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Perspective

Field enhanced photocatalytic disinfection

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An enormous number and tremendous diversity of microorganisms (such as bacteria and viruses) are surrounding us in our daily life, most of which we can live together in harmony under common circumstance. However, some of them are pathogenic and may cause serious disease and even death (i.e., Ebola hemorrhagic fever, cholera, flu and common cold). This type of microorganisms is featured with fast transmission from person to person through direct contact, body fluids, respiratory droplets, and aerosol particles. For instance, coronavirus 2019 (COVID-19) is one kind of serious pathogenic virus, which has the characteristic of rapid and wide spreading. To prevent the pandemic of pathogenic bacteria and viruses, a series of defense strategies have been developed in the past decades, including vaccines, disinfectants, antibiotics, and sterilization. Although certain achievements have been witnessed, pathogenic bacteria and viruses meanwhile exhibit their capacity of evolving rapidly to resist the defense systems we build. It gives rise to the formation of mutated bacteria and viruses with faster spreading speed and/or more virulent strain, thus leading to more difficult disinfection process. Fortunately, photocatalytic disinfection technology has emerged as an effective and viable alternative with superiorities of low cost and simplicity after the first report by Matsunaga et al. [1] in 1985. Significantly, unlike antibiotics, the photocatalyst-induced reactive oxygen species (ROS) attack bacteria through plenty of sites and multiple pathways, making the evolvement of antimicrobial resistance to photocatalysts almost impossible. In this regard, photocatalytic disinfection technology has revolutionized the field of disinfection for efficiently preventing pandemic and improving public health, showing significant social and economic benefits.

Principle and process of photocatalytic disinfection. Profiting from the progress of nano- and biological science as well as characterization technology, we are able to get deep insight into the mechanism of photocatalytic disinfection process. As shown in Fig. 1, when the light with energy equal to or higher than the energy band gap of semiconductor photocatalyst is introduced, the electrons in the valence band absorb light energy and then transfer to the conduction band, leaving the same number of photoexcited holes in valence band. A part of these photoexcited electrons and holes migrate to the surface of photocatalyst to take part in photocatalytic reduction and oxidation reactions, respectively. For the purpose of photocatalytic disinfection, the electrochemical reduction potential of photoexcited holes should be positive enough to oxidize water for the formation of hydroxyl radical ($\cdot$OH) and the potential of photoexcited electrons should be negative enough to reduce molecular oxygen for the generation of superoxide radical anion ($\cdot O_2^-$), singlet oxygen ($^1O_2$) and hydrogen peroxide (H_2O_2). The detailed generation process of these ROS can be summarized into the following five equations.

$$\text{Semiconductor} + h\upsilon \rightarrow e^- + h^+$$

$$H_2O + h^+ \rightarrow \cdot OH + H^+$$

$$O_2 + e^- \rightarrow \cdot O_2^-$$

$$\cdot O_2^- + e^- + 2H^+ \rightarrow H_2O_2$$

$$H_2O_2 + O_2 \rightarrow {}^1O_2 + 2 \cdot OH,$$

These generated ROS can subsequently attack and destroy the outer membrane, cytoplasmic membrane, and finally intracellular components of bacteria or viruses, leading to the inactivation of bacteria or viruses. It is worth noting that, for complete disinfection, the density of generated ROS should be higher than that bacteria can endure and protect against. On the other hand, ROS production rate is mainly dependent on the separation efficiency and lifetime of photoexcited carriers. However, most of the photoexcited carriers are inclined to recombine or dissipate in the forms of light or heat before participating photocatalytic redox reactions, which seriously limits the performance and efficiency of photocatalytic disinfection.

