Recent advances in surface-functionalised photosensitive antibacterials with synergistic effects

Peizi Liao, Jiahao Hu, Huagao Wang, Jinyang Li, Zuowan Zhou

Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, People’s Republic of China
E-mail: zzhou@swjtu.edu.cn

Abstract: The alarm has been ringing over the gradually increasing drug-resistant bacteria, which calls for the development of safer antibacterial materials. Photosensitive antibacterials are considered as a promising alternative solution due to their unique light-activated antimicrobial mechanism, which in-situ produces highly reactive oxygen species on the multiple and variable active sites for the inactivation of various microbes. However, there are some factors, including phototoxicity, oxygen consumption and the risk of microbial contamination, greatly limit the efficiency and application of photosensitisers (PSs) in practical biomedical applications. Some studies have explored the synergistic effects of PSs by antibiotics, photothermal agents, antibacterial nanoparticles and biofilm-disrupting enzymes. Moreover, novel synergistic methods for improving the antibacterial ability of PSs under low-energy irradiation, hypoxia conditions and dull conditions, have been rarely reviewed yet. Herein, the authors summarised some synergistic methods and related applications of surface-functionalised photosensitive antimicrobials, which were prepared with organic antimicrobial materials, superhydrophobic surfaces, upconversion nanoparticles and energy storage structures in recent years. Finally, the authors presented the advantages and challenges of these synergistic mechanisms, and further analysed the development trend and application prospects of the surface-functionalised photosensitive antibacterials in biomedical fields.

1 Introduction

It draws the attention of numerous researchers to resisting harmful bacteria [1, 2]. However, many antibiotic-resistant bacteria and even superbugs have emerged due to the overuse of antibiotics, leading to the bacterial generation of an efflux system through simple genetic mutation [3, 4]. The severity of the problem has been reported numerous times [5]. At the same time, researchers are constantly looking for alternative antibacterial approaches. Some non-drug sterilisation methods have been proposed, such as inorganic antibacterial agents, organic antibacterial agents, and physical sterilisation and so on. But there are some defects in many areas such as dispersibility, stability, safety and single mode or site of action, which greatly limit the application of these antimicrobials in biomedical field [6]. As one of the light-activated molecules, photosensitisers (PSs) are recognised as a promising candidate for defeating microbes [6], due to their low cost [7], multiple and variable sites of action [8, 9] controllability [10], diverse structure [11] and fast effect [12, 13].

Many research focused on the structural regulation and action mechanism of PS [8]. Most of PSs, including the synthetic PSs [14–16] natural PSs [17, 18] and nano-PSs [19, 20], have been reported to kill bacteria with a broad-spectrum. This unique antibacterial advantage comes from the generation of reactive oxygen species (ROS), following two distinctive mechanisms after light activation [21], as shown in Fig. 1. In type I, the light-activated PS produces ROS (‘O2, H2O2, •OH) via electron transfer [6, 22]; in type II, the light-activated PS generates singlet oxygen (‘O2) through energy transfer [23]. However, there are still some non-negligible defects when PSs is used, such as phototoxicity [24], oxygen consumption [25] and microbial contamination [26]. Previously it has been reviewed that these defects can be improved by taking advantage of the synergistic antimicrobial effects of antibiotics [27], photothermal agents [28], antibacterial nanoparticles [8] and biofilm-disrupting enzymes [29]. However, there are still some new surface functionalised PSs optimised by synergistic effect displaying excellent antimicrobial performance under low-energy irradiation, hypoxia conditions, and dull conditions. It has been reported that the use of PSs in these conditions can be improved by increasing the wavelength of irradiation [30], enhancing the selectivity capacity of PSs to bacteria [31], reducing the dosage of PSs [32], and broadening the ability to resist bacteria even in the dark [33].

The study of the synergistic effect of PSs has become a hot research topic, but the methods of synergistic mechanism are not well studied yet. And there are still many practical problems to be solved. In order to guide the research in this field, it is necessary to summarise the principles and characteristics of the newly emerging synergistic mechanism. Thus, in this paper, we review the research status and development prospects of the application of surface multi-functionality photosensitive antibacterial agents, which enhanced by four synergistic methods of adding organic antibacterial components, preparing superhydrophobic surfaces, introducing upconversion nanoparticles (UCNPs), and constructing capacity storage structures in recent years. We have also listed some key challenges, development trend and application prospects of the functionalised photosensitive antibacterials.

