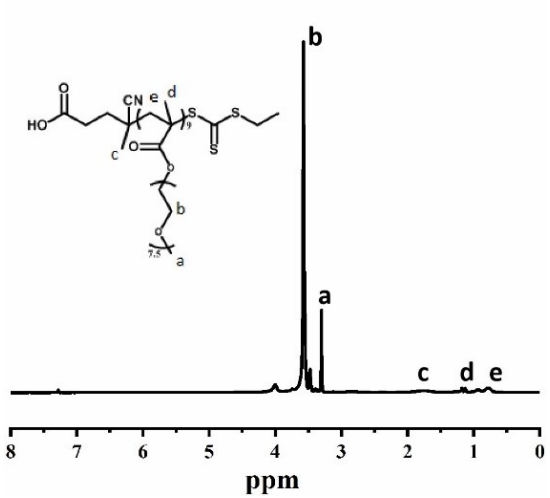


Figure S3. ^{1}H NMR spectrum of POEGMA in $CDCl_3$.

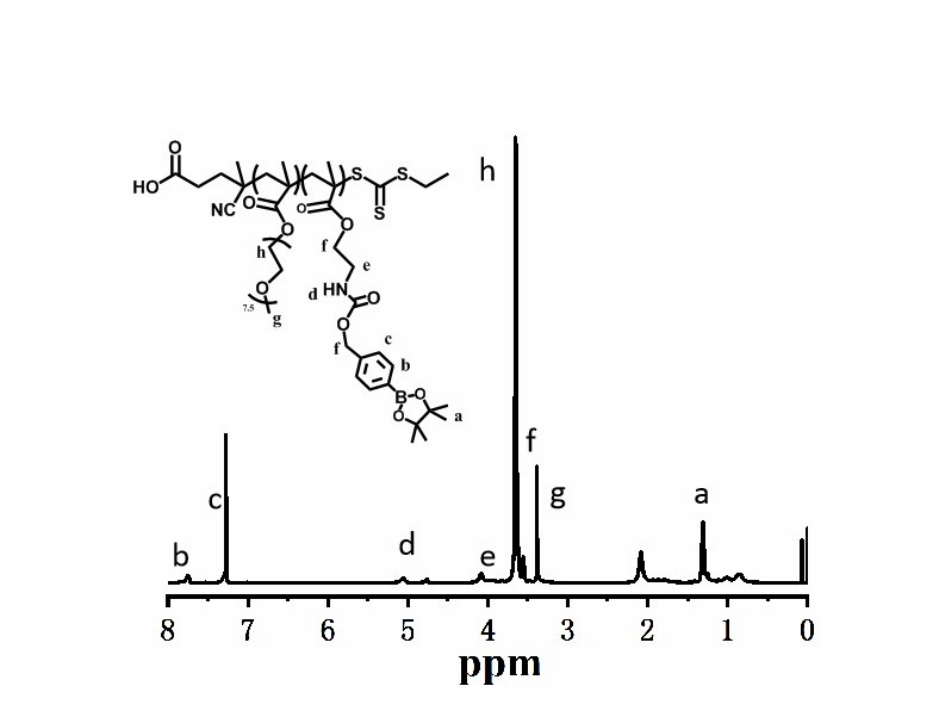


Figure S4. ^{1}H NMR spectrum of POEGMA-*b*-PBMA in $CDCl_3$.

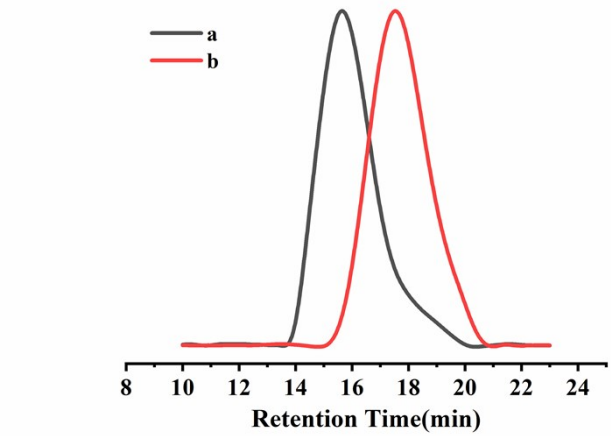


Figure S5. GPC curves of POEGMA-PBMA (a) and POEGMA (b).

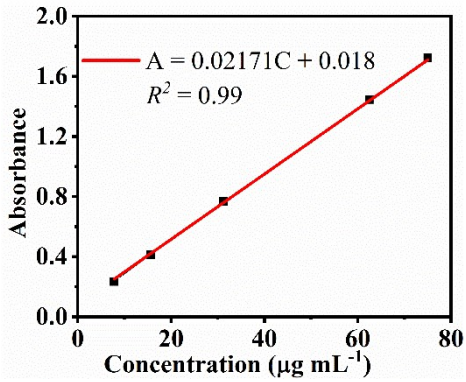


Figure S6. The UV-*vis* sbsorptance standard curve of TAPP.