To deal with the above critical issue, various attempts have been explored for promoting photoexcited charge separation, i.e., building internal electric field within photocatalysts by element doping, constructing hetero-nanostructures, and designing porous structures [2–5]. However, photocatalytic disinfection efficiency still necessitates further improvement due to the limitations of the abovementioned strategies. For example, the internal electric

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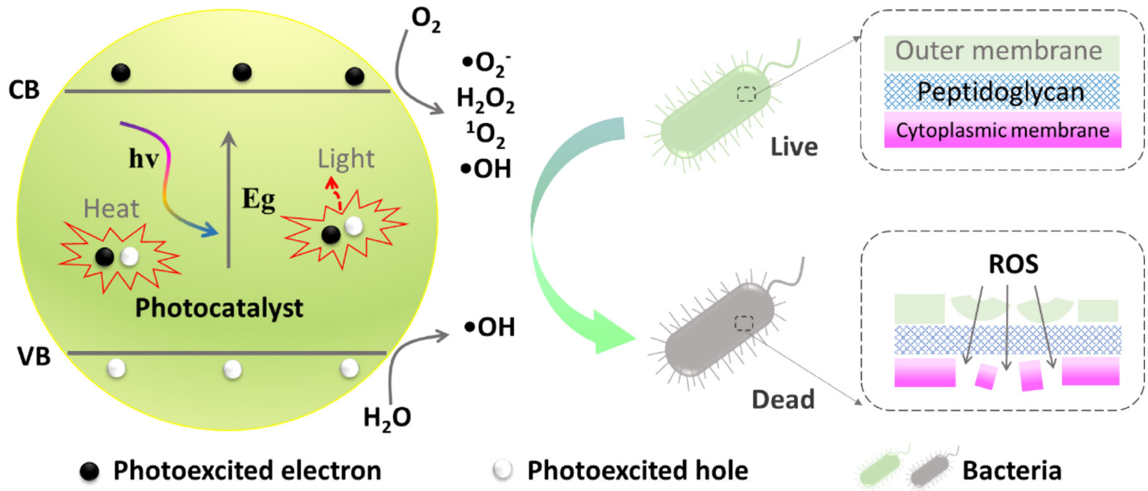

Fig. 1. (Color online) Schematic diagram of the basic principle and process of photocatalytic disinfection. Under light irradiation, photoexcited electrons and holes of photocatalyst are induced and react with oxygen and water to yield ROS (including .OH, .O_2^-, $^1O_2$ and H_2O_2), respectively. These ROS subsequently attack and damage outer membrane, followed by cytoplasmic membrane and finally intracellular components of bacteria.

fields originated from element-doped photocatalyst or heterojunctions are static and easy to be saturated by photoexcited carriers of photocatalysts and free charged ions from reactive solution, which dramatically hinders its promotion role in charge separation. Recently, enhancing photocatalysis through piezoelectric, pyroelectric and triboelectric fields has been proposed and substantiated as a promising pathway to facilitate carrier separation and prolong carrier lifetime, contributing to high-efficient photocatalytic degradation, disinfection, water splitting, and carbon dioxide conversion [6].

Piezoelectric field facilitating photocatalytic disinfection process. Piezoelectric field can be generated across piezoelectric semiconductors with noncentrosymmetric structures under external strain (such as mechanical force and ultrasonic vibration) due to the displacement of positive and negative ion centers of semiconductor crystal and the consequent dipole moment. This effect can be employed for disinfection by means of the following three main processes. First, piezoelectric field enables direct destructing of intracellular component and microbial outer structure via charge transfer and field-imparted electroporation, respectively. Secondly, piezoelectric field can also drive the generation of electron and hole pairs, and subsequently produce ROS for disinfection (named as piezo-catalysis) [7]. Thirdly, piezoelectric field is able to govern the separation and migration behavior of photoexcited carriers during photocatalysis on the basis of piezo-phototronic effect (Fig. 2a and d) [8]. Therefore, the synergistic effects between piezoelectric field and photocatalytic disinfection will give access to higher ROS production rate and increased photocatalytic disinfection efficiency.

Pyroelectric field enhancing photocatalytic disinfection performance. The pyroelectric effect is a two-way coupling of pyroelectric polarization and temperature variation that exists in a wide range of noncentrosymmetric semiconductor materials. When temperature increases, the electric dipoles will oscillate within a larger degree of spread angle due to the higher thermal motion, which leads to the decreases in pyroelectric polarization charges and surface potential. On the contrary, thermal cooling will result in a smaller angle for electric dipole oscillation and higher pyroelectric polarization potential. Hence, the surface potential of pyroelectric materials can be tuned by temperature changes and consequently drive the generation of ROS to realize pyro-catalytic disinfection process. For example, Gutmann and co-workers [9] investigated the disinfection property of nano- and microcrystalline $LiNbO_3$ and $LiTaO_3$ under a periodic temperature change between 20 and 45 °C. The results corroborated that the temperate variation-enabled pyroelectric potential of $LiNbO_3$ and $LiTaO_3$ could trigger the production of ROS, which finally inactivated *Escherichia coli* (*E. coli*) bacteria up to 95% within 60 min.

