Silver Nanomaterials In Antimicrobial Applications

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Abstract. The article provides an overview of the different preparation methods, antimicrobial mechanisms and antimicrobial applications of silver nanomaterials. The synthesis methods of silver nanomaterials are mainly divided into physical synthesis, chemical synthesis and biosynthesis, among which biosynthesis is widely used due to its high purity and environmentally friendly products. The antibacterial mechanism of silver nanomaterials is relatively complex, which is the result of multiple ways such as disrupting the integrity of cell membranes, interfering with protein synthesis, affecting cell signaling and inhibiting DNA replication. The antibacterial performance, as the main property of silver nanomaterials, is widely used in fields such as biomedicine, antibacterial materials and wastewater treatment.

Keywords: Silver nanomaterials, antibacterical mechanism, antimicrobial applications.

1. Introduction

With the developing of nanotechnology, nanomaterials exhibit unique optical, electrical and magnetic properties due to small size effect, surface effect, quantum size effect and macroscopic quantum tunneling effect, etc., which have important applications in the fields of electronics, chemical industry and medicine. Silver nanomaterials have been used in the fields of antimicrobial materials, biomedicine and wastewater treatment due to their wide range of antimicrobial properties[1]. It has been found that the properties of silver nanomaterials are directly related to their particle size, shape and surface chemical composition. At present, most of the applications and researches of silver nanomaterials focus on the application in the field of antimicrobial, for dozens of disease-causing microorganisms such as Escherichia coli, gonococcus, Chlamydia trachomatis and so on. Silver nanomaterials has a strong inhibition and killing effect, and will not produce drug resistance. In addition, to promote wound healing, cell growth and repair of damaged cells, silver nanomaterials has a broad development prospect in the field of antibacterial. This article outlines the different preparation methods of silver nanomaterials, as well as their antimicrobial mechanisms and their applications in the antimicrobial field.

2. Preparation of Silver Nanomaterials

2.1. Physical Synthesis

The synthesis of silver nanoparticles using physical methods involves the preparation of large silver monomers into nanoscale silver particles, which is characterized by higher purity and a simple process but higher energy consumption and production costs[2]. Therefore, physical methods have been less studied in recent years.

Lu et al. [3] Prepared silver nanoparticles with a particle size of about 30 nm using electrical discharge machining (EDM) at room temperature. As shown in Figure 1, fixed the silver electrode in the center of a conductive iron container which was connected to the negative electrode of the EDM machine, and the other silver electrode was connected to the servo system as the anode, and after the power was turned on, an electric spark was generated between the two electrodes, and then the surface of the silver electrode was evaporated by the high-temperature EDM melting and the silver vapors were gradually condensed under the cooling effect of the deionized water and then nucleated, and the silver vapors were adhered to the nucleus, and the atoms gradually grow to form silver nanoparticles.

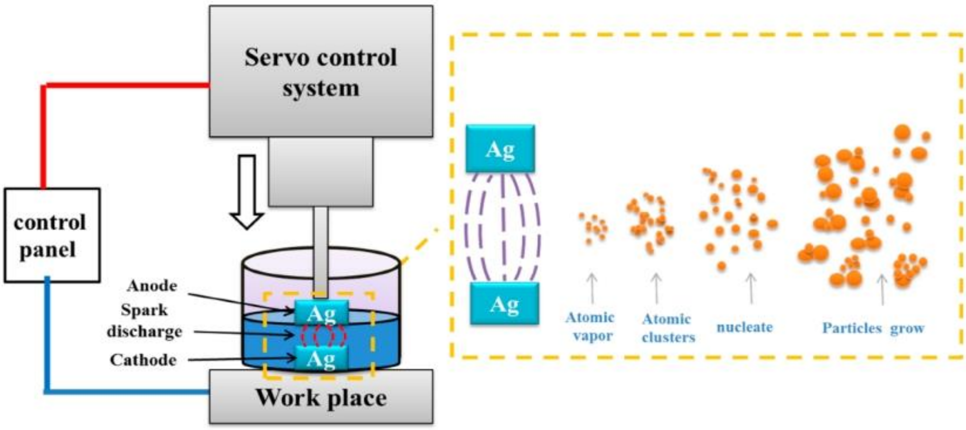

Fig 1. Schematic diagram of synthesis and preparation of silver nanoparticles [3].

