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Current Opinion in
Colloid & Interface Science

# Gold and silver nanoparticles as tools to combat multidrug-resistant pathogens

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**Abstract**
The sudden emergence and rapid spreading of viral, bacterial, and fungal infections and the usual development of resistance against traditional molecular drugs prompt the urgent need for alternative approaches to kill or inactivate pathogenic agents. This motivation has inspired a vast number of research works devoted to the design, synthesis, and application of nanomaterials, specifically inorganic plasmonic nanoparticles, as antimicrobial agents. We will pay special attention to articles from 2019 to 2023 where control of the colloidal properties, i.e., size, morphology, and colloidal stability, are properly considered. Here we will discuss the latest advancement in synthesis, colloidal characterization, and antimicrobial activity of Au and Ag nanoparticles, as well as hybrid systems based on combining metallic NPs with inorganic and organic materials. We will also consider contributions focusing on the green synthesis of plasmonic particles, highlighting the opportunities and the need for better control and predictivity of colloidal and functional properties.

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**Current Opinion in Colloid & Interface Science** 2023, **66:**101710

This review comes from a themed issue on **Biological (bio-inspired) Colloids and Interfaces (2023)**

Edited by **Martin Malmsten** and **Stefan Zauscher**

For complete overview about the section, refer Biological (bio-inspired) Colloids and Interfaces (2023)

**https://doi.org/10.1016/j.cocis.2023.101710**



## Introduction

Infectious diseases caused by pathogenic agents, such as bacteria, viruses, and fungi, pose a significant global threat, affecting millions of people worldwide each year. These microbial pathogens can rapidly spread through various pathways, such as ingestion of contaminated food and water, contact with untreated wounds, or airborne small liquid particles generated by coughing, sneezing, and breathing [1]. The rapid transmission of infectious diseases highlights the urgent need for effective treatments and prevention strategies, as demonstrated by the COVID-19 pandemic, which represents the most recent and significant example of how a viral infection can affect global human health and life [2,3]. Traditionally, a range of physical and chemical strategies, such as autoclaving, UV illumination, and chemical sterilization with ozone, alcohol, or chlorine, can be used to inactivate pathogens [4]. Antimicrobial and antiviral drugs can also prevent microbial growth by inhibiting their replication and proliferation. However, these traditional methods often fail against multidrug-resistant microbes, posing a significant challenge [5–8].

In recent years, inorganic colloidal nanomaterials have emerged as a promising solution to combat drug-resistant pathogens through physical and light-induced mechanisms [9] without developing antibiotic-resistant bacteria, showing distinct advantages over organic and polymeric materials.

Semiconductor nanomaterials and photosensitizers have provided, via photo-inactivation (i.e., photodynamic therapy (PDT)), a new route for systemic antimicrobial efficacy against a wide range of pathogens [10,11]. $TiO_2$, ZnO, and CuO nanoparticles (NPs) have been shown to effectively disinfect microbes if activated by UV–visible irradiation [12–14]. The reduction of microbial activity mainly relies on effects initiated by the semiconductor excitation, where the photo-generation of electron–hole pairs creates reactive oxygen species (ROS) and, consequently, consistent damage to pathogens. Specifically, ROS production damages bacteria and enveloped viruses by peroxidation, caused by hydroxyl radicals, or reduction of membrane lipids and DNA, caused by photogenerated electrons [15,16]. Although widespread, the application of these nanoparticles against different microbes is limited by several disadvantages. Specifically, their intrinsically extended band gap (Eg) requires UV illumination to promote electron excitation, which triggers collateral photochemical reactions and side effects. In most cases, the fast recombination of electron–hole pairs and the lack of specificity of these NPs reduce their effectiveness in bacterial inactivation.

Plasmonic metal nanoparticles have emerged as a flexible solution for eradicating fungal, bacterial, and viral pathogens through light- and thermal-induced means via adsorption of visible radiation [17–19]. This property is related to exceptional optical and photothermal features, high stability, and ease of manipulation, including fine-tuning of size, shape, and surface functionalization [20,21]. Combining these characteristics enhances the efficiency and selectivity of these nanomaterials, paving the way for a new era of antimicrobial nanoparticles that can be used both for *in-vivo* applications as well as for the engineering of antimicrobial coatings to prevent bacteria biofilm formation and proliferation on medical devices, fabrics, and coatings [22].

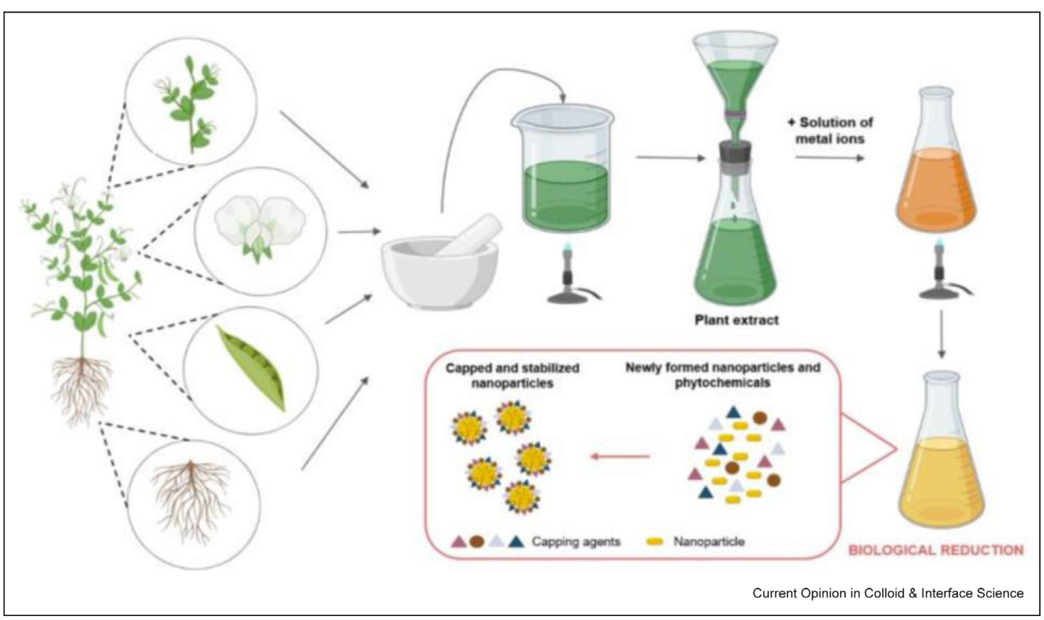
This review will discuss the latest developments in nanoplasmonic treatments against multiple microbial systems within the last three years. For previous reports, we refer the readers to recent review works [9,19,23]. Additionally, we will focus on the latest advancements in sustainable green production of antimicrobial metallic nanoparticles (Figure 1), which account for the growing need of environmentally friendly materials and related production processes [21].