Similar to the piezo-phototronic effect, pyroelectric potential can modulate the energy band structure at heterojunctions and thus effectively manipulate the separation as well as migration behavior of photoexcited carriers (named as pyro-phototronic effect) when pyroelectric photocatalysts or pyroelectric-photocatalytic composites are activated by light irradiation and temperature variation (Fig. 2b and d). Importantly, it has been demonstrated that pyroelectric field can not only immensely facilitate photocatalytic organic pollution degradation, but remarkably boost water splitting efficiency through inhibiting photoexcited carrier recombination [10]. Therefore, when pyroelectric field is introduced into photocatalytic disinfection process, an increasing number of photoexcited electrons and holes are anticipated to participate in redox reaction for yielding more ROS and realizing improved disinfection performance.

Triboelectric field increasing photocatalytic disinfection activity. Triboelectrification was recorded over 2600 years from ancient Greek civilization, which occurs for all known materials and substances in solid, liquid, and even gas states anywhere at any time. Electron transfer induced by the electron cloud overlapping of two materials upon mechanical force (i.e., pressure, friction) was proposed as the dominant mechanism of triboelectrification by Zhong Lin Wang [11]. Since the first report of triboelectric nanogenerator in 2012, a series of triboelectric materials and devices with ingenious structure and tailored composition have sprung up to scavenge ambient energy, including tribo-catalytic disinfection systems [12–14]. For example, Xie and co-workers [15] constructed a low-cost hand-powered water disinfection pump based on triboelectric effect, which showed excellent inactivation performance against four strains of bacteria, including gram-negative *E. coli* and *Enterobacter hormaechei*, as well as gram-positive *Bacillus subtilis* subsp. *subtilis* and *Staphylococcus epidermidis*. Significantly, it substantiated that the bacteria inactivation process was mainly caused by triboelectric field-induced electroporation (resulting in pores and ruptures in bacteria membrane, an instant sterilization process) and ROS inactivation (attacking bacteria cells, a sustainable disinfection process) [13]. Moreover, Kim et al. [16] reported a triboelectrification-imparted self-powered microbial