2 Photosensitive antibacterials with synergistic effects

2.1 Organic antibacterial materials and photosensitive antibacterials

Compensating the defects of PSs through the synergistic effect of antibacterial materials is a convenient method. Organic antibacterial agents can be combined with PSs by chemical bonds to change the water solubility and the molecular weight of PSs while exerting synergistic antibacterial action. The following
section will be focused on the surface functionalised PSs based on quaternary ammonium salt (QAS) and its synergistic antimicrobial activity. The addition of QAS, which attracts and kills bacteria by electrostatic adsorption [34], can improve the water solubility, bacterial targeting, and bactericidal ability of PSs [13, 31]. Quaternary ammonium cations can be directly bonded to the PS molecules by quaternisation, or bonded to the PS polymers by grafting or polymerisation. Cationic porphyrin derivatives [35] and cationic fullerenes [36] with quaternary ammonium groups are the focus of the current research.

Ma et al. [37] used 1,8-dibromooctane (DBO) for quaternisation and cross-linking reaction to obtain a linear pyridine polymer DBPE-DBO, which could effectively and rapidly inactivate the bacteria (E. coli and Staphylococcus epidermidis) via the \( \cdot O_2^\cdot \) produced under light and the antimicrobial activity of QAS. Zhao et al. [32] synthesised a cationic water-soluble oligo (thiopheneethynylene) (OTE) quaternised with CHI. This compound has half inhibitory concentrations values of S. epidermidis, S. aureus, E. coli, and R. solanacearum just in 8, 13, 24, and 52 ng/ml under irradiated status (white light for 30 min), and shows specific and extremely strong dark killing capability against S. aureus due to its quaternised pyridinium group (180 ng/ml for 30 min). While in Zhu’s [38] work, antibacterial polycations (EY-QEGED-R, \( R = CH_3 \) or \( CH_3H_2 \)), containing quaternary ammonium, PS (eosin Y), primary amine and hydroxyl species, were synthesised based on the ring-opening reaction and the quaternisation reaction (Fig. 2). The quaternary ammonium groups on the polymer lead to the superior dark antibacterial capability. The plentiful hydroxyl groups increased the potential antifouling capability (against dead bacteria) and good haemocompatibility. And the rich primary amine groups made EY-QEGED-R easily to be coated on various substrates via an adhesive PDA layer. These groups made the functionalised antibacterials promising for practical applications.

However, quaternised chitosan is often used in composite systems. Li et al. [39] used quaternised N-octyl chitosan (OC) as surface modification of UNCP (beta-NaYF\(_4\)·Yb/Er@NaYF\(_4\)) and then loaded with the PS (ZnPc) to get core–shell OC-UCNP-ZnPc nanomaterials, which produced \( \cdot O_2 \) under 980 nm irradiation, and had excellent antimicrobial effects on combat multi-drug resistant (MDR) bacteria. The quaternised chitosin in the system could increase the water solubility of nanomaterials [40], the conversion efficiency of UNCP, the specificity of bacteria and the bactericidal ability.

Similarly, quaternary phosphonium salts can also contribute to the water solubility, targeting and synergistic antimicrobial activity of the synergistic system [41]. Bresolí-Obach et al. [42] synthesised two different triphenylphosphonium PSs with phenalenone as PS. They were highly phototoxic to Gram-positive Staphylococcus aureus and Enterococcus faecalis, and the cationic groups in the synthenses mainly provided targeting properties.

2.2 Synergistic antibacterial of PSs and superhydrophobic surfaces

Superhydrophobic surfaces are effective in the removal of bacterial cells [43] and reducing the bacterial adhesion and the biofilm formation [44, 45]. Combined with the superhydrophobic surfaces and the photosensitive photobacterials, the photoactive surfaces are prevented from losing its effect due to the bacterial adhesion in the dark. Moreover, it will decrease the contact between system solution and PSs to reduce the dissolution loss of the PSs.