## Microbial agents

Microbial pathogens can be classified into three main groups: bacteria, fungi, and viruses. Generally, viruses share similar morphology, route of replication, and genome architecture; a virus can be classified as enveloped or non-enveloped, depending on interfacial composition, structure, and organization (Figure 2a) [25]. Non-enveloped viruses have a capsid, composed of protective shell proteins. In contrast, enveloped viruses, such as coronaviruses, have an additional external shell mainly composed of glycoproteins and lipids surrounding the nucleocapsid [26]. However, the classification of virus families is an evolving field, and some viral species remain unknown to the scientific world, emphasizing the urgent need for novel and flexible antiviral strategies.

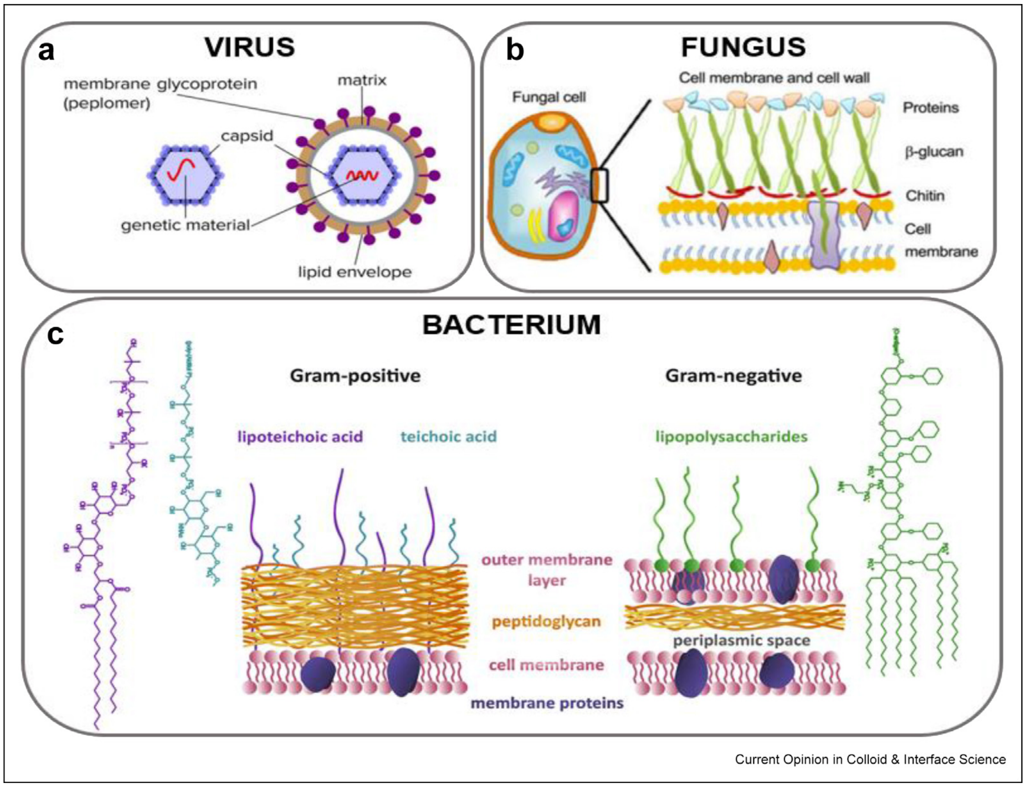
On the other hand, bacteria are divided into two main groups, Gram-positive and Gram-negative, for which cell walls' structure and chemical composition are significantly different (see Figure 2c). Gram-positive bacteria possess a thick peptidoglycan cell wall. In contrast, Gram-negative bacteria, like *Staphylococcus aureus*, also have an extra lipid membrane in addition to the cell wall and the standard plasma membrane [27]. This extra membrane provides enhanced resistance to antibiotics and nanoscale antimicrobial agents. In addition, the effectiveness of traditional antibiotic compounds is hampered by drug-resistant bacteria, such as methicillin-resistant *S. aureus* (MRSA), vancomycin-resistant Enterococcus (VRE), etc., making them an attractive target for antimicrobial plasmonic nanoparticles [28]. Finally, biofilms have received increased attention in antimicrobial treatment due to their consistent impact on the good conditions of the oral cavity, wounds, and implants [29]. Biofilms are a heterogeneous and complex matrix of bacteria interacting with polysaccharides, lipids, proteins, and nucleic acids, called excreted extracellular matrix (ECM) [30]. This complex architecture provides a rich environment for pathogens,

**Figure 1**




Schematic illustration of green synthesis of inorganic nanoparticles, readapted from the study by Rónavári et al. [24].

**Figure 2**




Examples of microbial species: enveloped and not-enveloped viruses (**a**), fungi (**b**), and Gram-positive and Gram-negative bacteria (**c**). Readapted from the study by Reddy et al., Pajerski et al., Chen et al. [35–37].

significantly improving bacterial stability and resistance to traditional treatment, necessitating novel pathways for their inactivation [31].

