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A Modified Flower Pollen-based Photosensitization Process for Enhanced Solar Water Disinfection: Photoelectric effect and Bactericidal Mechanisms

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Abstract

Solar disinfection (SODIS) is regarded as an affordable and effective point-of-use (POU) water disinfection treatment urgently needed in rural developing world. This work developed an enhanced SODIS scheme that utilized a novel flower pollen-based catalyst (Te-TRP). The bench-scale experiments demonstrated 100% photothermocatalytic inactivation of approximately 7-log *E. coli* K-12, *Spingopyxis sp.* BM1-1, or *S. aureus* bacterium by Te-TRP within 40-60 min. Moving toward practical device design, we constructed a flow-through reactor and demonstrated the outstanding water disinfection performance of Te-TRP. The in-depth mechanistic study revealed the synergetic effect between photocatalysis and photothermal conversion and identified the bacterial inactivation pathway. $^1O_2$ and $\bullet O_2^-$ were verified to be the dominant reactive oxygen species involved in the bacterial inactivation. The damage to bacterial cells caused by photothermocatalytic reactions was systematically investigated, demonstrating the cell membrane destruction, the loss of enzyme activity, the increased cell membrane permeability, and the complete inactivation of bacteria without the viable but nonculturable state cells. This work not only affords a facile approach to preparing biomaterial-based catalysts capable of efficient photothermocatalytic bacterial inactivation, but also proposes a prototype of POU water treatment, opening up an avenue for sustainable environmental remediation.

Keywords: Solar disinfection; Nature-inspired material; Photothermal; Photocatalytic; Bactericidal mechanism

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1. Introduction

Although huge efforts have been made in the last few decades to disinfect water, the lack of access to safe drinking water is still one of the greatest challenges worldwide, especially in low- and lower-middle-income countries. The population who has no access to safe water and sanitation services is as large as 4.5 billion (Ferreira et al., 2021), along with annual deaths of over half a million caused by the consumption of contaminated water (Loeb et al., 2018; Pichel et al., 2019). Driven by the urgent social needs for safe drinking water, the United Nations proposed a goal of "ensure access to water and sanitation for all" to be accomplished by 2030 (Ryberg et al., 2021). Therefore, affordable, low-cost, and effective water disinfection systems are urgently needed to achieve universal access to safe drinking water (Wang et al., 2019b).

In comparison with centralized water treatment, point-of-use (POU) water treatment demonstrates the advantages of low initial investment cost and easy operation, matching well with the needs from rural communities (Ryberg et al., 2018; Ryberg et al., 2020). Solar disinfection (SODIS) is one of the most intensively used POU water disinfection methods, taking advantage of the short-wavelength UV and the thermal effect of sunlight to inactivate hazardous microorganisms. However, SODIS suffers from the insufficient disinfection efficiency (e.g., less than 0.5-log inactivation of *E. coli* K-12 within 1 h) and the requirement for long-time exposure (e.g., 1-2 days) to sunlight (Cowie et al., 2020; Loeb et al., 2018; Ozores Diez et al., 2020; Zhang et al., 2020b). The use of additives such as photothermal catalysts is an effective strategy to improve the efficiency of SODIS. Thanks to the synergetic effect between

photocatalysis and photothermal conversion, photothermocatalytic materials potentially outperform their semiconductor and photothermal catalyst counterparts (Rommozzi et al., 2020). Our recent work reported a Ag-MnO_2 catalyst achieving significantly enhanced inactivation of *E. coli* K-12 upon sunlight irradiation, with the substantially increased temperature of the bulk water from 25 to 60 ℃ and the generation of reactive oxygen species (ROS) (Xia et al., 2019). However, the metal-based catalysts have certain drawbacks such as high cost, photo-corrosion, and metal leaching, which limit their large-scale practical applications (Chang et al., 2016; Taniguchi et al., 2020; Wang et al., 2020b). These issues drive researchers to explore low-cost and metal-free materials capable of efficient photothermocatalytic POU water disinfection (Ding et al., 2020; Li et al., 2019; Xia et al., 2015; Zhang et al., 2020a).

Learning from nature offers a promising approach for the development of cost-effective and metal-free biomaterials for water treatment. Plenty of biological sources in nature are qualified as environmental functional materials with minor modifications. Some of us have found that the treated rape pollen (TRP) was a promising biomass-derived photocatalyst exhibiting a high density of active sites and wide-spectrum response (Jiang et al., 2018; Wang et al., 2019a). It could inactivate 7-$\log_{10}$ cfu/mL of *E. coli* K-12 within 4 h under visible light. Given the good photocatalytic activity, TRP would be qualified as a photocatalyst candidate to be coupled with an effective photothermal material, thus realizing the synergetic photothermocatalytic bacterial inactivation.