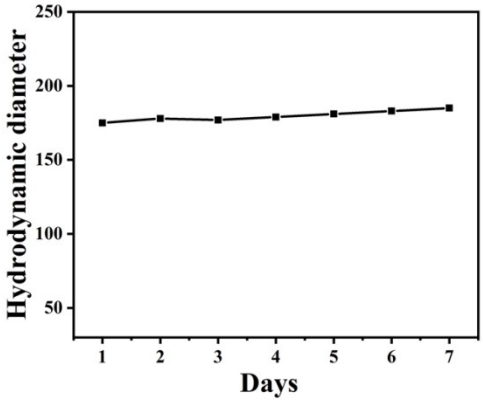
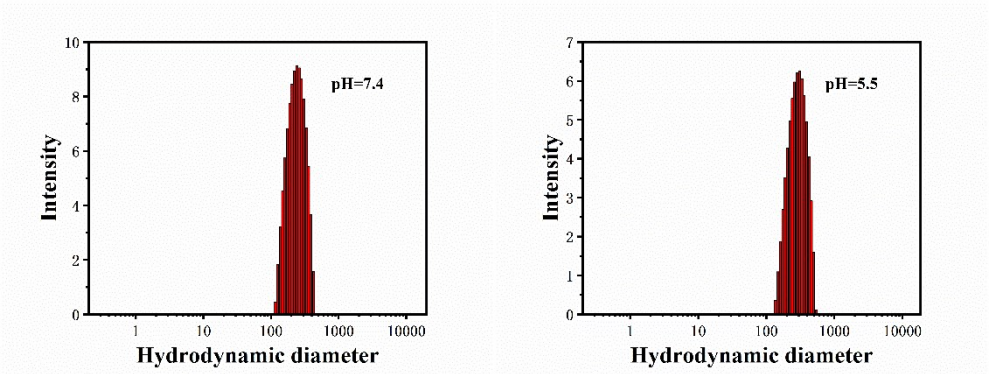


Figure S7. Changes of the hydrodynamic diameter of PT nanoparticles over a time period of seven days.



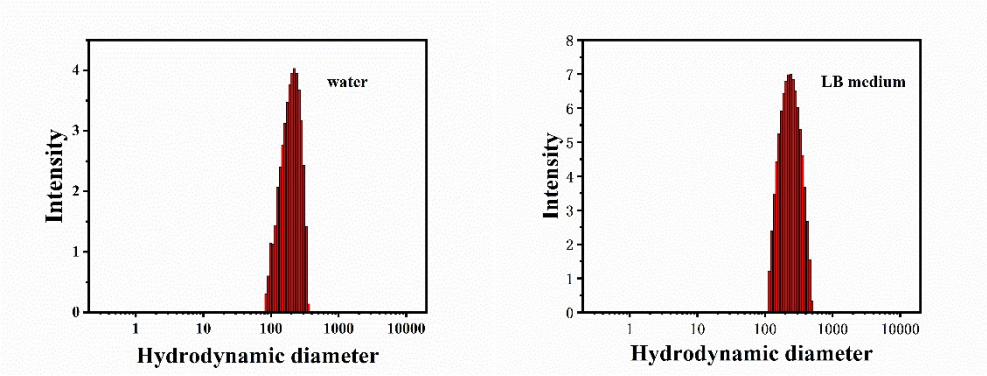


Figure S8. Hydrodynamic diameter of PT nanoparticles dispersed in different media.

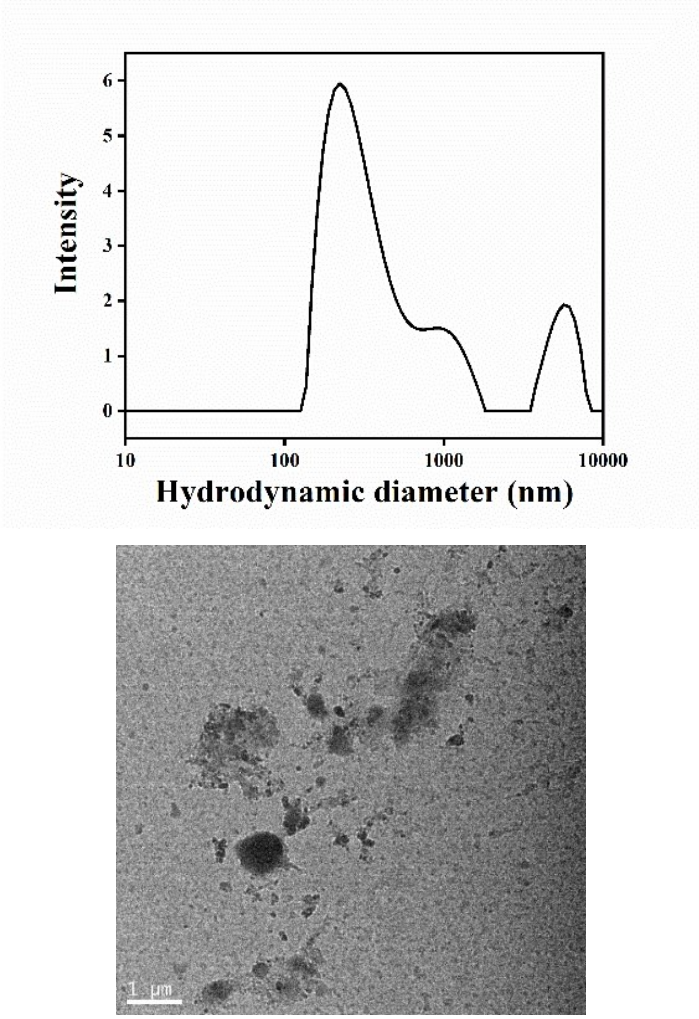


Figure S9. The diameter and TEM of the **PT** nanoparticles after treated with H_2O_2. Scare bar = 1um.