Hwang et al. [33] fabricated several self-cleaning and bactericidal surfaces by several paints, which were prepared by mixing titanium dioxide nanoparticles, fluoresilane and crystal violet (CV) or toluidine blue O (TBO) in ethanol solution. All of the painted surfaces (white, purple and blue), applied to paper, glass and polymer surface, showed superhydrophobicity in air (WCA>163°) (Fig. 3a). Meanwhile, they possessed good water resistance and self-cleaning property. Furthermore, the anti-adhesion rate of painted surfaces to the bacteria were >99.8%, and the surfaces with CV (purple) and TBO (blue) exhibited excellent antibacterial ability, owing to the generation of ROS, where the bactericidal rate against E. coli was about 99.50 and 99.99% under white light illumination within 3 h, respectively (Figs. 3b and c). Ghogare et al. [46] modified the silica device tip of the sensor by fluoresilane. The anti-adhesion tip showed a higher ROS production (10%) due to lesser microbial contamination. Additionally, Bartusik et al. [47] reported that fluorinated surfaces reduced the quenching of \( \cdot O_2^\cdot \) on the substrate so as to increase the lifetime of ROS.

Besides, there are other researchers using superhydrophobic surfaces to isolate the photosensitive antibacterials from the system liquid. Pushalkar et al. [26] fixed two PSs particles, loaded with phthalocyanine (PC) derivatives and chlorin \( \varepsilon \), to the surface of transparent polydimethylsiloxane posts array (SH) and then capped...
with inert silica nanoparticles to enhance the stability of the Cassie state. The PC-SH could rapidly produce \( \text{O}_2 \) and killed \( \geq 99.99\% \) of *Porphyromonas gingivalis* (\( >5 \log \)) in 15 min via 669 nm irradiation (270 kpm). The strong hydrophobic ability made the PSs between the arrays hardly come into contact with the liquid in the environment, except for \( \text{O}_2 \) [48]. In this way, the structural stability and safety can be improved. Furthermore, similar structures have been reported to discuss the difference in the activity of PS particles immobilised on different sites of PDMs, the influence of oxygen flux [48] and the resulting \( \text{O}_2 \) utilisation rate [49], and the practical application of this material in dental, water treatment and wound disinfection.

### 2.3 Photosensitive antibacterials materials based on UCNPs

In spite of some PSs that can be activated by an infrared laser, most of the currently developed PSs molecules need to be activated at relatively short wavelengths and low extinction coefficients [49]. However, it is well known that the ray with shorter wavelength has higher energy, shallower penetration depth, and greater impact on human body [50]. As a material that can convert the low-wavelength light source into a high-energy state, the UCNPs can be combined with PSs to greatly reduce the external irradiation source required for the action of PSs, even when using the NIR laser band (\( \lambda \geq 950 \) nm) as the activated source. The most commonly used UCNPs are the ones composed of fluorides (most commonly NaYF\(_4\)) doped with different levels of lanthanide ions (mostly one or several of Yb\(^{3+}\) and Er\(^{3+}\), Ho\(^{3+}\) and Tm\(^{3+}\)) [51]. The UCNPs can effectively convert infrared and near-infrared light (800–980 nm) into visible light or even ultraviolet light (290–540 nm) [52, 53], as shown in Fig. 4, and the combined PSs with light absorption in the corresponding absorption band can effectively kill bacteria by infrared and NIR laser irradiation. PSs usually have poor binding abilities with hydrophobic UNCPs, but this shortcoming can be solved by using a carrier, mostly silica layer [54] or amphiphilic polymer, wherein the coating of the amphiphilic polymer can effectively increase the water dispersion and stability of the nanoparticles [55]. Yin et al. [30] coated methylene blue (MB) on UNCP (NaYF\(_4\): Er\(^{3+}\)Yb\(^{3+}\)Mn\(^{2+}\)SiO\(_4\)) and then put them into quaternised chitosan hydrogel (CS-TM) with different ratio. These nanoparticles (UCNP/MB-doped QCS hydrogel) could produce a large amount of \( \text{O}_2 \) under NIR illumination at 980 nm, with 2% MB, and eliminated 89% of kanamycin-resistant *E. coli* after irradiation for 20 min. Also, the nanoparticles had a better antibacterial effect against oxacillin-resistant *S. aureus*. While Zhang et al. [53] coated the UNCP (LiYF\(_4\): Yb\(^{3+}\)Er\(^{3+}\)) with polyvinylpyrrolidone (PVP) and used the supported \( \beta \)-carbomethoxypthalocyanine zinc (CPZ) as PS, as shown in Fig. 5. The UNCPs-CPZ-PVP presented a high antibacterial activity against MDR bacteria (methicillin-resistant *S. aureus* (MRSA)) by 4.7 \( \log_{10} \) in 15 min with 980 nm light, and also had the bactericidal ability under 5 mm tissue samples. Ye et al. [56] validated the UNCPs-curcumin (NaYF\(_4\): Yb\(^{3+}\)Er\(^{3+}\)) conjugated by polyethyleneimine, not only showing inhibitory effects on MRSA with a MIC of 30 g/ml, which was less than curcumin (130 g/ml) at 980 nm for 30 min, but also exploring the MRSA-induced pneumonia in mice. In addition, some scholars have fixed the PSs to the UNCPs, with a silica shell, by covalent bonding [57].