The third class of pathogens we will consider in this report consists of fungi, a broad category of different eukaryotic species with various sizes and shapes, ranging from simple single-celled yeast to complex macroscopic mushrooms [32]. As eukaryotic organisms, they are characterized by a defined nucleus and cell organelles and obtain nutrients through absorption from the surrounding environment (Figure 2b). Some fungal species, such as Candida or Cryptococcus, cause severe diseases in animals, humans, and plants by producing mycotoxins, defeated only by a limited number of antimicrobial agents. Like bacteria, some fungi are drug-resistant pathogens, enhancing the need for alternative new antimicrobial species in recent years [33,34].

## Metallic nanoparticles

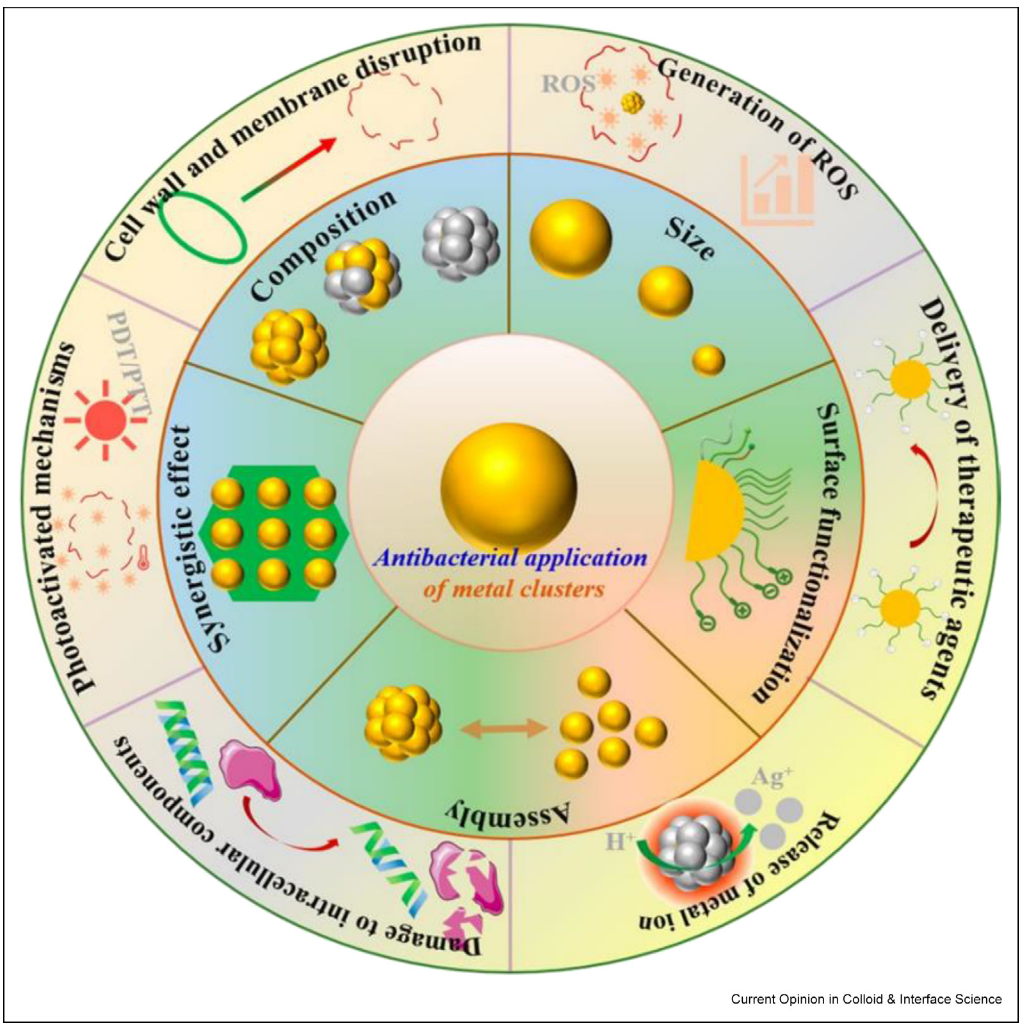
Plasmonic nanoparticles have a significant potential for biomedical applications due to their ease of synthesis and control over size and morphology, from a few to several hundred nanometers. Recently, there has been a growing interest in using metallic nanoparticles for antimicrobial applications [38]. Most reports involve synthetic methods with reducing agents such as sodium borohydride in solvents like chloroform, which pose risks to human health and the environment, prompting the use of green methods as a promising sustainable approach. Green synthesis involves using natural products, such as plant extracts or microorganisms, to reduce metallic salts instead of chemical agents, making it a cost-effective, easy-to-prepare, biocompatible, and non-toxic alternative. This innovative approach offers several benefits, such as natural redox molecules like aldehydes, fatty acids, alcohols, and flavonoids in plant extracts. These molecules can aid in the synthesis process and contribute to the reduction of environmental impact. Stable colloidal nanoparticles with relatively high purity can also be synthesized using physical methods, which are now considered as alternative green approaches by the scientific community. One such method is laser ablation in solution, which allows for the synthesis of biocompatible metallic nanoparticles without the presence of any potentially toxic sub-products [39,40].

The chemical stability of noble metals makes plasmonic NPs excellent candidates for biomedical applications. They are less susceptible to modifications caused by the surrounding media, such as degradation and dissolution. Additionally, the surface chemistry of metallic NPs can be tailored to improve biocompatibility and introduce targeting properties to specific sites while maximizing their colloidal stability. The ability of metallic NPs to absorb visible light through localized surface plasmon resonance (LSPR) is also significant. LSPR is sensitive to particle size, morphology, surface functionalization, chemical environment, and aggregative state, making it an effective tool for monitoring nanoparticle interactions in biological media and detecting, quantifying, and characterizing bacteria [41] and virus-like NPs [42,43]. Metallic NPs have also demonstrated potential as agents for the photothermic and photocatalytic treatment of microbial entities and cancer cells (see Figure 3 for the antibacterial mechanisms) [44]. By absorbing and dissipating the incident radiation as thermal energy, they can locally increase temperature and provoke the necrosis of bacteria and diseased cells.