Leclère et al. [4] synthesized silver nanoparticles by laser ablation in two different organic solvents, i.e., tetrahydrofuran and toluene, and explored the dispersion of liquid laser ablated silver nanoparticles in a polystyrene matrix. The laser ablation setup is shown in Figure 2. A laser was used to emit laser light at 20 Hz and 1064 nm to the silver foil in the solvent, and the pulse energy was continuously monitored using a 50-50 unpolarized beam splitter and a pyroelectric energy sensor, and different sizes of silver nanoparticles were ultimately obtained by setting different parameters.

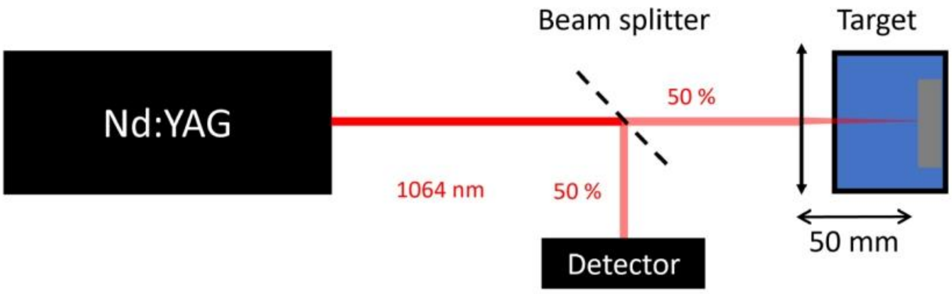

Fig 2. Simplified diagram of laser ablation device [4].

2.2. Chemical Synthesis

The preparation of silver nanoparticles by chemical reduction via organic and inorganic reducing agents is a relatively common method. Substances such as sodium citrate, ascorbic acid, sodium borohydride, Tollens reagent, *N*,*N*-dimethylformamide, etc. can be used to reduce silver ions in aqueous or nonaqueous solutions [5]. In addition, chemical methods such as microemulsion and hydrothermal methods can be used for the synthesis of silver nanoparticles.

Dong et al. [6] Synthesized silver nanoparticles with sizes between 10-20 nm and highly dispersed by oleylamine-mediated reduction of silver acetate via microemulsion method at 70 °C. It was explored that oleylamine helps in the synthesis of silver nanoparticles and the silver nanoparticles synthesized in this way are more stable and can be stored for about 6 months.

Wang et al. [7] Synthesized silver nanoparticles with an average particle size of 22.3 nm by hydrothermal method under alkaline conditions using 2, 2, 6, 6-tetramethylpiperidinium oxide oxidized nanocellulose as the sole carrier and dispersing agent, and $AgNO_3$ solution as the silver source and prepared silver nanoparticles/nanofibrillated cellulose composites. The carboxyl group introduced by oxidation of 2, 2, 6, 6-tetramethylpiperidinium oxide gave the dispersant a good dispersing effect, which enabled the added Ag^+ to be uniformly dispersed in the reaction system. During the hydrothermal reaction, the reducing terminal groups of the carrier can reduce Ag^+ to monomeric Ag which forms silver nanoparticles through nucleophilic interactions, and there is physical adsorption between the synthesized silver nanoparticles and the carrier to synthesize the silver nanoparticles/nanofibrillated cellulose composites.

Naderi-Samani et al. [8] Synthesized silver nanoparticles using silver nitrate as silver source, ethylenediamine as complexing agent, polyvinylpyrrolidone as stabilizer, hydrazine hydrate as reducing agent and deionized water as solvent.

Al-Bataineh et al. [9] Prepared silver nanoparticle stock solutions by dissolving ascorbic acid as stabilizer and trisodium citrate as reducing agent in deionized water.

Wojnicki et al. [10] Prepared silver nanoparticles by reducing silver nitrate using sodium borohydride at room temperature. First, prepared an appropriate amount of silver nitrate and trisodium citrate solution and mixed the two under magnetic stirring. Next, an appropriate amount of sodium borohydride was dissolved in deionized water and added to the solution containing silver ions to obtain a light yellow solution of silver nanoparticles.

2.3. Biosynthesis

Traditional techniques such as chemical reduction, commonly used to prepare silver nanoparticles, are costly and environmentally unfavorable. Therefore, researchers have developed greener ways of biosynthesis. Biosynthesis can be categorized into three types: the use of plants and their extracts; the use of microorganisms such as yeast, fungi and microalgae; and the use of membranes and DNA [11].