Noble metals (e.g., Au, Ag, and Pt, etc.) with localized surface plasmon resonance (LSPR) effect have been intensively used as photothermal materials (Fan et al., 2016; Seh et al., 2012; Wang et al., 2018a; Xia et al., 2018b; Zhang et al., 2019; Zhou et al., 2016; Zhou et al., 2017; Zielinski et al., 2016). These noble metals can generate hot charge carriers and dissipate their energy by local heating of the surroundings (Kale et al., 2013; Mateo et al., 2021), favorable for the photocatalytic and photothermal reactions. However, considering the low investment cost of POU water treatment at a rural household level, noble metals are cost-prohibitive. This motivates researchers to search non-noble metals as alternative photothermal catalysts. Recently, the semi-metallic tellurium (Te) has been demonstrated to exhibit broadband solar energy harvesting and efficient photothermal conversion. Te nanoparticles show broad optical absorption up to 3500 nm, making Te nanoparticles rapidly increase from 29 to 85 ℃ within 100 s irradiated by a halogen tungsten lamp with the spectrum similar to sunlight (Han et al., 2018; Ma et al., 2018; Ou et al., 2020; Yu et al., 2018; Zhang et al., 2014; Zhang et al., 2018). In addition, the small bandgap (0.35 eV) of Te may facilitate the separation of charge carriers of a Te-loaded semiconductor and thus contribute to the photocatalytic performance. The unique three-dimensional porous structure of TRP provides large accessible surface areas for loading Te nanomaterials. Therefore, we hypothesize that the combination of Te with TRP would lead to the desirable properties for water disinfection.

In this work, the Te nanowires loaded TRP (Te-TRP) was for the first time developed and applied to SODIS. The rapid 100% bacterial inactivation of 7.13-log *E.*

coli K-12 was achieved by Te-TRP under simulated sunlight within 60 min. Mechanistic study showed that Te-TRP exhibited altered wettability, synergetic photocatalytic and photothermal effect, and improved photocatalytic properties, leading to the efficient SODIS performance. To realize a real-world POU water treatment, the flow-through SODIS system was established and the performance of Te-TRP catalyst was examined. The mechanisms of the significantly increased activity of Te-TRP was systematically investigated, followed by the study of bactericidal pathway in the photothermocatalytic treatment to guide future design of advanced catalysts.

2. Experimental

2.1. Materials

All chemicals used in this work are analytical grade and used without further purification. Sodium tellurite (Na_2TeO_3), 5,5-dimethyl-1-pyrroline-N-oxide ($C_6H_{11}NO$, 97%), 2,4,6-Trimethylpyridine ($C_8H_{11}N$,99%), TEMPOL ($C_9H_{18}NO_2$), and glutaraldehyde ($C_5H_8O_2$, 50% aqueous solution) were purchased from Aladdin Chemical Reagent Co., Ltd., polyvinylpyrrolidone (PVP, Mw~40000) and hydrazine hydrate ($N_2H_4 \cdot H_2O$,80%) were purchased from Tianjin Bodi Chemical Co., Ltd., isopropanol was purchased from Tianjin Damao Chemical Reagent Factory. LB broth and LB agar were purchased from Guangdong Huankai Microbial Technology Co., LTD. Rape pollen (RP) was purchased from Henan Zhuoyu Bee Products Co., Ltd. Distilled water was used in all experiments.

2.2. Synthesis of Materials

2.2.1 Preparation of TRP

TRP was prepared following the procedure reported by Jiang et al. (2018). Typically, 10 g of RP was suspended in 100-mL deionized water under ultrasonication until a homogeneous bright yellow suspension formed. Then, RP was collected by filtration and washed using absolute ethanol and deionized water 3 times. Subsequently, RP was fixed in a mixture of 50-mL absolute ethanol and 50-mL formaldehyde solution with continuous stirring for 2 h, collected by filtration, and washed with deionized water 3 times. After that, RP was immersed in 100 mL of concentrated sulfuric acid (12 mol/L) and stirred vigorously at 80 ℃ for 4-5 h. The product was filtered and washed with deionized water till the solution pH reached 7. After vacuum drying at 60 ℃ for 48 h, the dark brown TRP powder was obtained.

2.2.2 Fabrication of Te-TRP

The ultrafine Te nanowires loaded TRP was fabricated by a hydrothermal method (He et al., 2016; Liang et al., 2013). Typically, 0.05 g of the as-prepared TRP, 0.08 g of sodium tellurite (Na_2TeO_3), and 0.5 g of polyvinylpyrrolidone (PVP) were dispersed in 50 mL of deionized water under violent stirring with the assistance of ultrasound. Then, 3.5 mL of $NH_3 \cdot H_2O$ and 1.5 mL of $N_2H_4 \cdot H_2O$ were added as reducing agents and stirred for another 1 h. After that, the mixture was transferred into a 100-mL autoclave, and heated in an oven at 200 °C for 10 h. After cooling to room temperature, the resultant product was centrifuged at 10000 rpm/min for 10 min and washed with deionized water until the solution pH turned neutral. After vacuum drying at 60 ℃ for 24 h, the Te-TRP composite with the Te to TRP mass ratio of being 1:1 was obtained.

In addition, the Te-TRP composites with the Te:TRP mass ratio of 1:2, 2:1, and 4:1 were prepared by varying the dosage of Na_2TeO_3 being 0.08, 0.32, and 0.64 g, respectively. Unless otherwise specified, the Te:TRP mass ratio in Te-TRP is 1:1.