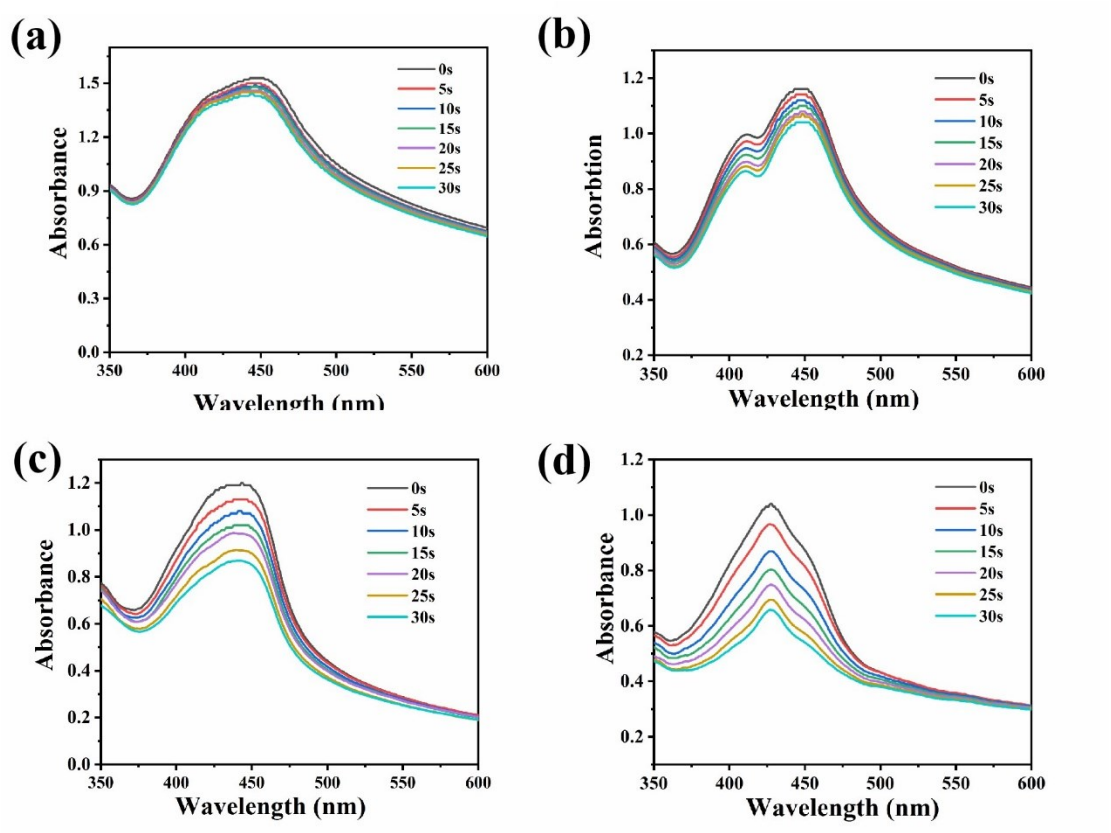


Figure S10. The UV-*vis* absorptance spectra of DPBF with laser irradiation. (a) pH = 7.4 (b) pH = 5.5. (c) pH = 7.4 + H_2O_2 (d) pH = 5.5+H_2O_2.