LSPR also acts as a localized nano-lens, generating an intense electric field near the metallic surface. This local enhancement of the electric field can promote the excitation of photoactive molecules coupled to the metallic surface, improving the excitation rate of photosensitizers and promoting their bactericidal activity. Light adsorption can also trigger the formation of hot electrons that can be transferred to unoccupied molecular orbitals of molecules near the metal surface, triggering photocatalytic processes for the inactivation of microbes.

In addition, the interactions of these NPs with membranes and their translocation into intracellular

**Figure 3**




Metal NC-based nano antibiotics for combating bacterial infections. Physicochemical factors of NPs (inner layer) and mechanisms of action (outer layer) associated with the antibacterial behavior. Adapted from the study by Zheng et al. [46]. Copyright © 2022, Youkun Zheng et al.

compartments may affect DNA/RNA replication, enzyme function, and protein denaturation. Considering that the overall antimicrobial activity of plasmonic NPs is light- and not light-dependent, they are suitable for both in-vivo treatments and as central components of antimicrobial coating of surfaces.

While the specific antimicrobial action mechanisms of metallic nanoparticles are beyond the scope of this report, the reader is referred to previous comprehensive reports on this particular aspect [19,45].

This review will discuss the latest advancement in synthesis, colloidal characterization, and antimicrobial activity of Au and Ag nanoparticles, as well as hybrid systems based on combining metallic NPs with inorganic and organic materials.

## Gold nanoparticles

Gold nanoparticles are widely used in the biomedical field as antimicrobial agents due to their high stability and low degradability. The effectiveness of Au nanoparticles and their inactivation mechanisms depend on multiple factors, including their size, shape, surface functionalization, and chemical compounds used in their synthesis. While spherical AuNPs have been extensively studied against a wide range of pathogens, the efficiency of more complex nanoparticle architectures remains an active research topic. As mentioned in the introduction, the adsorption of photosensitizers on the metal surface promotes the production of ROS, inducing damage to different microbes [47]. The generation of ROS depends on plasmonic absorption, which can be enhanced and regulated by the shape anisotropy of NPs and, consequently, the localized electric field generated [37]. For example, Rossi et al. demonstrated for the first time that the inclusion of anisotropic gold nanorods (AuNRs) in a polyurethane (PU) matrix with a photosensitizer dye enables the formation of a highly efficient light-activated antimicrobial films [48]. The specificity towards biofilms can be adjusted by exploiting the different inactivation capabilities of AuNRs and Au nanostars (AuNSs) against Gram-negative and Gram-positive bacteria, allowing a more targeted approach. Increased production of ROS due to the anisotropy of plasmon resonance is not the only advantage offered by this class of particles. Facets, edges, and vertices on the surface of NPs act as binding sites for different ligands, which can be exploited to increase their antimicrobial activity. For example, concave cubic AuNPs functionalized with natural antioxidant molecules (lipoic acid and glutathione) showed excellent antibacterial activity by inducing fatty acid oxidation and membrane pore formation while remaining highly biocompatible for human red blood cells and HeLa, L929, and Chinese hamster ovary-green fluorescent protein cells [49]. Biocompatibility and elevated antimicrobial activity can also be preserved in ultrasmall gold nanoclusters (AuNCs) with less than 2 nm sizes. They exhibit well-defined geometric structures, molecular-like properties, and tunable luminescence ranges from ultraviolet to near-infrared (NIR) [50]. By combining fluorescence and electron microscopy, Linklater et al. demonstrated that the small size of these nanoclusters promotes their internalization into the internal compartments of common pathogens, such as *S. aureus* and *Pseudomonas aeruginosa*, inducing metabolic imbalance, ROS production, and irreversible intracellular damage [51]. Their antimicrobial efficacy can be enhanced by exploiting appropriate surface ligands. Imidazole-stabilized nanoclusters have been shown to induce metabolic imbalances, leading to bacterial death [52]. Ligand exchange of imidazole with biotiolated intracellular biomolecules, involved in cellular redox balance, leads to the accumulation of oxidizing species and, consequently, bacterial death (Figure 4).

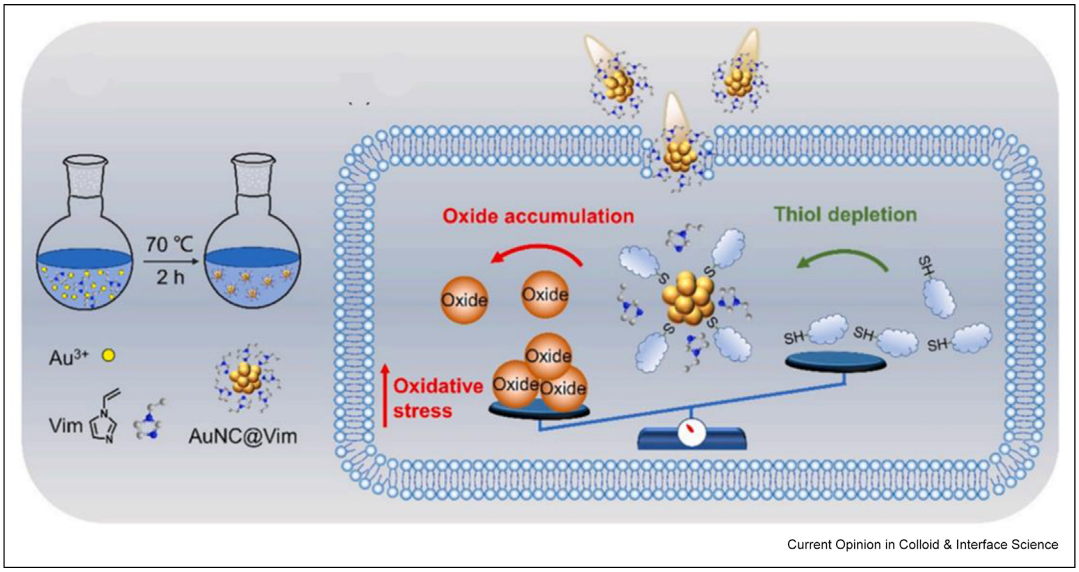
The synthesis of AuNPs for medical applications by chemical routes is a well-established method, with known environmental hazards posed by toxic reagents. However, new green-synthetic strategies have recently emerged to address these concerns.