Al-Mhyawi. [12] Obtained face-centered cubic metallic silver nanoparticles by using biosynthesis. Tobacco leaves were ground and mixed with deionized water, after heating, stirring, filtration and centrifugation to obtain the plant extract. Afterwards, silver nitrate and deionized water were mixed, and the reaction was continued by adding the plant extract and the prepared salt solution after thorough shaking and mixing. After filtration, centrifugation and heating, the powder form of face centered cubic metallic silver nanoparticles was produced.

Ali et al. [13] prepared silver nanoparticles using flaxseed extract mixed with silver nitrate solution left to stand for about 5 hours. Since the flaxseed extract contains antioxidants, it indicated that silver nanoparticles were produced when the solution produced a distinctive red color, which confirmed by UV-Vis spectroscopy.

Yun et al [14]. Synthesized spherical chitosan/silver nanocomposites using ginger extract. Dried ginger was mixed with deionized water and boiled. After cooling, filtration and sonication, silver nitrate solution was mixed with ginger extract and heated. When the color of the reaction mixture changed from clear to shining yellow to brown, it indicated that silver nanoparticles were synthesized. The formation of silver nanoparticles was confirmed by UV-Vis absorption spectrophotometer at throughout the reaction.

Yassin et al. [15] Synthesized silver nanoparticles using the fungus Penicillium verrucosum. Cell-free cultures of Penicillium verrucosum were mixed with an aqueous silver nitrate solution and incubated at 25 °C protected from light. Silver nanoparticles obtained using this green synthesis method were collected by centrifugation. Experiments were conducted using flasks containing a fungal filtrate without silver nitrate solution as a control.

Shantkriti et al. [16] Obtained silver nanoparticles by reduction of silver nitrate using aqueous extract of Duchenne saltgrass. The study found that the color of the solution changed after 15 minutes of contact between silver nitrate and microalgae extract, suggesting that silver nanoparticles were synthesized by a method that is fast and environmentally friendly compared to traditional physical and chemical methods.

Schöbel et al. [17] Synthesized spherical silver nanoparticles using brewer's yeast. The cell-free culture supernatant of brewer's yeast was mixed with silver nitrate solution. Silver nanoparticles of different size ranges were obtained by varying reaction conditions, including reaction temperature, reaction time, light intensity and so on. It was explored that the reaction time for obtaining high quality silver nanoparticles was 72 hours and the reaction temperature was 50 °C, while light could shorten the synthesis time.

Ai et al. [18] prepared DNA-templated silver nanoparticles by adding silver nitrate solution to a mixture of oligonucleotides and phosphate-buffered saline in an ice bath, followed by the addition of sodium borohydride solution, which was vigorously oscillated and then sonicated to obtain DNA-templated silver nanoparticles, which were characterized by fluorescence spectroscopy and transmission electron microscopy. By varying the length of DNA and its molar ratio to silver nitrate, the optimal choice of DNA strands of different lengths as templates for the synthesis of silver nanoparticles and the best molar ratio for the synthesis of silver nanoparticles were found.

3. Antimicrobial Mechanism of Silver Nanomaterials

As shown in Fig. 3, the mechanism of the antimicrobial effect of silver nanoparticles is complex and has four main aspects: disrupting the integrity of cell membranes, interfering with protein synthesis, affecting cell signaling and inhibiting DNA replication.