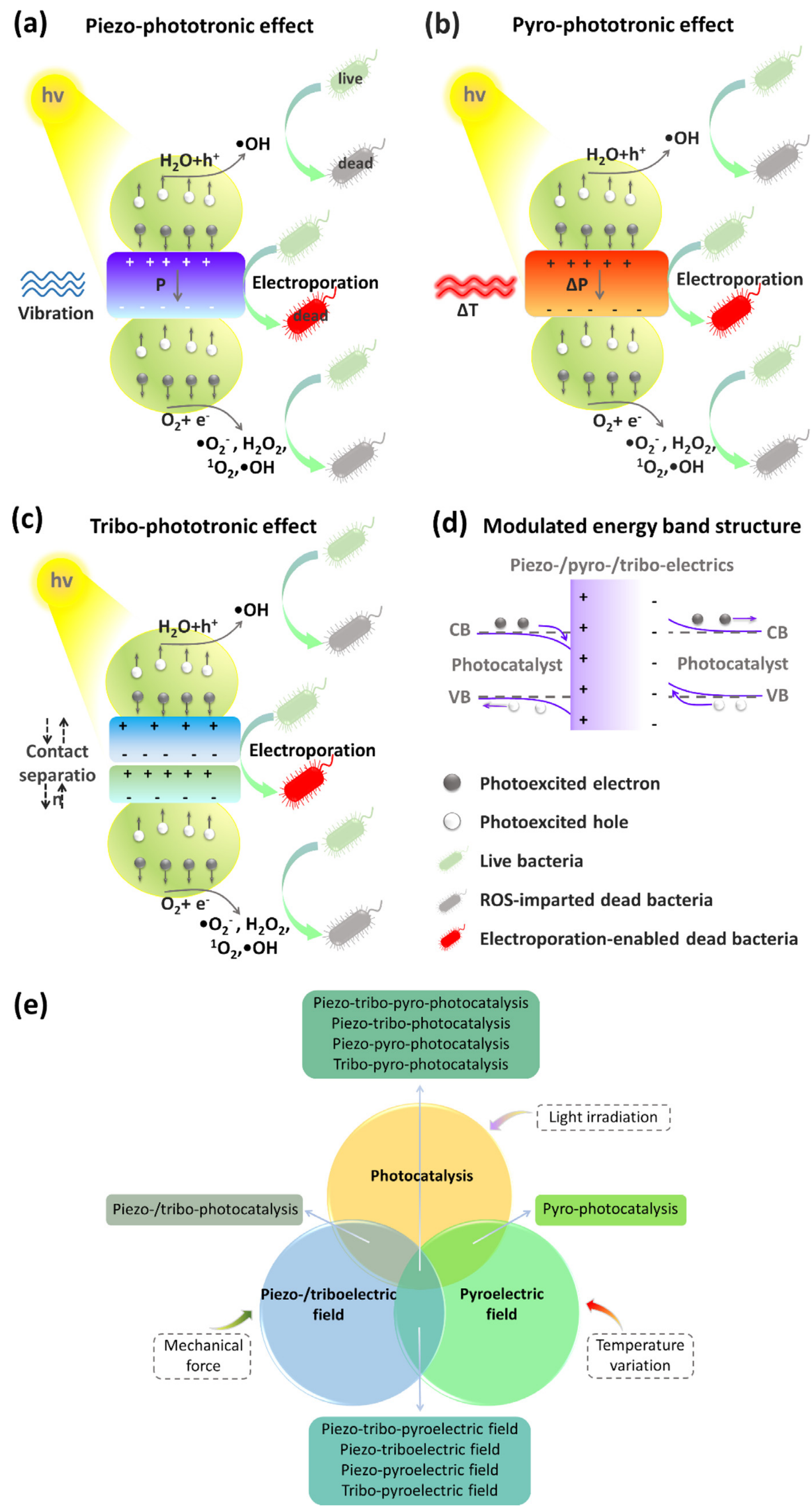

Fig. 2. (Color online) Schematic diagrams of (a) piezoelectric field, (b) pyroelectric field, (c) triboelectric field enhancing photocatalytic disinfection performance via piezo-phototronic effect, pyro-phototronic effect and tribo-phototronic effect, respectively. (d) The corresponding energy band structure as well as (e) carrier migration behavior of photocatalyst modulated by the field originated form piezo-/pyro-/triboelectric effects.

air disinfection system based on nanowire structure ($Cu(OH)_2$ nanowire-modified Cu electrode), which effectively attacked and destroyed the outer structures of bacteria *E. coli* and *Bacillus subtilis*, and virus bacteriophage MS2 via electroporation. It provided an efficient route to fulfill the urgent need for protecting public health through inactivating air-transmitted bacteria and viruses.

On the other hand, triboelectric field has been employed to enhance photocatalytic degradation of formaldehyde in air and rhodamine B in water [17]. It implied that, in addition to introducing electroporation process and triggering the generation of ROS, triboelectric field could be utilized to modulate the energy band structure of photocatalysts at heterojunction surfaces and interfaces, and thus tune the separation and migration behavior of photoexcited electron-hole pairs (named as tribo-phototronic effect), as depicted in Fig. 2c and d. Therefore, the production rate of ROS will be enhanced, and photocatalytic disinfection performance will be boosted.

Coupling effect on photocatalytic disinfection. Fig. 2e depicts the schematic diagram of the coupling among piezoelectric field, pyroelectric field, triboelectric field and photocatalysis. It indicates that, through reasonable material and structure designs, these viable and robust coupling effects are expected to greatly enhance photocatalytic disinfection performance. Notably, different types of natural energy source (such as solar light, mechanical force, and temperature variation) can be synergistically utilized (Table S1 online) to increase energy conversion efficiency and alleviate worldwide energy crisis.