Concerning green AuNPs for antimicrobial purposes, an interesting example reports the production of 8−15 nm AuNPs with different shapes using Brazilian red propolis (BRP) as the reducing and capping agent [53]. The presence of bioactive BRP molecules on the surface of the NPs makes the resulting AuNPs highly efficient against bacteria and fungi. Another relevant natural plant extract is Silybin, a potent flavonoid with antimicrobial, antioxidant, and hepato−protective activities that can reduce and stabilize metal nanoparticles. For the first time, Islam et al. demonstrated the green synthesis of sibylin-coated AuNPs for rapid (less than 1 h) inactivation of drug-resistant pathogens, particularly *P. aeruginosa* and E. Coli, as shown by microscopic assessment of the cell viability [54].

Green antimicrobial nanomaterials can be produced using various enzymes (metabolites) derived from fungal biomass. Specifically, metabolites from the fungal strain of *Trichoderma saturnisporum* have been successfully employed in the mycosynthesis of AuNPs. Azab et al. performed a complete physicochemical characterization of 8−30 nm AuNPs, demonstrating that such biogenic gold nanoparticles inhibit the viability of drug-resistant Gram-negative and Gram-positive bacteria, biofilm proliferation, antioxidant, and anticancer activity against cancer cells without affecting the toxicity of healthy cell lines [55].

Also, green AuNPs can be coupled with photosensitizer ligands. Maliszewska et al. produced monodisperse AuNPs from the mycelium of *Mucor plumbeus* [56]. The NPs enhance the effectiveness of methylene blue

**Figure 4**




Schematic representation of the oxidative stress caused by gold nanocluster functionalized with 1-vynilimadazole (Vim). Reprinted from the study by Gong et al. [52], Copyright (2022), with permission from Elsevier.

photosensitizer in forming ROS, inducing light-activated death in *S. aureus* and *Escherichia coli* using low light intensities. The results demonstrate that mycosynthesized AuNPs can be used in photodynamic therapy in combination with photosensitizing molecules, decreasing the photobleaching of dyes and, consequently, enhancing their photoactivity.

## Silver nanoparticles

In recent decades, silver nanoparticles have emerged as the most used and commercialized class of metallic nanoparticles for medical and biomedical applications, including household antiseptic sprays and antimicrobial coatings for medical devices [57]. The antimicrobial effect of AgNPs is primarily attributed to the release of silver ions from their surface. By binding to the cell wall through electrostatic interactions, AgNPs can denature membrane proteins, leading to alterations in the exchange of biological species with the external environment. Moreover, Ag ions can increase the membrane permeability of AgNPs in microorganisms determining morphological deformations in their structure. The antimicrobial effect of AgNPs extends beyond their adhesion to the cell surface and can also be ascribed to their penetration into the intracellular lumen and interaction with organelles, leading to cell damage by modifying their cellular functions. Ag ions generate intracellular ROS and induce genotoxicity by interfering with DNA/RNA replication, disrupting cell structure. Excessive release of $Ag+$ and side effects can occur with high amounts of AgNPs.

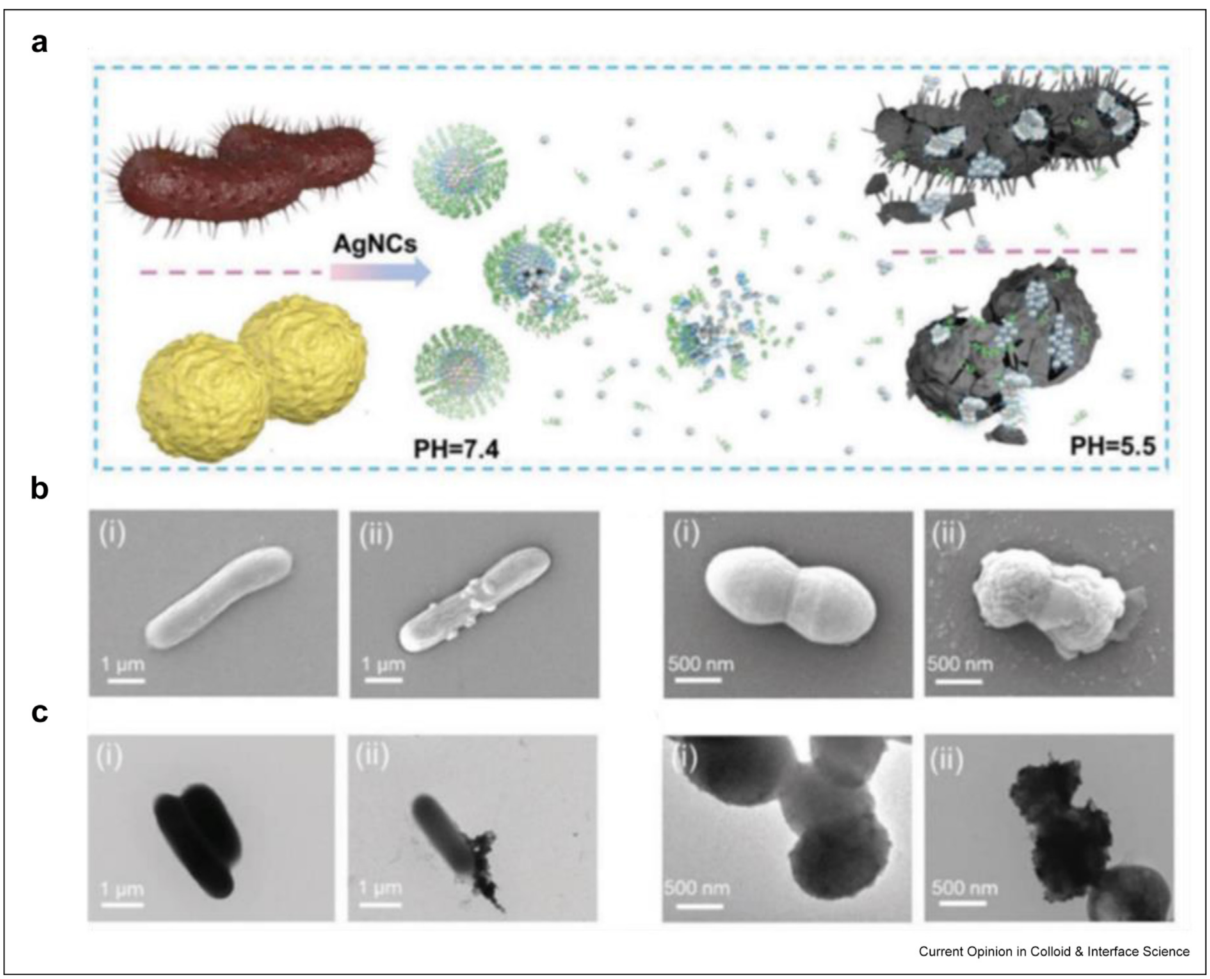
Consequently, researchers have focused on synthesizing different AgNP formulations with lower minimum bactericidal concentrations (MBC), the lowest concentration that kills 99.9% of bacteria. Functionalizing AgNPs with targeting agents, such as antimicrobial peptides (AMPs) or polycations, represents a strategic solution to overcome dose-related side effects [58]. AMPs prevent the adaptive immunity of bacteria by acting on the microbes' membrane without entering the cell. Furthermore, the synergistic effect of AMPs–AgNPs complexes allows the reduction of the dosage of AgNPs, significantly improving their biosafety. For instance, Alotaibi et al. combined commercial AgNPs with several antimicrobial agents (ampicillin, kanamycin, vancomycin, ciprofloxacin, colistin, and rifampicin), demonstrating their synergic effects against Gram-Negative bacteria with minimal toxicity to mammalian cells [59].