2.3 Material characterizations

The X-ray diffraction (XRD) patterns of samples were recorded on a RIGAKU D-MAX 2200 diffractometer with monochromatic Cu Kα radiation at a scanning speed of 8º/s from 10.0º to 80.0º. The morphology of samples was investigated by a Quanta 400F thermal field emission scanning electron microscopy (SEM, Shimazhu, Japan). Fourier transform infrared (FTIR) spectra were recorded using a Nicolet iS10 FTIR spectrometer (Thermofisher Scientific, U.S.A.) with 0.2 cm^{-1} resolution. UV-Vis-NIR diffuse reflectance spectra (DRS) were measured by a Lambda 950 UV-Vis-NIR spectrophotometer (PerkinElmer, U.S.A.). Photoelectrochemical experiments were carried out in 1.0 M Na_2SO_4 solution with a CHI 660D electrochemical workstation using a three-electrode system, in which a platinum electrode was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. Photothermal conversion performance of Te-TRP in water (0.5 mg/mL) was investigated by an infrared thermal imager FLIR-C3 under simulated sunlight irradiation. The solid-state infrared thermographic images of the powdered samples were recorded by an infrared thermal imager (Fotric 226s, U.S.A.). The wettability of samples was investigated by a contact angle tester (Kruss DSA25, Germany). The submerged thermocouple microprobe was used to monitor the solution temperature under irradiation.

2.4 Photothermocatalytic bacterial inactivation

E. coli K-12 was chosen as the model bacterium to evaluate the bacterial inactivation. Bacterial cells were cultured in 25 mL of nutrient broth (NB) at 37 ℃ for 16 h under shaking. Then, 10 mL of the *E. coli* K-12 suspension was collected, centrifugated at 5,000 rpm for 5 min, and washed with sterilized water twice. Subsequently, 2.5 mg of catalyst was added into 5 mL of deionized water containing 10^7 cfu/mL of *E. coli* K-12 and irradiated by the simulated sunlight (light intensity = ~200 mW/cm^2, spectrum is shown in Fig. S2) provided by a xenon lamp (PLS-SXE300D, China). At given time intervals, samples were collected and spread on agar plates for incubation. The viable cells were counted after incubation at 37 °C for 24 h. To investigate the effectivity of Te-TRP to inactivate other types of bacteria, *Spingopyxis sp*. BM1-1 and *Staphylococcus (S.) aureus* were also used.

To evaluate the reusability and stability, the photothermocatalytic bacterial inactivation was repeated 5 times using the recycled Te-TRP. Before each run, Te-TRP was recovered by filtration, thoroughly washed with ethanol and deionized water to remove the adhered bacterial residues and other substances, and dried at 60 ℃ overnight.

To move toward practical POU operations, a continuous flow-through disinfection system was built to examine the disinfection performance of Te-TRP in flowing water under natural sunlight irradiation (35 mW/cm^2). As shown in Fig. 4a-c, this system consisted of a circulating pump, a bench-scale reactor, and a triangle bottle with a magnetic stirrer. Upon bacterial inactivation, the water flow was cycled through the

flow-through disinfection system. The concentration of Te-TRP catalyst was 0.2 mg/mL. The initial *E. coli* K-12 concentration was 3.7 $\log_{10}$ cfu/mL, close to that in natural water. The suspended Te-TRP catalyst in water was removed by a floating method, as shown in Fig. 4g-i. To estimate the catalyst removal rate using this method, the Te-TRP residues in the purified water (from outlet) were collected by filtration for weight measurement.

2.5 ROS analysis

ROS were detected and analyzed by an electron spin resonance (ESR) spectrometer (Bruker A300). Spin traps can capture ROS and produce spin adducts. 2,4,6-trimethylpyridine (TEMP) aqueous solution, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) in dimethyl sulfoxide (DMSO) solution, and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) aqueous solution were used to trap $^1O_2$, $\bullet O_2^-$ and •OH, respectively. To identify the ROS generated via photothermocatalytic, photocatalytic, and photothermal reactions, respectively, the ESR spectra for each ROS were recorded under various conditions: (1) irradiated by simulated sunlight without temperature adjustment; (2) irradiated by simulated sunlight with temperature adjustment (fixed at 25 ℃) to allow photocatalysis alone; and (3) without irradiation but with temperature adjustment (fixed at 55 ℃) to simulate the photothermal process. In addition to ESR, a scavenger study was carried out to evaluate the roles of reactive species in the bacterial inactivation process. 2 mM of sodium azide (NaN_3), TEMPOL, and isopropyl alcohol (IPA) were used to quench $^1O_2$, $\bullet O_2^-$ and •OH, respectively.

2.6. Biomolecule oxidation assay and enzyme activity

Cell viability assay, SEM imaging, qualification of superoxide dismutase (SOD) and catalase (CAT) enzymes, analysis of bacterial membrane permeability, and determination of single-cell activity were shown in Supplementary Text S2.