Applications of field improved photocatalytic disinfection. On the basis of piezo-phototronic effect, Lin et al. [18] developed a new type of piezoelectric photocatalytic nanomaterial Au-MoS_2@carbon fibers (CFs), in which single- and few-layered MoS_2 functioned as piezoelectric photocatalyst to generate photoexcited electron-hole pairs and piezoelectric field under the synergistic effects of visible light irradiation and mechanical vibration. The much higher disinfection rate of gram-negative bacterium *E. coli* was achieved due to the piezo-phototronic effect, which gave rise to increased separation rate of photoexcited electron-hole pairs and consequently enhanced production rate of ROS. Additionally, Wang et al. [19] proposed a multilayered coaxial heterostructure nanorod array (TiO_2/$BaTiO_3$/Au) with piezoelectric $BaTiO_3$ nanolayer inserted between TiO_2 nanorod and Au nanoparticles. The constructed heterostructure nanorod array exhibited obviously boosted ROS ($\cdot O_2^-$ and $\cdot OH$) production efficiency and higher inactivation rates of gram-negative bacterium *E. coli* as well as gram-positive bacterium *S. aureus*. The enhancement was predominately ascribed to the piezo-phototronic effect of $BaTiO_3$: the piezoelectric potential of $BaTiO_3$ modulated the energy band structure between TiO_2 and $BaTiO_3$, and thus benefited the charge separation and transport among Au, TiO_2, and $BaTiO_3$. It is worth mentioning that the superior photocatalytic inactivation property could be further achieved by simultaneously coupling with piezo-phototronic effect and localized surface plasmon resonance (LSPR) effect. In detail, hot electrons originated from the LSPR decay processes of Au nanoparticles were injected into piezoelectric $BaTiO_3$ and migrated to the surface of TiO_2 driven by piezoelectric field for further promoting the ROS production efficiency. Therefore, more appealing research works focusing on piezoelectric field-boosted photocatalytic disinfection are anticipated in the near future, including exploring self-powered piezo-photocatalytic disinfection system with subtle and viable material structure and composition design, investigating the mechanism of disinfection process, and coupling with other fascinating effects (for instance, photothermal effect, photoacoustic effect, magnetic effect).

Similar to piezo-phototronic effect, pyro-phototronic, tribo-phototronic effects and their coupling effects also possess great potential in promoting photocatalytic disinfection performance. However, there is no report about pyroelectric, triboelectric, piezo-pyroelectric, piezo-triboelectric, pyro-triboelectric, and piezo-pyro-triboelectric fields enhanced photocatalytic disinfection to the best of our knowledge. It is highly desirable to explore and develop ferroelectric photocatalysts (possessing piezoelectric, pyroelectric and photocatalytic properties), triboelectric photocatalysts, and ferroelectric-photocatalytic/triboelectric-photocatalytic/ferro-tribo-photocatalytic composites with excellent sterilization activity for improving public health. In addition, deep investigations on the mechanism with respect to how piezo-/pyro-/tribo-phototronic and their coupling effects modulate the photocatalytic disinfection process is favorable for providing fundamental guidelines to the researchers who are interested in photocatalysis, piezoelectrics, pyroelectrics, triboelectrics, disinfection and other relative fields, in a multi-discipline perspective ranging from material design and structure construction to energy utilization and system integration.

Piezoelectric/pyroelectric/triboelectric field can be exclusively generated upon mechanical trigger/temperature variation/mechanical force through piezoelectric/pyroelectric/triboelectric effect, which can directly destroy bacteria membrane and viruses through electroporation process or cause the generation of ROS (similar to photocatalytic disinfection process) to attack bacteria and virus cells. Particularly, in consideration of photocatalysis, the induced piezoelectric/pyroelectric/triboelectric field can function as a gate to modulate the energy band structure and thus tune carrier behavior on the basis of piezo-/pyro-/tribo-phototronic effect, boosting the formation of ROS and consequently facilitating photocatalytic inactivation performance. The studies focusing on field-enhanced photocatalytic disinfection are very limited at present and more innovative progresses are highly desired. Specifically, piezoelectric/pyroelectric/triboelectric photocatalysts and their composites with ingenious structure and composition designs are anticipated to achieve multi-stimuli-driven electric fields synergistically improving photocatalytic disinfection performance. Furthermore, exploring and developing self-powered field boosted photocatalytic disinfection systems are also a significant and promising trend to alleviate the current energy shortage issues and worldwide public health problems.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/10.1016/j.scib.2022.01.007.