AMPs are designed to have targeted functionality. However, they can be degraded in biological environments due to changes in pH and temperature, leading to a loss of their antimicrobial properties. Recent work has addressed this issue by incorporating an osteogenic natural agent, i.e., silk fibroin (SF), into AMPs–AgNP complexes. SF acts as a stabilizer, improving the colloidal stability of nanoparticles and preventing the inactivation of AMPs, thereby maintaining antibacterial and anti-biofilm activities against *S. aureus* pathogens [58]. Although the targeting capabilities of these functionalizations are well established, other negatively charged interfaces in biological fluids may still interfere with them. More efficient targeting antibacterial agents were developed using stimuli-responsive Ag nanoparticles to address these concerns. Xie et al. report the preparation of silver nanoclusters (AgNCs) stabilized by pH-triggered functional polymers against MRSA and *E. coli* [60]. The ortho ester moiety of the polymer is hydrolyzed under acidic conditions, using a pH-triggered reassembly process, resulting in the collapse of AgNCs and release of Ag+ in the proximity of the acidic microenvironment of bacterial membranes (for the antimicrobial mechanisms and effect on the bacteria membranes see Figure 5a–c).

Synthesis of metallic nanoparticles as antimicrobials faces various challenges, including high cost, stability, scalability, and toxic reagents. The current trend in the large-scale production of antibacterial NPs is to move towards more environmentally friendly processes using various biological systems, such as bacteria, fungi, algae, plants, and earthworms. Reusable bio-sources are being sought to maintain the easy scalability of nanoparticle production, with a focus on metallotolerant fungal strains. Recently, eleven different metallotolerant fungal strains were isolated, identified, and screened for the production of AgNPs [61]. By a combination of X-ray diffraction (XRD) spectroscopy, energy-dispersive X-ray spectroscopy (EDX), and scanning electron microscopy (SEM) with antimicrobial analysis, the synthesized AgNPs demonstrated high antibacterial activity against various bacterial strains, such as *E. coli*, *Bacillus subtilis*, *S. aureus*, *P. aeruginosa*, *Enterococcus faecalis*, and *Listeria innocua*.

Recently, many green approaches have used fungal strain extracts to synthesize antimicrobial AgNPs with promising bactericidal, antioxidant, and cytotoxic properties [62–64]. Biogenic AgNPs with relevant antimicrobial properties have also been synthesized from plant extracts such as *Citrus limon* zest, *Moringa oleifera* flower,

**Figure 5**




*In-vitro* antibacterial mechanism AgNCs (**a**), SEM/TEM images of *E. coli*. and MRSA untreated (i) and treated (ii) by AgNCs (**b–c**). Adapted from the study by Xie et al. [60].

and banana waste peduncles demonstrating antimicrobial effects [65–67]. Lately, promising and effective green antibacterial AgNPs have been synthesized via laser ablation. These AgNPs have demonstrated the capability to inhibit the proliferation of various types of bacteria, both in their free form and in biofilms [68–70].

## Hybrid nanoparticles

In recent years, combining different antimicrobial agents has emerged as a new strategy for treating multidrug-resistant bacteria (MDR) mutations. The synergistic action of individual antimicrobial agents provides enhanced cytotoxicity against MDR, improving biological activity while reducing side effects. The combination of nanomaterials, such as multimetallic NPs, is an efficient MDR. Multimetallic NPs comprise two or more metals integrated into hybrid materials with tunable functionalities and optical properties. The synergistic effects of these components are controlled by various parameters, such as structure, chemical composition, and morphology, which influence the overall properties of the hybrid, such as the electronic structure and the total electric charge.