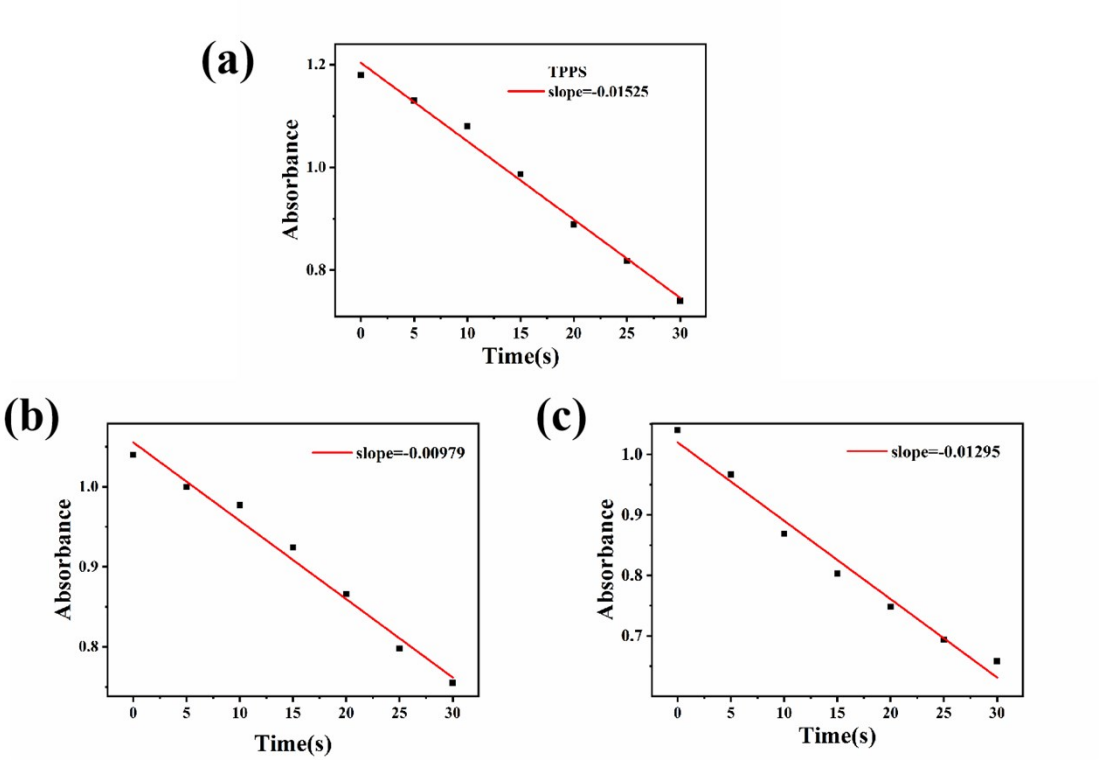


Figure S11. The UV-*vis* absorptance spectra of DPBF with laser irradiation. (a) TPPS (b) PT nanoparticles in pH = 7.4 (c) PT nanoparticles in pH = 5.5.

Table S.1. Singlet oxygen yield of PT nanoparticles

Samples	ΦΔ
pH = 7.4	0.45
pH = 5.5	0.60

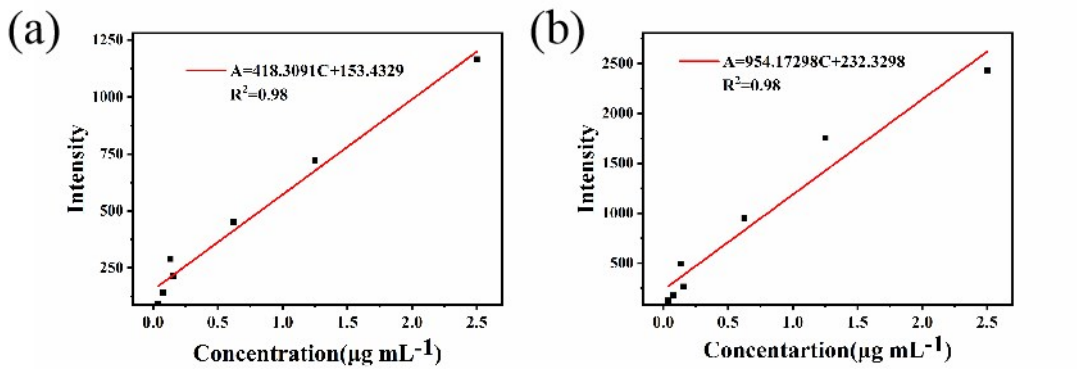


Figure S12. The fluorescence standard curves of TAPP (a) pH = 7.4 (b) pH = 5.5.

Bacterial culture. The pre-frozen bacterial fluid was transferred to fresh LB medium, and then shaken at 220 rpm overnight at 37°C. Diluted the overnight bacterial solution 1:100 and shook for another 2 h to make sure the bacteria in log growth phase before experiment.

Morphological characterization of bacteria. After incubating the bacteria with **PT** nanoparticles according to the antibacterial experiments section and washed three times with PBS, the bacterial suspensions were fixed with 2.5% glutaraldehyde in 0°C. After 12 h, the bacterial suspensions were dehydrated through sequential treatments of 30%, 50%, 70%, 80%, 90%, and 100% × 2 ethanol for 6 min. At last, the specimens were coated with gold before being inspected by Scanning Electron

Microscope.

Animal Experiments: All KM mice used in the experiment were purchased from Shanghai Jessie Experimental Animal Co., Ltd. All animal experiments were performed according to the guidelines for the protection of animal life and protocols.

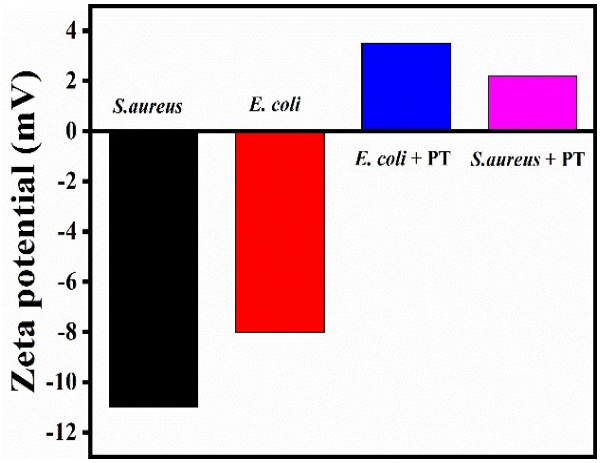


Figure S13. The zeta potential of bacteria before and after treated with **PT** nanoparticles.