By adding other functional materials to form a core–shell structure during the preparation of UNCPs, multifunctional photosensitive antimicrobials can be obtained [58]. Wang et al. [59] constructed a multifunctional multi-stage core–shell structure nanoparticles (Fe@UCNP-HMME) for both dual-modality imaging and photo/sonodynamic antimicrobial through wrapped UNCP (NaGdF\(_4\) Yb\(^{3+}\)Er\(^{3+}\)) on Fe\(_3\)O\(_4\), and then continued to coat quaternised chitosan (HACC) and photo/sonosensitisser hematoporphyrin monomethyl ether (HMME). When 125 mg/ml Fe@UCNP-HMME was added, 70% of *E. coli* was killed by \( \text{O}_2 \) after 10 min of illumination at 980 nm, and the rest *E. coli* could be all eliminated with another 10 min of ultrasonication.

### 2.4 Photosensitive antibacterial agent and energy storage structure

The above methods all utilise a new bactericidal component or anti-adhesion component to achieve the synergistic purpose, while the energy storage mechanism can pit microbes in the dark without introducing new antibacterial materials. It converts and stores energy or active oxygen when light irradiates, and then releases ROS in the dark. The following sections mainly introduce the delayed luminescent particles, the preservation of the light-absorbing transient (LAT), and the active oxygen storage mechanism.
2.4.1 Persistent luminescent materials (PLNPs): With a similar structure to the UNCPs, the above-mentioned, PLNPs possess particular energy-traps that can store excitation light under irradiation, by forming electrons or holes via embedding of metal ions in certain inorganic matrices. After excitation, carriers are released from the defects and produce persistent luminescence by radiation recombination at certain ions [60, 61]. Generally, the excitation source of PLNPs is ultraviolet light, and the delayed luminescent light can be modulated in the visible to infrared band by different dopant ions [62]. Ozdemir et al. [63] bounded the BODIPY derivative to PLNP (Zn$_{2.78}$Ga$_{1.68}$Ge$_{1.00}$O$_8$: Cr$_{0.01}$) and improved the strength and persistence of luminescence by co-depositing PPy/Co$^3+$. After ultraviolet charging (254 nm for 5 min), energy in the trap would transfer and excite the bounded BODIPY with continuous production of $^1$O$_2$ in darkness for at least 30 min. In addition, it has been reported that polyethylene glycol-modified PLNP (Zn$_{2.99}$Cr$_{0.005}$O$_4$) can produce $\bullet O_2^-$ under ultraviolet irradiation [64].

Xu’s team studied the synergistic antimicrobial effects of chemiluminescent materials and used PS. Luminol is a bioluminescent molecule which emitted blue light (400–55 nm) in the dark with the presence of alkaline and hydrogen peroxide [65]. A cationic oligo (p-phenylene vinylene) (OPV) (350–550 nm) was used as a PS to construct bioluminescence resonance energy transfer (BRET). The BRET killed 98% of Candida albicans within 30 min in darkness [66]. Based on this system, they developed an electrochemiluminescent antimicrobial hydrogel. Combining with the characteristics of electroluminescence, the hydrogel showed more controllability, luminescent intensity and time. After 5 s of electrification, the hydrogel could emit light for $>10$ min and exhibit premium antibacterial ability to E. coli, S. aureus and C. albicans [67].