Noble metals, such as Au, Ag, and the platinum group elements, have been used in alloys, core–shell, and clusters of nanoparticles due to their multiple properties, including catalytic activity, chemical inertness, surface plasmon resonance, and antimicrobial activity. Incorporating a noble metal nanomaterial in implant-associated infections can prevent bacterial proliferation. An efficient approach has been recently demonstrated by combining Ag with an electrochemically more noble metal, like a platinum (Pt) group element, which enhances the $Ag^{+}$ release based on the principle of sacrificial anode. Bimetallic AgPt NPs have been synthesized by a wet-chemical method, focusing on the cytotoxicity against cells and bacteria, demonstrating the prominent role of the relative Ag and Pt content for simultaneous antimicrobial and osteopromotive effects. In particular, an increase in silver content improves the bactericidal effect. The highest synergistic effect is obtained for 50 %mol of silver and platinum, for which good antibacterial and osteopromotive activities are observed [71]. Furthermore, Ag–Pt alloys are emerging in nanomedicine not only for the properties mentioned above but also for the remarkable anticancer activity of platinum and its potential in bioimaging [72].

Efficient antibacterial activity in bimetallic NPs can also be achieved by conjugating metals with metal oxides, like Ag/Ag2O. D'Lima and coworkers have synthesized and thoroughly characterized these hybrid nanoparticles [73]. Performing DLS, XRD, SEM, and HRTEM experiments, they unraveled the morphology and crystalline structure of the NPs and demonstrated that this combination is lethal to MDR *P. aeruginosa*.

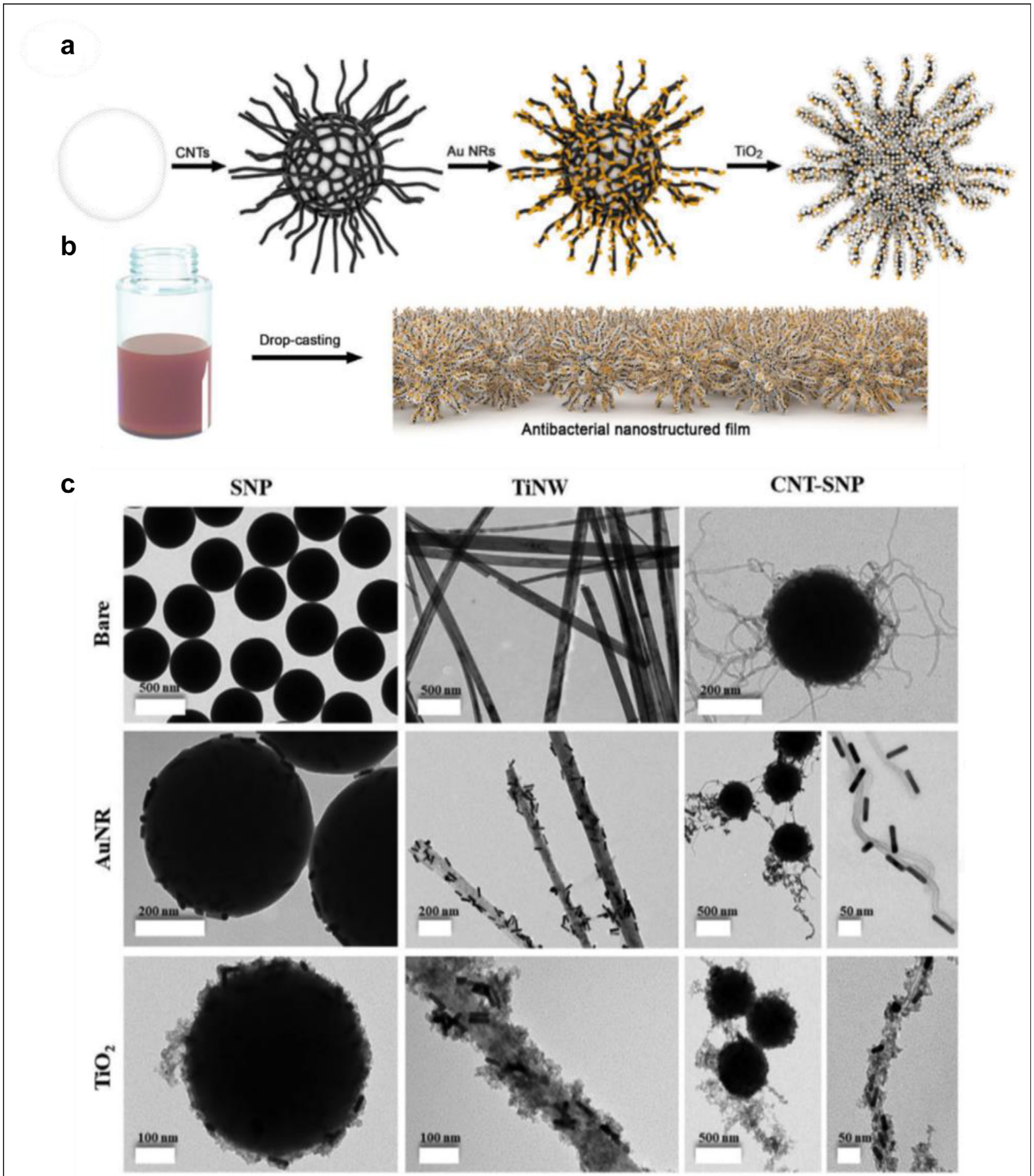
As mentioned in the introduction, $TiO_2$NPs and ZnONPs have been considered viable options for destroying many classes of microorganisms due to their photocatalytic properties. However, their photocatalytic efficiency needs to be extended from the UV to the visible and near-infrared (NIR) region, which can be achieved by incorporating plasmonic noble metal NPs [74]. Their significant absorption and scattering-cross sections prompt their use as sensitizers to inject electrons in the semiconductor conduction bands and generate ROS [75]. In this framework, Zhang et al. presented an efficient and eco-friendly preparation of Ag/$TiO_2$ nanocomposites with small size and narrow distribution by cold plasma treatment [76]. Well-dispersed silver nanoparticles were grown directly on the titanium oxide surface without reducing agents or stabilizers. The Ag$TiO_2$ nanocomposites exhibit enhanced photodegradation of methylene blue and pronounced deactivation of *E. coli* and *S. aureus* proliferation.