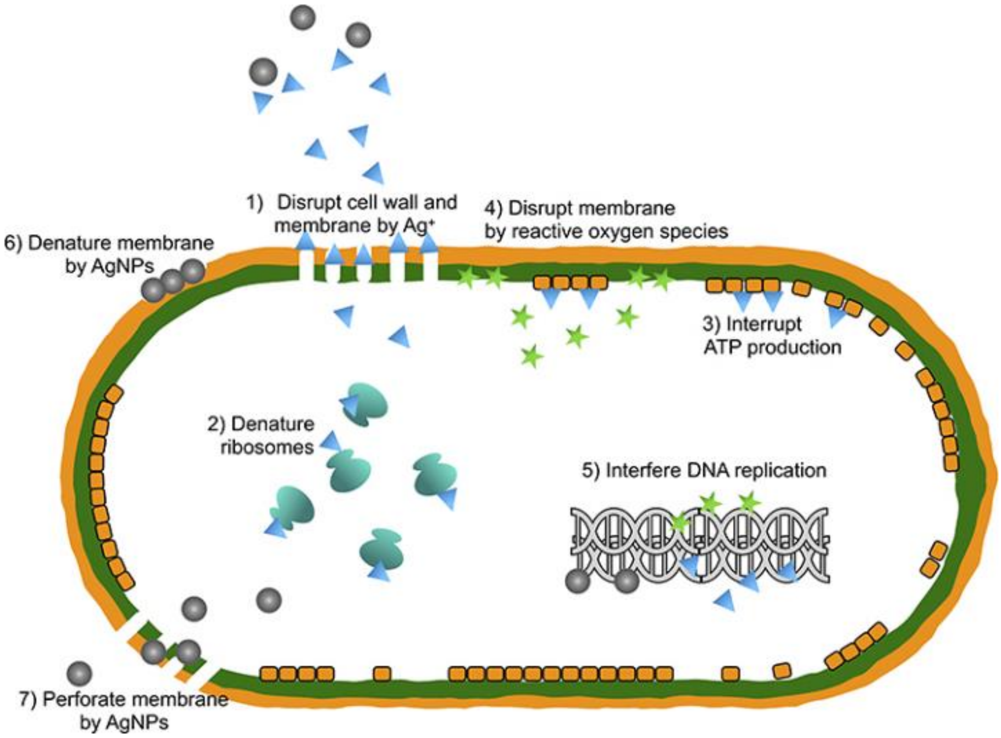

Fig 3. Antimicrobial mechanism of silver nanoparticles [22].

Silver nanoparticles release silver ions that can adhere to or cross cell walls or cytoplasmic membranes and alter the permeability of the cell membrane. Silver nanoparticles can also have a direct effect on bacterial cells by accumulating in pits in the bacterial cell wall and denaturing the cell membrane, or by directly penetrating the bacterial cell wall and altering the structure of the cell membrane, which affects the osmotic pressure inside and outside of the bacterium, causing the cell to swell or even rupture, which leads to leakage of the bacterial contents [19, 20].

As silver ions inactivate respiratory enzymes in the cytoplasmic membrane, production of adenosine triphosphate is terminated, and free silver ions or silver nanoparticles arrive in the cell and damage proteins through the formation of Ag-S bonds, leading to respiratory chain dysfunction and membrane pump damage [20]. At the same time, silver also stimulates the production of reactive oxygen species, resulting in oxidative stress, which can exacerbate the destruction of cell membranes and damage biomolecules such as DNA, affecting cell metabolism and accelerating apoptosis [21]. In addition, silver ions can inhibit protein synthesis by denaturing ribosomes in the cytoplasm, leading to microbial dysfunction [22].

In addition, silver nanoparticles can be involved in bacterial signaling. Bacterial signaling is affected by phosphorylation of protein substrates, and nanoparticles can dephosphorylate tyrosine residues on peptide substrates [22]. Disruption of signaling can lead to apoptosis and termination of cell proliferation.

The roles of sulfur and phosphorus are crucial as the main elements in the formation of deoxyribonucleic acid modifications. The interaction of silver ions with sulfur and phosphorus leads to DNA condensation and inhibits its replication process, leading to problems in cell reproduction and even microbial apoptosis [22].

4. Application of Silver Nanomaterials in Antimicrobial Field

In recent years, nanosilver has been widely used in biomedicine, antimicrobial materials, wastewater treatment and other fields due to its broad-spectrum antimicrobial properties. Studies have shown that silver-based nanoparticles are able to kill about 99.99% of microorganisms such as E. coli and MS2 phage viruses. In addition, silver-based porous nanocomposites can also effectively inactivate bacteria and viruses in drinking water up to 99%-100% [23].

4.1. Biomedicine

Marsich et al. [24] prepared an alginate/hydroxyapatite composite scaffold containing nano-silver, which was tested against human osteosarcoma cells MG63 and Saos-2 by the MTS method and showed that the composite scaffold did not adversely affect osteoblast proliferation, and at the same time, it had a significant bactericidal effect against four Gram-positive and Gram-negative bacteria, which made the biocompatible antimicrobial composite scaffold an ideal material for use in bone grafts.