3. Results and discussion

3.1 Material characterizations

XRD was used to analyze the crystal structure and phase composition of Te nanowires, TRP, and Te-TRP. As shown in Fig. 1a, pure Te nanowires displayed sharp and strong diffraction peaks at 2θ = 23.04°, 27.56°, 38.26°, 40.45°, 43.33°, 45.9°, 47.05°, 49.63°, 51.24°, 51.94°, 56.88°, and 62.81°, which were well indexed to the t-Te phase (JCPDS No. 36-1452). The XRD patterns of bare TRP only exhibited a wide diffraction peak at around 20°, revealing the amorphous structure (Jiang et al., 2018; Wang et al., 2019a). The Te-TRP composites showed the same diffraction peak positions as Te, but the intensity of some diffraction peaks varied, which was attributed to the changed surface exposure of Te nanowires after loading on TRP.

The FTIR spectra (Fig. 1b) showed that TRP was mainly composed of C=O, -CH_3, and -CH=CH- bonds. Peaks appeared at 1720 cm^{-1} and 1230 cm^{-1} indicated the presence of C=O bond in TRP. The peak at 2930 cm^{-1} was assigned to the stretching of C-H (Wang et al., 2019a). The FTIR spectrum of Te-TRP mainly followed suit, indicating the preserved TPR structure upon Te loading. The UV-Vis-NIR DRS spectra were performed to investigate the optical property of TRP and Te-TRP. As shown in Fig. 1c, Te-TRP exhibited strong and broad absorption in UV, visible, and even infrared (IR)

regions, while TRP showed strong UV but insufficient visible-light absorption, indicating the significantly extended spectral response and improved light-harvesting capacity of Te-TRP.

SEM images were recorded to examine the morphologies of TRP before and after Te loading. As shown in Fig. 2a, Te nanowires exhibited a uniform ultrafine nanowire structure. Fig. 2b showed the unique three-dimensional porous hollow structure of TRP, with an average particle diameter of 1-2 μm. This structure would not only provide abundant surface sites for the growth of Te nanowires, but also favor the contact with bacterial cells. SEM images of Te-TRP clearly showed the well-loaded Te nanowires on either the inner or outer surface of TRP. Regarding the Te nanowires on the TPR outer surface, they primarily concentrated on the pollen framework, with a small portion across the pores. The unique distribution of Te nanowires would affect the near-field optical intensity of Te-TRP upon irradiation, which will be discussed in section 3.3.

It has been acknowledged that TRP was not suitable for liquid-phase operations due to its high hydrophobicity (Xiao et al., 2019). The loading of Te nanowires, a hydrophilic material, on TRP, is expected to change the wettability and enable Te-TRP for effective water disinfection. We then measured the water contact angle (WCA) to evaluate the wettability of our samples. As shown in Fig. 2e, the WCA of bare Te nanowires was 24.6 °, revealing the strong hydrophilicity. While the WCA of bare TRP was 110 ° (Fig. 2g), which demonstrated that TRP had strong hydrophobicity, unfavorable for water disinfection operations. As expected, the WCA of the Te-TRP

composites was reduced to 45.2 ° (Fig. 2f), revealing that the loading of Te nanowires could improve the hydrophilicity of TRP, thereby favoring the dispersion of the composites in water and facilitating the contact between Te-TRP and bacterial cells.

3.2 Solar-driven photothermocatalytic bacterial inactivation performance

Bench-scale experiments. To evaluate the photothermocatalytic performance, we started by investigating the bacterial inactivation of *E. coli* K-12, one of the most commonly detected bacteria in contaminated water, using the benchmark bacterial cell density (1×10^7 cfu/mL) (Wang et al., 2019a). As shown in Fig. 3a, the Te-TRP composite completely inactivated 7.13-log *E. coli* K-12 within 1 h, significantly outperforming its counterparts, bare TRP and Te nanowires, which achieved only 3.52- and 3.89-log inactivation of *E. coli* K-12, respectively. The outstanding photothermocatalytic activity of Te-TRP was primarily attributed to the synergetic effect of TRP and Te, which will be discussed in section 3.3. The negligible biotoxicity of Te-TRP was verified by the tiny decrease in cell population in the presence of Te-TRP in dark. Sunlight alone (without catalyst) only inactivated 0.57-log *E. coli* K-12 cells, indicating that sunlight had almost no photolysis to bacterial cells.

To verify whether the Te-TRP catalyst is UV or visible-NIR favored in the SODIS process, the photothermocatalytic bacterial inactivation was also carried out under visible-NIR irradiation, using the UV cut-off simulated sunlight. As shown in Fig. S3, the visible-NIR light-driven antibacterial efficiency was slightly lower than that irradiated by full sunlight, with 5.36-log *E. coli* K-12 cells inactivated within 1 h. Therefore, Te-TRP is visible-NIR favored in the SODIS operation.