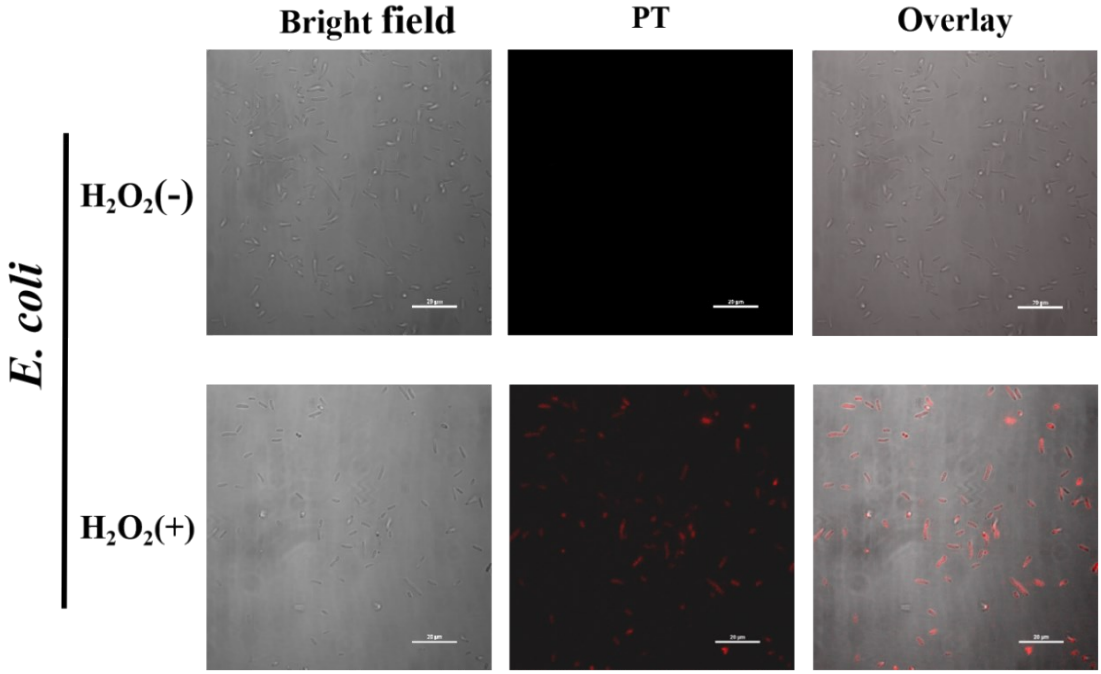


Figure S14. Confocal images of *E. coli* after incubation with the **PT** nanoparticles under different conditions for 1h at pH = 5.5.

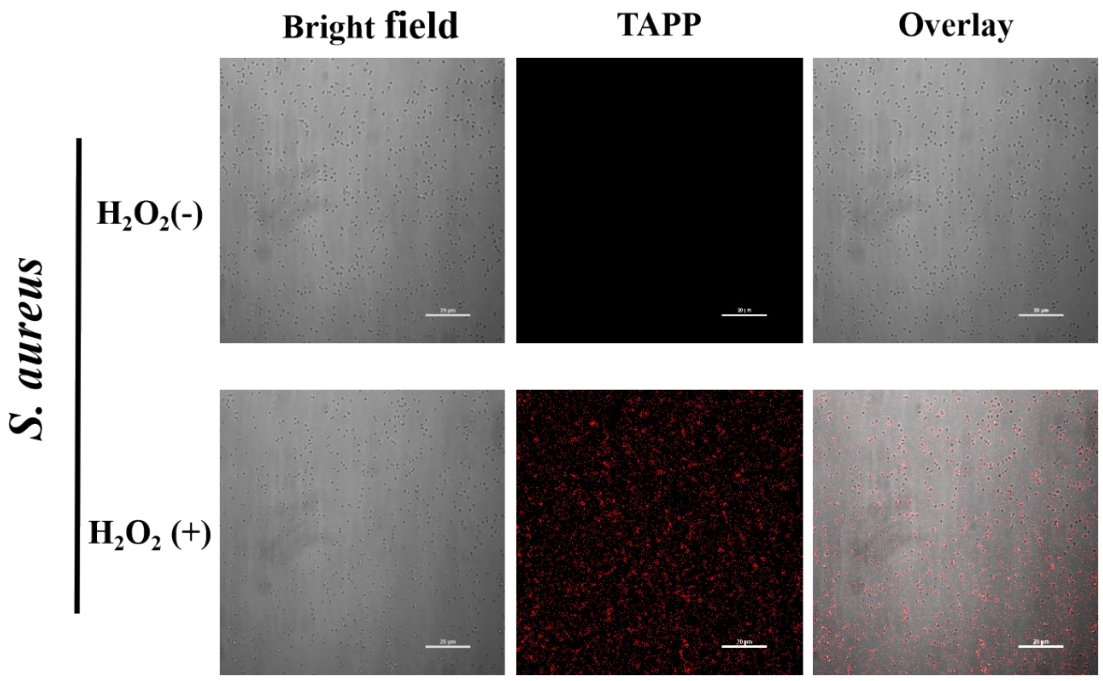


Figure S15. Confocal images of *S.aureas* after incubation with the **PT** nanoparticles under different conditions for 1h at pH = 5.5.