Rai et al. [25] synthesized silver nanoparticles using grits rice leaf extract and silver nitrate and developed antimicrobial shampoos, soaps and ointments for the treatment of animal skin diseases. The silver nanoparticles were characterized by using UV-Vis spectrophotometer, Fourier Transform Infrared Spectroscopy, Transmission Electron Microscopy, and compared the antibacterial activity of this nanosilver and phytomedicinal oils against Aspergillus niger, Aspergillus fumigatus, Staphylococcus aureus, and Escherichia coli isolated from the skin of animals. And bioactivity experiments were also conducted using injured rabbits, which demonstrated that this blend of nanosilver and phytomedicinal oils showed maximum antimicrobial activity. Then prepared shampoos, soaps and ointments using the nanosilver-phytomedicine oil blend and evaluated the antimicrobial properties, which indicated that the nanosilver-phytomedicine oil blend could be used to develop antimicrobial shampoos, soaps and ointments for veterinary use to reduce skin infections and enhance wound healing activity in animals.

Baygar [26] synthesized a silk suture loaded with propolis and silver nanoparticles and evaluated its antimicrobial properties and biocompatibility. It was found that the antimicrobial activity of the silver nanoparticle-coated suture against Escherichia coli and Staphylococcus aureus was significantly enhanced compared to the uncoated silk suture, and the suture did not have a significant effect on the activity and proliferation of 3T3 fibroblasts. Since E. coli and S. aureus are multidrug-resistant bacteria that cause hospital-acquired infections, the suture can help inhibit bacterial infections and accelerate wound healing, and can be used as a novel antimicrobial material for biomedical applications and clinical practice.

Xiong et al. [27] Prepared a porous AgPd bimetallic alloy nanocage through a current displacement method using silver nanocubes and explored its antimicrobial properties and biocompatibility. It was shown that the nanocage exhibited complete broad-spectrum antimicrobial resistance, and cytotoxicity tests were performed on four mammalian cells, which indicated that the nanocage was able to preferentially kill bacteria over mammalian cells in vitro. Then tested the nanocage in vivo under pathological conditions using mice infected with Pseudomonas aeruginosa, and showed that the application of the nanocage effectively suppressed the acute inflammatory response caused by bacterial infection and did not damage the five major organs, suggesting that the nanocage retained its antimicrobial activity and did not suffer off-target toxicity, even under the complex pathological conditions in vivo.

Antezana et al. [28] Added different concentrations of silver nanoparticles to collagen hydrogels and explored the effect of controlled release of bactericidal silver ions from collagen hydrogels on the persistence of antimicrobial materials. They evaluated the bactericidal activity of nanosilver against Gram-negative (Pseudomonas aeruginosa) and Gram-positive (Staphylococcus aureus) bacteria, and showed that nanosilver was able to completely inhibit the growth of Pseudomonas aeruginosa and Staphylococcus aureus. After that, doped the nanosilver into collagen hydrogels to develop antimicrobial scaffolds for wound healing. Considering the need for biocompatibility for clinical applications, they tested its cytotoxicity on MDCK epithelial cells by MTT colorimetric assay. The study showed that accumulated silver ions may be harmful to the cells, so added cannabis oil to improve its biocompatibility.

Geerts et al. [29] doped gum arabic-nanosilver complexes synthesized by green method into toothpaste to reduce pathogenic microorganisms in the oral cavity, after which proved its antimicrobial activity against oral microorganisms such as Gram-positive, Gram-negative and fungal strains and further cytotoxicity assessment determined that the complexes do not cause damage to human cells within a short period of time, making this complex a good candidate for dental care with good biocompatibility, thus the complex has a promising application in dental care.

Ambrogi et al. [30] prepared an oleogel containing silica-silver based nanomaterials for use as a potential antimicrobial treatment for the prevention and cure of skin infections. The composite was tested and showed good antimicrobial activity against Gram-negative Pseudomonas aeruginosa and Gram-positive bacteria Staphylococcus aureus and Staphylococcus epidermidis. Afterwards, tested the cytotoxicity of the composite using human dermal fibroblasts and human keratinocytes, and the results showed that the composite had no cytotoxicity or very low cytotoxicity for both of these cells, indicating that the composite meets the basic conditions for use as an antimicrobial treatment.