Optimization of Te to TRP mass ratio and catalyst concentration. To achieve the highest photothermocatalytic efficiency, parameters such as Te to TRP mass ratio and catalyst concentration were optimized. First, the performance of the Te-TRP composites with various Te/TRP mass ratios was evaluated. As shown in Fig. 3b, the Te-TRP composite with Te/TRP mass ratio of 1:1 showed the most efficient bacterial inactivation, while the lower bactericidal efficiency was observed by either increasing or decreasing the Te content. Te-TRP (2:1), Te-TRP (4:1), and Te-TRP (1:2) achieved 5.84, 4.77, and 4.65 $\log_{10}$ cfu/mL of bacterial inactivation within 1 h, respectively. Given the fact that the photothermal effect of Te-TRP is primarily due to the presence of Te nanowires (will be shown later), on the one hand, the insufficient Te loading would lead to the lower photothermal conversion efficiency, which is unfavorable for bacterial inactivation; on the other hand, the excessive loading of Te nanowires on TRP would cause a heavy coverage of the photoactive sites on TRP surface and thus suppress the photocatalytic reactions. Subsequently, the concentration of Te-TRP catalyst was optimized using the best-performing Te-TRP composite (Te/TRP mass ratio = 1:1). As shown in Fig. 3c, the bactericidal efficiency decreased when further increasing the Te-TRP concentration from 0.5 to 1.0 mg/mL or above. The results were ascribed to the reduced light penetration and insufficient light-harvesting owing to the excessive dosage of Te-TRP. Decreasing the catalyst concentration from 0.5 to 0.25 mg/mL also led to a lower bactericidal efficiency, which was due to the ineffective photothermal conversion and the limited number of photoactive sites.

Photothermocatalytic inactivation of other bacteria. Considering the presence

of bacteria other than *E. coli* in water matrixes, the photothermocatalytic inactivation of other bacteria, i.e., Gram-negative *Spingopyxis sp*. BM1-1 and Gram-positive *S. aureus* bacteria were studied. *Spingopyxis sp.* BM1-1 is highly resistant to chlorine and would survive in sewage after chlorination treatment. Impressively, Te-TRP completely inactivated 7.1-log *Spingopyxis sp.* BM1-1 cells within 40 min under simulated sunlight, representing an efficiency even higher than that towards *E. coli* K-12. In comparison with *Spingopyxis sp.* BM1-1, it took longer (90 min) to inactivate *S. aureus* (6.7-log) under the same condition, but the efficiency was still satisfactory. It could be deduced that Te-TRP would be more applicable for the inactivation of Gram-negative bacteria. The above results emphasized the great potential of Te-TRP in inactivating a wide range of bacteria, especially Gram-negative organisms.

Stability and reusability of Te-TRP. The stability and reusability of catalysts are important for their practical applications. As such, we evaluated the stability and reusability of our catalyst by repeating the photothermocatalytic experiments 5 times and examining the morphology of Te-TRP by SEM after multiple reuses. As shown in Fig. 4a, the bactericidal efficiency slightly decreased after each cycle, which was mainly due to the mass loss of Te-TRP and the accumulation of bacterial residues on Te-TRP. But Te-TRP still realized 6-log *E. coli* K-12 inactivation in the 5^{th} run, corresponding to as high as 99% inactivation efficiency. The SEM images of Te-TRP before and after 5 cycle runs showed negligible changes (Fig. 4b and c). Therefore, the structure of Te-TRP remained intact after multiple runs. These results demonstrated the high stability and reusability of Te-TRP.

Flow-through water disinfection. To evaluate the potential of our catalysts for more practical POU operations, a pilot-scale circulating flow-through disinfection system was constructed and used for SODIS. The diagram and photographs of the flow-through reactor are presented in Fig. 5a-c. As shown in Fig. 5d, after being irradiated by natural sunlight for 60 min, *E. coli* K-12 bacteria in the flow-through disinfection system were completely inactivated by Te-TRP, whereas sunlight alone and bare TRP achieved 0.18- and 0.58-log bacterial inactivation under the same conditions, respectively, indicating the significantly enhanced disinfection by Te-TRP. In addition, the spread plate assay (Fig. 5e and f) showed that the bacteria after 60-min treatment were non-culturable, demonstrating the complete bacterial inactivation by Te-TRP. The affordable recovery of catalysts for reuse is important in a real-world water treatment. As shown in Fig. 5g-i, thanks to the low material density of Te-TRP, as much as 99.67% of Te-TRP was recovered via a floating strategy in 30 min without additional energy supply. The preliminary cost of this flow-through water disinfection system was estimated to be ca. \$0.001/L (Text S3), it was similar with or even lower than that of other POU water disinfection methods, such as edible dye-enhanced SODIS (\$0.001−0.002/L) (Ryberg et al., 2018) and water boiling (\$0.001−0.007/L) (Clasen et al., 2008a; Clasen et al., 2008b). Thus, Te-TRP showed great potential for cost-effective bacterial inactivation in practical water treatment operations.