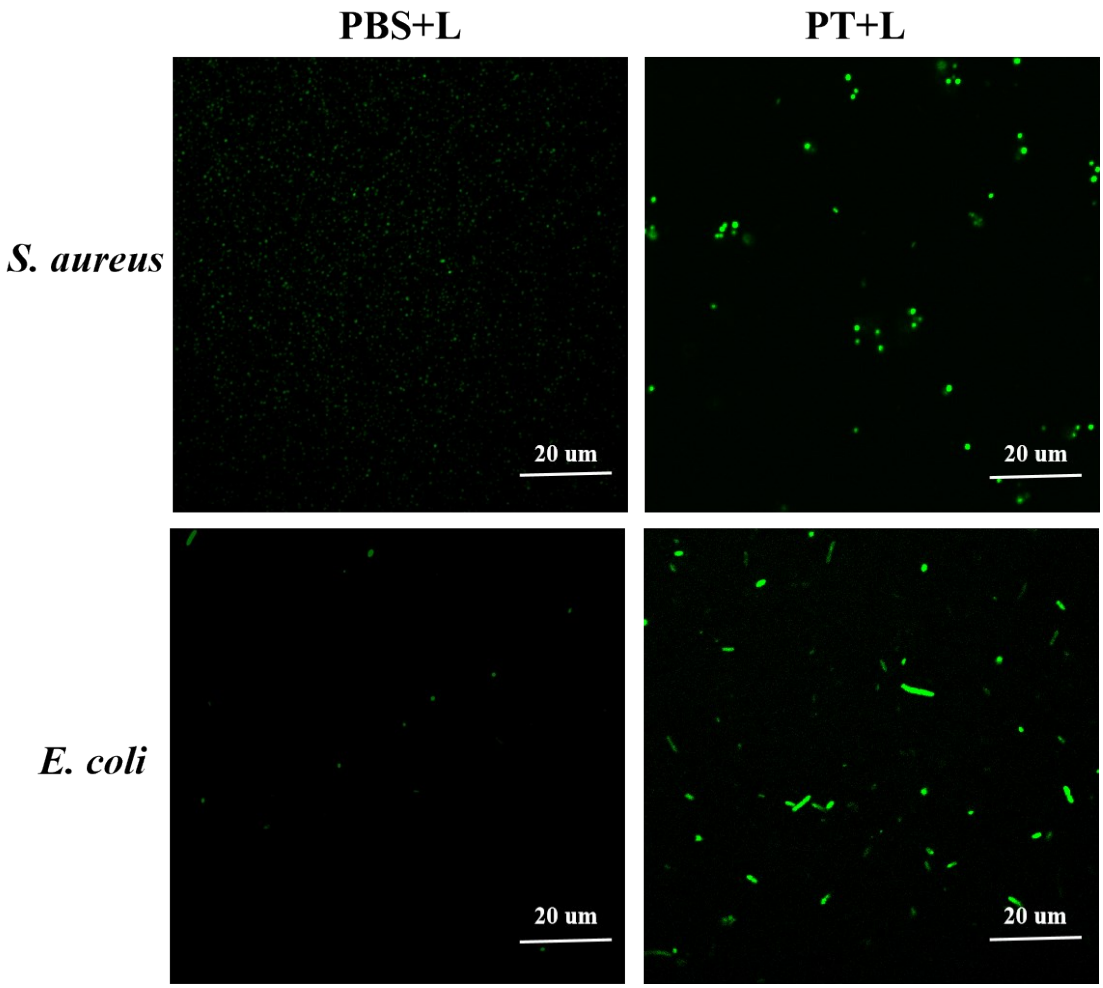


Figure S16. ROS production of bacteria incubated with PBS and **PT** nanoparticles under laser irradiation

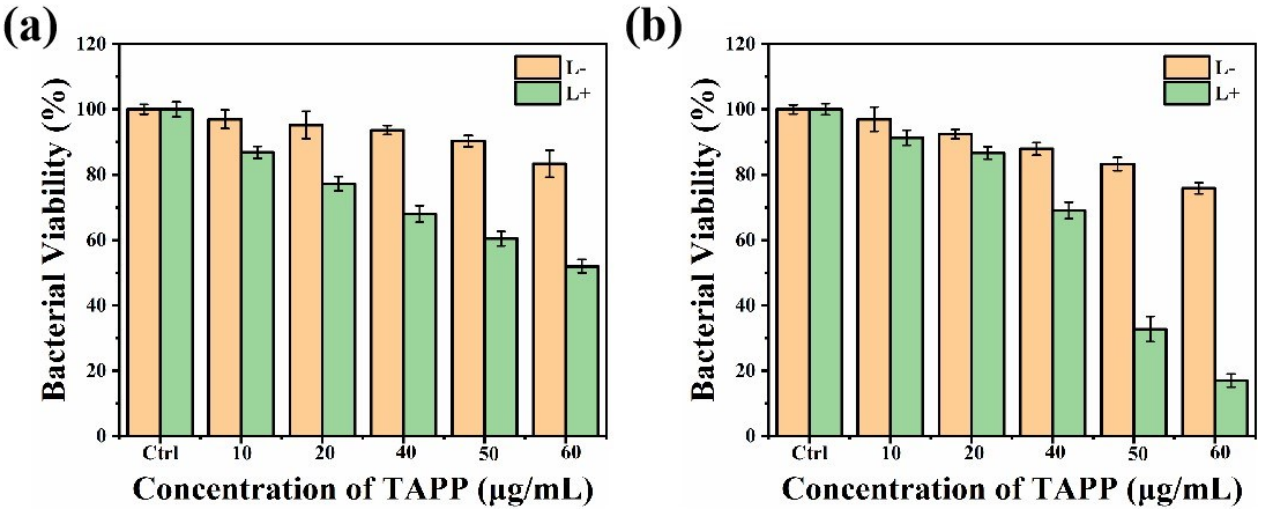


Figure S17. The viability of *S. aureus* treated with **PT** nanoparticles (a) pH = 7.4 (b) pH = 5.5 with the addition of H_2O_2.