2.4.2 Light-absorbing transient: Despite being a common photoinitiator, benzophenone has been shown to have antimicrobial activity by producing ROS ($\bullet O_2^-$, $H_2O_2$, $\bullet OH^-$) via generation of radicals under ultraviolet or sunlight [68, 69]. Park et al. found that benzophenone modified materials had an antimicrobial effect in the dark after ultraviolet irradiation [70], but did not give much explanation.

Si et al. [71] prepared a daylight-driven rechargeable antibacterial and antiviral nanofibrous membranes (RNMs) based on the structure of benzophenone. After solely driven by the daylight, if the free-radical benzophenone did not transfer energy in time, most of the structures would capture the electrons and rearrange to form LAT, as shown in Fig. 6. When the LAT contacted water and oxygen again in the dark, RNMs could produce ROS ($H_2O_2$ and $\bullet OH^-$) by catalysing oxygen and restore to ground state; the other part of the free-radicals were reduced to diphenyl methanol (DPM), no longer being photoactive. Based on the structure of benzophenone, the RNMs could reduce $6 \log_{10}$ of E. coli in 60 min under daylight, and the same effect could be achieved at 120 min in dark conditions after being charged against E. coli, as well as better antibacterial ability against L. innocua and T7 bacteriophage (Figs. 6c and d). The RNMs have been applied to masks and protective clothing with mass preparation.

2.4.3 Singlet oxygen storage trap: By forming internal peroxide as an oxidation product, many organic ring compounds are capable of reversibly capturing and storing singlet oxygen with high efficiency [72]. And 2-pyrrolidone derivatives are found to store and release singlet oxygen in response to heat [73]. Changtong et al. [74] synthesised a four 2-pyrrolidone molecularly modified porphyrin compound, named Tetraphenylporphyrin, which has the function of generating, trapping, storing and releasing $\bullet O_2^-$. Turan et al. [25] designed a 2-pyrrolidone modified boron dipyrromethene derivative (PYR6), which produced singlet oxygen under illumination (665 nm) and stores a portion of $\bullet O_2^-$ with the structural transformation to 2-pyrroline endoperoxide (EPO7). While in dark conditions, the EPO7 released $\bullet O_2^-$ by thermal cyclisation reaction, thence avoided excessive consumption of oxygen in the system. This process could be cycled multiple times with being highly cytotoxic.

In another paper, Tan et al. [24] prepared a composite antibacterial film (PPMS/BPS films), constructed by black phosphorus (BP) as PS and poly(4-pyridonemethylstyrene) (PPMS) by solution bonding. The films generated and trapped $\bullet O_2^-$ under visible light (660 nm), and killed 99.3% E. coli and 99.2% S. aureus just in 10 min. And in dark condition, the $\bullet O_2^-$ stored in the PPMS-EPO/BPS film was released with different rate relayed on different temperatures, as shown in Fig. 7b, which brought about the antibacterial rates against E. coli and S. aureus at 76.5 and 69.7% at 37°C, respectively. Due to the co-protection of hydrophobic PPMS and an oxide layer on the surface, the BPS had good stability and prevented further degradation.
3 Conclusion and outlook

We summarised the progress in the preparation of functional photosensitive antimicrobial surfaces by several synergistic components. The QAS improves the targeting and antibacterial ability of the photosensitive antibacterials to the bacteria, which helps the photocative surfaces to reduce the demand for light and oxygen, while still maintaining the sterilising ability in the dark. QAS-PSs of different scales, from small molecules to supra-molecules and to polymers, have tremendous advantages serving as antibacterials, surface modifiers, and composite components, which can be employed in water treatment [78], wound treatment [58, 76, 77], medical devices [78, 79], and cell imaging probes [37, 80, 81]. In the future, the QAS-PSs should be designed with more controllable antimicrobial and surface properties, excellent safety and long-term efficacy, based on the characteristics of QAS. In addition, other effective antimicrobial components such as quaternary phosphonium salts [34] and haloamine [82] compounds can also be considered.