3.3. Mechanistic investigations

Bulk Water Heating. To explore the photothermocatalytic bacterial inactivation mechanisms, we started by evaluating the photothermal conversion performance by

monitoring the bulk water heating. The thermo-images (Fig. 6a) showed that the temperature of Te-TRP suspension increased from ca. 27 ℃ to 55-60 °C within 30 min under sunlight irradiation, enabling the photothermal effect and promoting the photocatalytic reactions. By contrast, the thermo-images of pure water (Fig. 6b) showed a negligible temperature increase within 30 min under the same condition. The solid-state infrared thermographic images (Fig. 6c) demonstrated that the local temperature of Te-TRP powder (99.3 ℃) was higher than that of Te (86.5 ℃) and TRP (61.9 ℃) powders. The localized high temperature of catalysts would heat the surrounding environment and attack bacterial cells. The *in-situ* temperature measurement (Fig. 6d) showed that the temperature of Te-TRP suspension rapidly increased from 27 to 57 ℃ within 20 min and stayed at this value afterward. For pure water and TRP suspension, their temperature increased to 38.5 °C and 42.3 °C after 10 min and remained unchanged with prolonged irradiation. These results revealed that Te-TRP exhibited an efficient photothermal conversion of sunlight and rapidly heated the bulk water to a relatively high temperature capable of facilitating bacterial inactivation (Ni et al., 2015).

Simulation of the near-field electric/optical intensity. To better understand the photothermal mechanisms, the simulation of electric/optical intensity near TRP and Te-TRP particles upon irradiation was carried out (Text S1). The catalyst models were constructed based on the SEM results (Fig. 2b and Fig. 2d), where the quantity ratio of Te nanowires located on TRP framework, Te nanowires located on TRP pores, and TRP pores was estimated to be 13:1:1. As shown in Fig. 7 and Supplementary Fig. S4, when the plane wave reached the surface of TRP and Te-TRP, the distribution of electric field

exhibited a heterogeneity with periodic oscillation due to the scattering effect of samples. For bare TRP (Fig. 7a and Fig. S4b), high optical intensity was observed in pores and partial regions of the inside hollow space (intensity higher than the plane wave). Therefore, the porous and hollow structures of TRP would favor light-harvesting and the subsequent photothermal conversion. Regarding the Te-TRP composite with all Te nanowires on the framework (Fig. 7b and Fig. S4c), the optical intensity upon light irradiation almost remained unchanged compared with that of bare TRP, indicating that such Te distribution played a negligible role in alerting the optical properties of Te-TRP. By contrast, Te nanowires on the TPR pores could significantly improve the optical intensity, with the average enhancement locally reaching up to approximately 5 times of incident light intensity compared to the values observed in Fig. 7b. The results revealed that the enhanced near-field optical intensity of Te-TRP was primarily ascribed to the presence of Te nanowires located on the TRP pores. It should be noted that although Te nanowires on TRP framework showed an insignificant effect on the optical intensity, their contributions to photothermocatalytic treatment cannot be underestimated due to their LSPR effect and important roles in facilitating charger transfer and reducing the recombination of electron-hole pairs, as we will show later.

ROS analysis. To verify the generated ROS from Te-TRP via photocatalytic, photothermal, and photothermocatalytic processes, ESR measurement was carried out under different conditions. As shown in Fig. 8a, the peak of DMPO-•O_2^- complexes with a quadruple characteristic peak (peak intensity = 1:1:1:1) were observed in the photothermocatalytic system (Wang et al., 2021b), whereas such peaks were absent in

photocatalytic and photothermal systems, indicating that the generation of $\bullet O_2^-$ required the synergy of photocatalysis and photothermal conversion. The peak intensity of DMPO-$\bullet O_2^-$ at 2 min was close to that at 5 min (Fig. 8b), thus the concentration of the steady-state $\bullet O_2^-$ was stable after 2 min. As displayed in Fig. 8c, TEMP-$^1O_2$ signals with triple characteristic peaks (peak intensity = 1:1:1) appeared in all systems, whereas the signals in photothermocatalytic system were stronger than those in the other two systems, suggesting the generation of more $^1O_2$ by photothermocatalytic behaviors. The presence of DMPO-•OH peaks (peak intensity = 1:2:2:1) in photothermocatalytic and photocatalytic systems and the absence of DMPO-•OH peaks in photothermal system were observed (Fig. 8e), indicating that the photothermal process could hardly produce •OH radicals. Given the slightly higher intensities of DMPO-•OH peaks in photothermocatalytic system than that in photocatalytic systems, •OH radicals should be mainly produced via photocatalysis.

To obtain an in-depth understanding of the roles of $\bullet O_2^-$, $^1O_2$, and •OH in bacterial inactivation, scavenging studies were carried out using the specific scavengers to quench the individual ROS and verify its contribution to bacterial inactivation. As shown in Fig. 8g, the significant decrease in bacterial inactivation efficiencies after adding TEMPOL and NaN_3 unveiled the crucial roles of $\bullet O_2^-$ and $^1O_2$. The moderate decrease of cell density from 7.14 to 3.69 $\log_{10}$ cfu/mL indicated that •OH radicals were involved in bacterial inactivation, but they were not the major contributor.