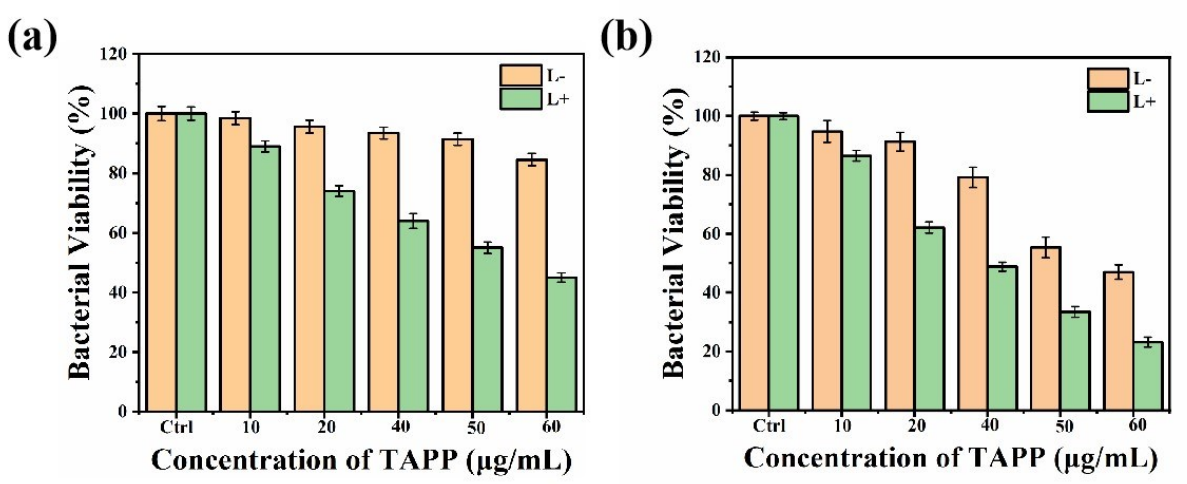


Figure S18. The viability of *E. coli* treated with **PT** nanoparticles (a) pH = 7.4 (b) pH = 5.5 with the addition of H_2O_2.

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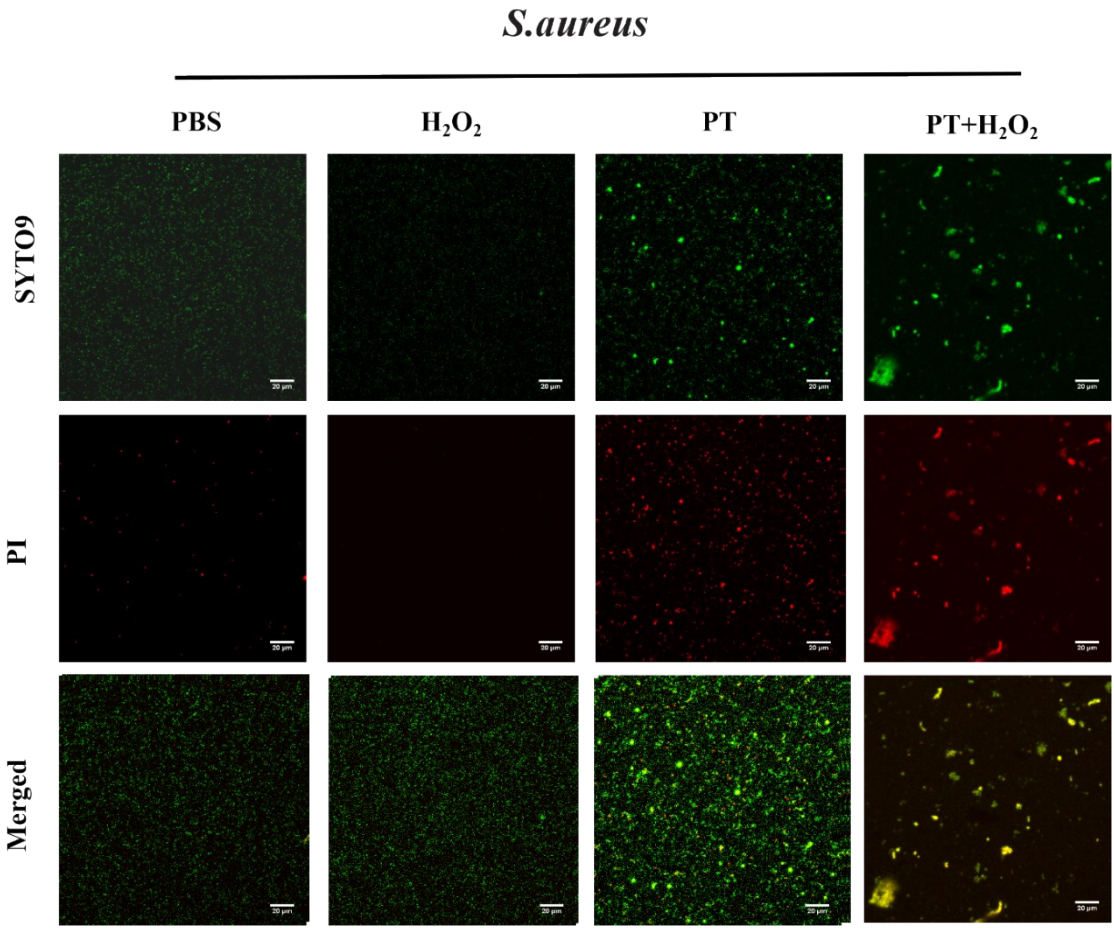