4.2. Antimicrobial Materials

Ye et al. [31] synthesized two new multifunctional nanocomposites modified with silver nanoparticles modified with epoxide using microemulsion and precipitation polymerization methods. The nanomaterials were tested and showed significant destructive properties against Escherichia coli, and a comparison of the antimicrobial effects before and after silver nanoparticle modification showed that the composites modified with silver nanoparticles exhibited better antimicrobial effects against E. coli.

Wei et al. [32] prepared a waterborne polyacrylate-nanosilver wood coatings with excellent antimicrobial properties and tested them using the contact antimicrobial method, which showed that the coatings had excellent resistance to both Escherichia coli and Staphylococcus aureus, which was attributed to the fact that nanosilver disrupts the respiratory chain-binding enzyme and inhibits ribosomal subunit proteins as well as the enzyme-expression-associated ATP production process, which influences the DNA replication results. Antimicrobial coatings not only protect wood, but are also important in stopping the spread of pathogens.

Kasemsiri et al. [33] synthesized silver nanoparticle coating that can be applied to paper using mangosteen bark extract and demonstrated that the coating exhibited antimicrobial activity against both Gram-positive and Gram-negative bacteria, and that it was less resistant to Gram-negative bacteria than Gram-positive bacteria. In addition, they concluded that the good dispersion of silver nanoparticles in the polymer matrix increased the ability of this coating to penetrate the cell wall, thus enhancing antibacterial activity.

Boivin et al. [34] Incorporated silver nanoparticles into an acrylic latex for use in wood protective coatings and evaluated the effect of initiator type on the antifungal properties of silver nanoparticles embedded in the acrylic latex. The latex was explored for its ability to effectively inhibit the colonization of the black spot fungus and when a water-soluble initiator such as potassium persulfate was used, the silver nanoparticles became more aggregated and produced higher antifungal activity against Aspergillus branched-chain.

Chaisen et al. [35] Synthesized and characterized cotton fabrics loaded with silver nanoparticles and hemp straw activated carbon composites and evaluated their antimicrobial activity. The results of the study showed significant antimicrobial activity against Escherichia coli and Staphylococcus aureus, which can be used for active food packaging and biomedical applications.

4.3. Sewage Treatment and Air Purification

Darwish et al. [36] Synthesized composites with antimicrobial activity by embedding silver nanoparticles and samarium-doped zinc oxide nanorods in aragonite fish bone. It was shown that the composite exhibited significant eradication of Staphylococcus aureus, Pseudomonas aeruginosa and Schistosoma mansoni under both dark and light conditions. Therefore, the composite can be used to inhibit the growth of pathogenic bacteria (Staphylococcus aureus and Pseudomonas aeruginosa) in wastewater and is expected to be used as a new wastewater sterilization and disinfection material.

Bechelany et al. [37] synthesized a novel silver/polyacrylonitrile electrostatically spun fiber deposited on nonwoven fabrics for air purification. Silver/polyacrylonitrile nanofibers were synthesized using the electrostatic spinning method with *N*, *N*-dimethylformamide and silver nitrate, characterized and evaluated for filtration properties, quality factor and antimicrobial activity. The study found that the nature and concentration of the antimicrobial agent, the type and concentration of bacteria, and the contact time between the bacteria and the antimicrobial agent affect the antimicrobial effect of the antimicrobial agent, and that spherical silver nanoparticles smaller than 5 nm in diameter favored the antimicrobial activity against Escherichia coli. Therefore, the fiber material can effectively remove airborne bacteria and has a broad application prospect in the fields of masks, clean rooms and airline cabins.

5. Conclusion

In recent years, silver nanomaterials have received special attention from researchers due to their potent antimicrobial activity, which has been widely explored in the fields of antimicrobial therapy, food packaging, antimicrobial coatings, and wastewater treatment, thus providing a good opportunity for the development of smart nanosystems with antimicrobial activity.

However, as nanomaterials become more widely used and people come into contact with them more frequently, nanotoxicology and biosafety assessments cannot be ignored. For example, studies have shown that exposure to lower levels of silver can lead to silver deposition on the skin and other parts of the body, whereas prolonged exposure to high levels can lead to psoriasis, exposure to high airborne levels can lead to respiratory problems, lung and throat irritation, and stomach pains, and skin contact with silver can lead to mild allergic reactions [38]. Therefore, it is also essential to understand the toxic effects of nanomaterials and to develop proper countermeasures.

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