Synergetic effect between photothermal conversion and photocatalysis. Although the high photothermal activity of Te-TRP was confirmed, the individual

contribution of photothermal effect to photothermocatalytic bacterial inactivation and the synergy between photocatalytic and photothermal inactivation are unclear. Therefore, a water bath was used in bacterial inactivation experiments to control the environment temperature and to differentiate the roles of photocatalysis and photothermal effect. Experiments were first carried out at a fixed room temperature under sunlight irradiation to eliminate the photothermal conversion. As displayed in Fig. 8h, only 3.29-log *E. coli* K-12 cells were inactivated within 1 h. In addition, the bacterial inactivation experiment was performed at 55 °C in dark to simulate the photothermal conversion alone. Such temperature was the same as the photothermocatalytic system using Te-TRP upon sunlight irradiation (Fig. 6d). In this case, 3.58-log *E. coli* K-12 was inactivated, similar as that in photocatalysis. Therefore, photothermal effect and photocatalysis almost contributed equally to bacterial inactivation in the photothermocatalytic process. Given the efficient 7.13-log bacterial inactivation by photothermocatalytic treatment, we argue that the photothermal effect and photocatalysis show a synergetic effect that enables the more efficient bacterial inactivation.

Band structure characterization and photoelectrochemical properties. To further investigate the mechanism of the enhanced photothermocatalytic activity of Te-TRP, the band structures and photoelectrochemical properties of TRP and Te-TRP were analyzed. The positive slopes of Mott-Schottky plots (Fig. 9a) revealed the n-type semiconductor feature of TRP and Te-TRP. Therefore, the conduction band minimum (CBM) position was close to the flat potential, which was -0.39 V and -0.45 V *vs.*

Saturated Calomel Electrode (SCE) for TRP and Te-TRP, respectively, determined by the intercept of X-axis. The equation E(NHE) = E(SCE) − 0.24 V was applied to convert SCE to Normal Hydrogen Electrode (NHE) (Xu et al., 2018). As a result, the CBM positions were -0.63 V and -0.69 V *vs.* NHE for TRP and Te-TRP, respectively. The bandgap of TRP and Te-TRP was calculated to be 1.85 eV and 1.01 eV, respectively, as shown in the Tauc plots (Fig. 9b). The narrowed bandgap of Te-TRP could lead to easier photo-excitation and better light-harvesting. According to Kubelka–Munk function (Wang et al., 2018c), the valence band maximum (VBM) positions of TRP and Te-TRP were estimated to be +1.22 and +0.32 eV, respectively.

The band structure characterization allows us to further investigate the generation of ROS by Te-TRP. Theoretically, the photogenerated e^- at the conduction band of Te-TRP is negative enough to convert O_2/H_2O into $^1O_2$ (-0.11 V) (Xia et al., 2018a), as shown in Eqn. 2, which was validated by the critical role of $^1O_2$ in bacterial inactivation (Fig. 8g). As shown in Eqn. 3, the photogenerated e^- by Te-TRP was able to reduce the dissolved oxygen to $\bullet O_2^-$ (-0.33 eV) (Wang et al., 2020a; Xia et al., 2016). The generated $\bullet O_2^-$ could further transfer into $^1O_2$ and H_2O_2 (Eqn. 4). The photogenerated h^+ from VB of Te-TRP (+0.32 V) is not positive enough to convert O_2/H_2O into •OH (2.8 V) (Xia et al., 2015), causing the insignificant bactericidal role of •OH. The generation of •OH, as confirmed in the earlier ESR result, should be achieved via a multi-step pathway, as shown in Eqn.3-5. Electrons generated by TRP would enrich on Te nanowires and thus inhibited the recombination of electrons and holes, so that the adsorbed O_2/H_2O could capture electrons more efficiently to form ROS. Furthermore,

1 the heat generated by the photothermal conversion could attack cell membrane and
2 facilitate the damage from ROS to bacterial cells. Based on the above discussion, the
3 process of photothermocatalytic *E. coli* K-12 inactivation over Te-TRP was shown in
4 Eqn. 1−6.

$$\text{Te-TRP} + \text{sunlight} \rightarrow h^+ + e^- \quad (1)$$

$$O_2 + h^+ \rightarrow {}^1O_2 \quad (2)$$

$$e^- + O_2 \rightarrow \bullet O_2^- \quad (3)$$

$$\bullet O_2^- + H_2O \rightarrow {}^1O_2 + H_2O_2 + OH^- \quad (4)$$

$$H_2O_2 + h\nu \rightarrow 2\bullet OH \quad (5)$$

$$\bullet OH/\bullet O_2^-/{}^1O_2 + \text{heat} + \textit{E. coli} \rightarrow \text{cell debris} \quad (6)$$

5 To evaluate the recombination of electron-hole pairs and the charge transfer
6 behaviors, photoelectrochemical measurements were conducted. The smaller arc radius
7 of electrochemical impedance spectra (EIS) plots of Te-TRP than pristine TRP indicated
8 the lower charge transfer resistance (Fig. 9c) (Wang et al., 2018c). In addition, the
9 higher photocurrent density of Te-TRP than TRP revealed the more abundant charge
10 carriers and the more efficient charge transfer in Te-TRP (Fig. 9d), benefiting the
11 photocatalytic reactions.