Although there are not only studies on superhydrophobic photosensitive surfaces, the superhydrophobic properties can effectively prevent the bacteria from contaminating the photocative surfaces, especially in the absence of light, protect the PSs from liquid, and improve the stability and long-term effectiveness of the structure. At the same time, based on a variety of construction methods, various superhydrophobic photosensitive antibacterial surfaces can be quickly and effectively combined on various substrates for long-term applications. The presence of the surface and layer can effectively increase the oxygen content and the survival time of $^{1}$O$_2$. These materials can be utilised in dental [26], water treatment [27], and wound disinfection [33]. But how to improve the utilisation of $^{1}$O$_2$ is the focus of future research.

UNCPs construct the functionalisation of the photosensitive surface by effectively reducing the wavelength of excitation light source and increasing the depth of action on photocative surfaces. And the dispersion and antimicrobial of UNCP-PSs can be improved with selected coating materials. Combining with the emitting light of UNCPs, in vivo therapeutic exercise can be designed with imaging tracking function, especially in the treatment of inflammation [83, 84] and cancer [54, 85] in deep tissues. Multifunctional UNCP-PS with multi-layer core–shell structure is a hot research topic, such as a composite nanoparticle with all magnetic resonance (MRI) imaging, upconversion luminescence (UCL) imaging, photodynamic/sonodynamic antibacterial and quaternised surface layer [56]. However, how to adjust the range and intensity of the UNCPs emission band through the selection, content and distribution of doping elements still needs further study, especially on the optimisation of upconversion efficiency. The overlap between emission band and PS absorption band is an important factor affecting this system. The appropriate band matching and strong binding mode are the research direction of UNCP-PSs. In addition, surface-modified UNCPs and their morphology and size control are also constantly explored.

The energy storage structure can help photosensitive surfaces retain their bactericidal ability by releasing ROS in darkness. However, related research is so deficient that more attention is needed. Applications of PLNPs and electrochemiluminescent molecules in PDT have been heavily reported [61, 86]. Guided by the same principle, they can be rapidly extended to the field of antimicrobials. And these luminescent materials can be used as an imaging agent for excitation when they are used as exciting light sources in the dark [87, 88]. There is only one definite report found on photosensitive antibacterials based on LAT energy storage mode and applied in protective clothing [69]. However, it is difficult for LAT to store energy in the presence of oxygen and water, and the maximum absorption wavelength of benzophenone, usually in ultraviolet band, also limits its application. As for the PSs with singlet oxygen storage trap, they are the most reported and the most used materials. As a kind of synergistic 2-pyrollidone can be firmly combined with PSs through covalent bonds, so as to control the release rate of $\bullet{O}_2$ by regulating temperature, as well as to reduce the dependence of PSs on light and oxygen. By combining with 2-pyrollidone, the surface functionalised PSs can be explored for cancer treatment [25] and surface-modification devices [34]. While the capture efficiency, structural stability and cycling ability of $O_2$* are key to improvement, other organic ring compounds, such as diphenylanthracene derivatives [89, 90] pyrrolidine derivatives [91, 92], also deserve attention.

Surface-functionalised photosensitive antibacterials, which are modified by synergistic components, exhibit more adaptable and excellent antimicrobial ability in vitro and in vivo antimicrobials, and avoid many hazards. They can be applied to medical devices, implant materials, inflammation treatment, wound treatment, dental, protective materials, water treatment and other aspects, as well as in cancer treatment, self-cleaning and organic degradation.

Additionally, luminescent materials and PSs can also bring imaging tracking effect due to their visible light or fluorescence emission. It seems that the future development will focus on the multifunctional UNCPs composite system that can excite several PSs, smart photosensitive antibacterials with light-activation, PSs with oxygen carrier components and photosensitive antibacterial system with multiple synergistic mechanisms for further improving the antibacterial efficiency and reduction of the biotoxicity of these photo-induced antibacterials, the colour display function brought by luminescent materials in sensors that also has storage mechanisms with controllable release and the prospects in promoting energy conversion.

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