Antibacterial and antifungal activity of hybrid composites was also achieved by modulating the physico-chemical properties of the photocatalysts, including electrostatic interactions or/and crystallite/NPs', and combining them with multiple multifunctional materials [77]. For instance, a significant influence on the photocatalytic properties of the $TiO_2$ nanocomposite is associated with the size and shape of $TiO_2$NPs. In particular, $TiO_2$ nanorods have been shown to exhibit enhanced PDT capacity due to the larger surface area. Iqbal et al. synthesized biocompatible multifunctional heterostructures of Ag-decorated $TiO_2$ hybrid nanorods (HNRs) for photodynamic therapy and antibacterial activity [78]. They employed a straightforward approach to bind 4–5 nm AgNPs onto the surface of titanium oxide nanorods by hydrothermal procedure and thermal decomposition. Biocompatibility was achieved by functionalizing the surface of NPs with FDA-approved Pluronic® F-127 polymers. The synthesized HNRs show remarkable ROS production under UV irradiation in tumor cells and 90% killing efficiency against Gram-negative and Gram-positive bacteria strains and represent a promising heterostructure for dual therapy applications.

Enhanced efficacy of antibacterial AgNPs against bacterial biofilms can be achieved by combining them with magnetic elements (Fe or Co) synthesized via laser ablation. This method is not only a valuable example of synergism that combines degradation due to magnetophoretic movements with ROS production for Ag+ release, but it also represents a contaminant-free and environmentally friendly approach to producing antimicrobial agents [79,80].

The efficacy of combining different materials was recently expanded to composite materials consisting of

**Figure 6**




Current Opinion in Colloid & Interface Science

**Top:** Illustration of the synthetic method employed for the fabrication of the CNTs-coated SiO2 particles plasmonic nanocomposites, used as a template for the (**a**) sequential deposition of AuNRs and TiO2 NPs, and the (**b**) formation of a nanostructured film employing a drop-casting approach of the dispersion of the plasmonic nanocomposites. **Bottom:** Relative TEM images of the different colloidal nanostructures (SNP, TINW, and CNT-SNP) used as templates (first row); coated with AuNRs (second row), and further coated with TiO2 NPs (third row). Copyright 2021 [82], published by Wiley-VCH GmbH.

three -or more-different scaffolds. Mohaghegh and co-authors reported the fabrication of multifunctional Apatite (HA)/Ag/AgBr/$TiO_2$ composites by a facile deposition−precipitation protocol [81]. The obtained NPs are highly effective against yeast fungi and Gram-negative bacteria according to different deactivation pathways under visible light and dark conditions. By performing microscopy investigations, they demonstrated that under light irradiation, both microbes are decomposed by oxidation. At the same time, under dark conditions, only their growth is inhibited due to the absorption of the photocatalyst on their surface.

To increase the plasmonic photosensitization of $TiO_2$, the use of Au is often preferred thanks to its high chemical robustness and resistance to oxidation. These nanocomposites mainly involve Au nanorods and are currently investigated as novel sunlight-sensitive coatings with antibacterial properties. In this area, composite AuNR@$TiO_2$ materials -growth on different supports, like silica nanoparticles (SNP), multi-walled carbon nanotubes arranged as branches over silica nanoparticles (CNT-SNP), and titanate nanowires (TiNW)- have demonstrated their photocatalytic and antibacterial properties in the visible and near-infrared ranges (Figure 6) [82].

## Conclusions

This report reviews some of the recent applications of plasmonic NPs as antimicrobial agents. Recently, these NPs have emerged as promising candidates in medical formulations against pathogenic threats, which have the potential to affect the lives of billions of people in the world. Metallic NPs can kill or inhibit the proliferation-of pathogens through several interaction mechanisms, both light-dependent and non-light-dependent. Plasmonic NPs can absorb light and dissipate it via heat generation, transfer electrons to photosensitizers adsorbed or grafted on their surface, and locally increase the E-field, thereby enhancing ROS production. In addition, the non-photon-induced inhibition can involve particle adhesion to the membrane and their translocation into intracellular compartments, influencing the DNA/RNA replication, enzyme function, and protein denaturation and affecting the metabolite balance. All these mechanisms are mainly controlled by the physico-chemical characteristics of the nanoparticles, such as size, shape, surface functionalization, and compositions, expanding the possibilities of targeted-antimicrobial therapies. For these reasons, researchers are currently focusing on synthesizing novel multi-component nanomaterials to improve antimicrobial efficacy. Metals can be combined with semiconductor NPs (TiO2, ZnO) and act as sensitizers to enhance their photoactivity by extending their excitation range from the UV to the visible and near-infrared (NIR) region. Multifunctional hybrid NPs may also be designed by combining two metals, one of which is more electrochemically stable and acts as a sacrificial anode, boosting the release of ions. More sophisticated heterostructures involve several components, each rationally designed with controlled functionalities for targeted applications. All these combination strategies aim to exploit the synergistic effect of individual components to reduce the minimum particle concentration required to kill pathogens. Several reports are recently focusing on green approach to develop innovative antimicrobial materials, using natural extracts from plants, fruits, and microorganisms provides high-performance colloidal NPs, minimizing toxic reaction waste. To the best of our knowledge, these methods are mostly limited to preparing single-component antimicrobial materials. Although very interesting and with high potential impact, this specific field needs a more robust physicochemical approach to guarantee reproducibility of size, morphology, and function across batches and a higher control on these parameters, overcoming the typical limitations of NPs production with sodium citrate, that, despite considered relatively green, is generally characterized by a limited control over size and morphology and low stability. We believe that this should be one of the priorities in the field, together with the synthesis of multi-component antimicrobial nanomaterials via green approaches.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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** of outstanding interest

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