12 **3.4 Damage to bacterial cells**

13 **Destruction of bacterial cells.** To look into the destruction process of bacterial
14 cells upon photothermaocatalytic treatment, we first identified the cell activity with a
15 fluorescence microscope, where cells were stained by Live/Dead BacLight Bacterial
16 Viability Kit. As shown in Fig. 10a-c, almost all *E. coli* K-12 exhibited green

fluorescence, revealing that the cell membrane of *E. coli* K-12 was intact before treatment. After being irradiated by sunlight for 10 min, a small number of *E. coli* K-12 cells showed red fluorescence, indicating the partial inactivation of bacteria. When the reaction time was extended to 60 min, all the bacteria displayed red fluorescence, demonstrating the complete inactivation of *E. coli* K-12.

The SEM images of *E. coli* K-12 cells were recorded to monitor the damage of cell membrane. As shown in Fig. 10d-f, *E. coli* K-12 cells showed a typical rod shape with intact cell membrane structure before treatment. Meanwhile, a large number of *E. coli* K-12 cells were adsorbed on the surface of Te-TRP. This would be favorable for photothermocatalytic bacterial inactivation because many photocatalytic and thermal reactions necessitate the short-range contact between catalysts and targets. With the treatment for 10 minutes, the cell membranes of *E. coli* K-12 shrunk and became unsmooth, indicating the heavy attacks on cell membranes (Wang et al., 2018b). Finally, the cell membrane was seriously broken when the treatment was prolonged to 60 min, resulting in the disability of energy-dependent reactions as well as the oxidation and/or leakage of the cytoplasmic substances.

Enzyme activity. The bacterial cell membrane was responsible for the production of enzymes to resist external attacks. Therefore, the activity of anti-oxidative enzymes was detected by measuring the generation of superoxide dismutase (SOD) and catalase (CAT) by cells. SOD can react with $\bullet O_2^-$ to form O_2 and H_2O_2, and CAT can trigger H_2O_2 to form O_2 and H_2O, thus reducing the attack of these ROS (Xiao et al., 2019). As shown in Fig. 10g, in the first 30 min, the contents of these two enzymes increased

gradually. At the beginning of the photothermocatalytic treatment, the stress antioxidant system of the cell membrane produced sufficient SOD and CAT to fight against ROS. After 30 min, the cell membrane of *E. coli* was seriously damaged and lost the ability to produce antioxidant enzymes owing to the persistent attacks of ROS, as suggested by the decreased concentration of SOD and CAT.

Cell membrane permeability. The inner membrane (cytoplasmic membrane) permeability of bacteria was investigated by ONPG. A higher value of OD_{420} indicates the increased bacterial inner membrane permeability. As shown in Fig. 10h, in the photothermal system, OD_{420} increased from 0.011 to 0.046 within 60 min, indicating that the photothermal effect of Te-TRP would slightly increase the membrane permeability. Regarding the photocatalytic system, OD_{420} reached to 0.084 at 60 min, suggesting that photocatalysis contributed more to altering the membrane permeability than the photothermal effect. Compared with the individual photocatalytic and photothermal system, OD_{420} values in the photothermocatalytic system were significantly higher, indicating that photocatalysis and photothermal conversion had a synergistic effect on attacking the cell inner membrane.

VBNC analysis. Under certain environmental conditions, bacteria would present a viable but non-culturable (VBNC) state. Although cells in the VBNC state cannot form colonies, they remain alive and can recover the culturability in appropriate conditions (Zhang et al., 2015). Therefore, the D_2O-labeled confocal Raman micro-spectroscopy was utilized to verify if VBNC bacteria are completely inactivated. VBNC cells can absorb D_2O and form C-D bonds, showing a broad peak at 2040-2300 cm^{-1} in

the Raman spectrum; while C-D peaks are absent or appear at very low levels in the Raman spectrum of dead cells (Wang et al., 2021a). As shown in Fig. 10i, strong C-D peaks were observed before treatment, indicating the presence of the VBNC-state bacterial cells. Upon the photothermocatalytic treatment by Te-TRP for 60 min, C-D peaks almost disappeared, suggesting that nearly all bacterial cells, including but not limited to VBNC-state ones, were completely killed.

4. Conclusions

In this work, ultrafine Te nanowires were successfully loaded on porous TRP by a hydrothermal method to form the Te-TRP composites, which achieved superior photothermocatalytic inactivation of bacteria under sunlight. On one hand, Te-TRP composites exhibited increased hydrophilicity due to the loading of highly hydrophilic Te nanowires, favoring the liquid-phase reactions. On the other hand, Te nanowires and TRP exhibited a synergetic effect between photocatalytic and photothermal conversion, leading to the outstanding photothermocatalytic activity towards bacterial inactivation such as *E. coli* K-12, *Spingopyxis sp.* BM1-1, and *S. aureus*. Te-TRP also performed well in a flow-through water disinfection system, suggesting the great potential of using Te-TRP in the practical water treatment devices. The mechanistic study showed that ROS such as $^1O_2$ and $\bullet O_2^-$ were the most important contributors in bacterial inactivation. The damage to bacterial cells was studied by monitoring the cell membrane destruction, examining the enzyme activity, and semi-quantifying the VBNC-state cells. This study

provides a green strategy to turn biological materials into functional photothermocatalytic materials for efficient water disinfection operations.

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