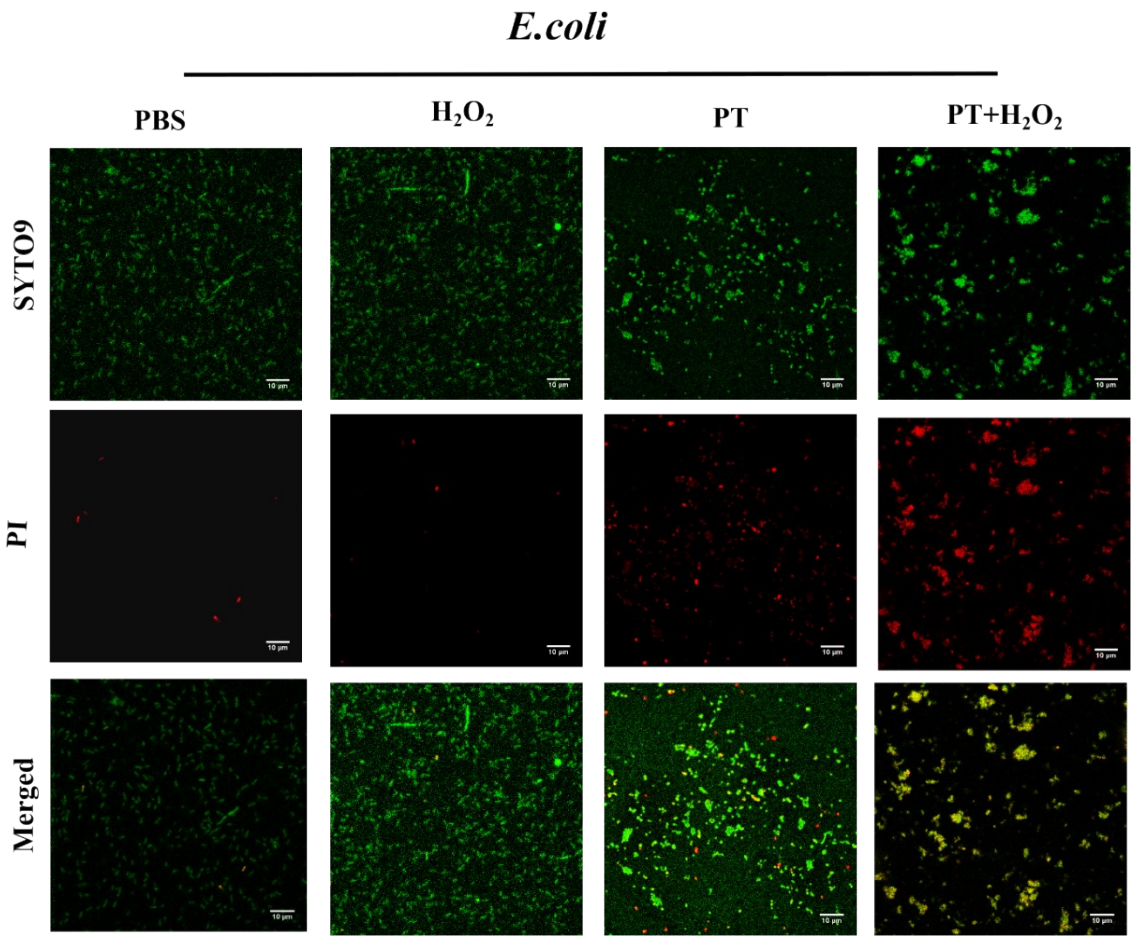

Figure S19. Live/dead bacterial cell observation of *S.aureus* and *E.coli* before and after treated with **PT** nanoparticles under irradiation at pH = 5.5, respectively. Scare bar = 20 μm.

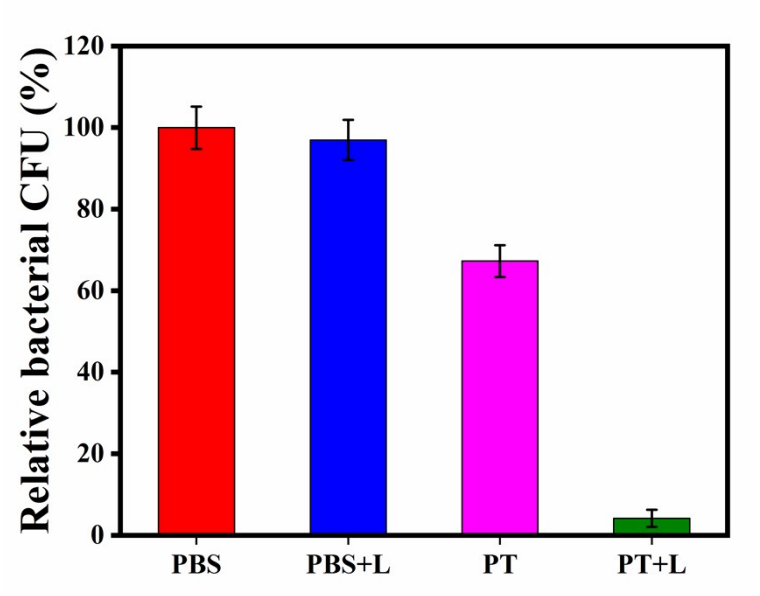

Figure S20. The CFU count of bacteria living in the catheter.

References

1. C. Wang, P. Zhao, G. Yang, X. Chen, Y. Jiang, X. Jiang, Y. Wu, Y. Liu, W. Zhang and W. Bu, *Materials Horizons*, 2020, **7**, 1180-1185.
2. Y. Zhu, C. Chen, G. Yang, Q. Wu, J. Tian, E. Hao, H. Cao, Y. Gao and W. Zhang, *ACS Appl Mater Interfaces*, 2020, **12**, 44523-44533.