References

[1] Matsunaga T, Tomoda R, Nakajima T, et al. Photoelectrochemical sterilization of microbial cells by semiconductor powders. FEMS Microbiol Lett 1985;29:211–4.
[2] Wang L, Liu J, Wang H, et al. Forming electron traps deactivates self-assembled crystalline organic nanosheets toward photocatalytic overall water splitting. Sci Bull 2021;66:265–74.
[3] Shi L, Zhou Z, Zhang Y, et al. Photocatalytic conversion of Co to fuels with water by B-doped graphene/g-C_3N_4 heterostructure. Sci Bull 2021;66:1186–93.
[4] Chen Y, Yang D, Yoon YJ, et al. Hairy uniform permanently ligated hollow nanoparticles with precise dimension control and tunable optical properties. J Am Chem Soc 2017;139:12956–67.
[5] Liu Q, Chen C, Yuan K, et al. Robust route to highly porous graphitic carbon nitride microtubes with preferred adsorption ability via rational design of one-dimension supramolecular precursors for efficient photocatalytic CO_2 conversion. Nano Energy 2020;77:105104.
[6] Wang M, Wang B, Huang F, et al. Enabling piezopotential in piezoelectric semiconductors for enhanced catalytic activities. Angew Chem Int Ed 2019;58:7526–36.
[7] Xia D, Tang Z, Wang Y, et al. Piezo-catalytic persulfate activation system for water advanced disinfection: process efficiency and inactivation mechanisms. Chem Eng J 2020;400:125894.
[8] Wang ZL. Piezopotential gated nanowire devices: piezotronics and piezo-phototronics. Nano Today 2010;5:540–52.
[9] Gutmann E, Benke A, Gerth K, et al. Pyroelectrocatalytic disinfection using the pyroelectric effect of nano- and microcrystalline $LiNbO_3$ and $LiTaO_3$ particles. J Phys Chem C 2012;116:5383–93.
[10] Dai B, Fang J, Yu Y, et al. Construction of infrared-light-responsive photoinduced carriers driver for enhanced photocatalytic hydrogen evolution. Adv Mater 2020;32:1906361.
[11] Wang ZL, Wang AC. On the origin of contact-electrification. Mater Today 2019;30:34–51.
[12] Xu Q, Fang Y, Jing Q, et al. A portable triboelectric spirometer for wireless pulmonary function monitoring. Biosen Bioelectron 2021;187:113329.
[13] Tian J, Feng H, Yan L, et al. A self-powered sterilization system with both instant and sustainable anti-bacterial ability. Nano Energy 2017;36:241–9.
[14] Wang G, Feng H, Hu L, et al. An antibacterial platform based on capacitive carbon-doped TiO_2 nanotubes after direct or alternating current charging. Nat Commun 2018;9:2055.
[15] Ding W, Zhou J, Cheng J, et al. Tribopump: a low-cost, hand-powered water disinfection system. Adv Energy Mater 2019;9:1901320.
[16] Huo Z, Kim Y, Suh I, et al. Triboelectrification induced self-powered microbial disinfection using nanowire-enhanced localized electric field. Nat Commun 2021;12:3693.
[17] Feng Y, Ling L, Nie J, et al. Self-powered electrostatic filter with enhanced photocatalytic degradation of formaldehyde based on built-in triboelectric nanogenerators. ACS Nano 2017;11:12411–8.
[18] Chou T, Chan S, Lin Y, et al. A highly efficient Au-MoS_2 nanocatalyst for tunable piezocatalytic and photocatalytic water disinfection. Nano Energy 2019;57:14–21.
[19] Yu X, Wang S, Zhang X, et al. Heterostructured nanorod array with piezophototronic and plasmonic effect for photodynamic bacteria killing and wound healing. Nano Energy 2018;46:29–38.

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