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«Green» synthesis of metal nanoparticles. Application and future perspective

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Metal nanoparticles are currently one of the most researched materials in the field of science and technology. These materials are up to one hundred nanometers in size and differ from ordinary metals in their unique physical and chemical properties.

The use of metal nanoparticles in biomedicine is one of the most promising areas of their application. For example, gold nanoparticles can be used to diagnose and treat cancer. Gold nanoparticles can be coated with various molecules that can target and interact with cancer cells, allowing cancer to be detected and staged. Silver nanoparticles can be used as antimicrobial agents, since silver has a high activity against bacteria and fungi. Also, silver nanoparticles can be used to treat wounds, as they promote rapid healing and prevent infections.

Metal nanoparticles are also applied in other industries *e.g.* to produce electronics, improve the properties of materials, manufacture catalysts, and many other things that are used both in everyday life and in the production and improvement of technological processes. This article discusses the use of metal nanoparticles of silver (AgNPs), zinc (ZnNPs), titanium oxide (TiO₂NPs), and gold (AuNPs) in biomedicine and other fields.

Keywords: green biosynthesis, nanoparticles, nanometals, microorganisms.

Introduction

Nanoparticles are currently increasingly capturing scientific spaces with their diverse and practical properties. Their main features are the size and shape, which result in the diver-

sity compared to chemical analogs [1–3]. The technologies for obtaining nanoparticles with physical and chemical methods are very time-consuming but recent discoveries make it pos-

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sible to speed up this process thanks to the «green» method of obtaining nanoparticles using biological agents, such as bacteria, fungi, algae, *etc.* [4]. Microorganisms and biological systems play an important role in the production of nanoparticles of various metals. The use of living organisms in this area leads to the rapid development of nanoparticle production technologies due to their properties of forming elementary metal particles and an environmentally friendly way of their extraction, since this process does not require the use of toxic substances that can enter the environment [1–3].

Some of the plants produce nanoparticles of palladium and platinum. For example, nanoplatinum is synthesized by leaves of the *Doipyros kaki* plant, and the leaves of *Gardenia jasminoides* and *Glycine max* reduce elemental palladium; the fruits of the *Musa paradisiaca* plant and the bark of the *Pinus resinosa* and *Cinnamom zeylanicum* plants produce palladium nanoparticles, and the bark of the *Pinus resinosa* plant is able to reduce platinum from its salts to elementary nanoparticles [1, 7].

Due to the ability of microorganisms to quickly accumulate biomass and synthesize biologically active substances, they can be candidates for obtaining metal nanoparticles in laboratory conditions, and later in industry [1, 3].

Microorganisms such as bacteria, fungi, yeast, and algae, most of which are capable of synthesizing nanoparticles, are the main bioobjects used in green synthesis. The main principle of the synthesis is the reduction of metal ions to nanoparticles [5].

Various microbes have been reported to synthesize nanoparticles of silver, gold, and

other metals. Silver and gold are given much more attention compared to others. Nanoparticles of these metals have been used in various fields and are biocompatible and low toxic. This makes them excellent drug delivery systems and carrier material for sensors in diagnostic tools [6].

Thus, bacteria of the genera *Bacillus*, *Pseudomonas*, *Lactobacillus*, *Klebsiella*, *Corynebacterium*, *Staphylococcus*, *Enterobacter* act as biocarriers for silver nanoparticles; fungi of the genera *Cladosporium*, *Fusarium*, *Trichoderma*, *Penicillium*, *Aspergillus*, *Phaenerochaete*; *Candida* yeast; and algae of the genus *Plectonema* [7]. ZnO nanoparticles are produced by bacteria of the genera *Aeromonas*, *Lactobacillus*, *Enterococcus* and *Bacillus*; fungi of the genera *Aspergillus* and *Fusarium*; algae of the genera *Marine*, *Caulerpa*, *Hypnea* and *Sargassum* [8, 9].

Nanoparticles of titanium dioxide TiO₂ can be synthesized by bacteria genera *Bacillus*, *Aeromonas*, *Lactobacillus* and *Halomonas*; fungi of the genera *Aspergillus*, *Volvariella*, *Saccharomyces*, *Streptomyces* and *Lecanora* [5].

Bacteria of the genera *Bacillus*, *Pseudomonas*, *Rhodococcus*, *Rhodopseudomonas*, *Ureibacillus* and *Nocardia* can be producers for gold nanometal; fungi of the genera *Fusarium*, *Colletotrichum*, *Yarrowia* and *Neurospora*; algae of the genera *Shewanella*, *Sargassum* and *Plectonema* [7, 9].

The fungus *Fusarium oxysporum*, yeast *Schizosaccharomyces pombe* and *Candida glabrata* are also used for the synthesis of cadmium sulfide nanoparticles [1, 7].

Cobalt nanoparticles are recovered with the help of the bacterium *Pyrobaculum islandicum*, and nanometal lead is produced

from the bacterium *Desulfovibrio desulfuricans* [7].

Plants and their parts are also often used for the synthesis of metal nanoparticles. Thus, the leaves of *Argemone maxicana*, *Acalypha indica*, *Mangifera indica*, *Cassia fistula*, *Catharanthus roseus*, *Clerodendrum inerme*, *Murraya koenigii*, *Aloe vera*, *Piper betle*, *Ocimum tenuiflorum*, *Coleus aromaticus* and *Apiin* are often used for silver synthesis; fruits of plants *Emblica officinalis*, *Carica papaya* and *Tanacetum vulgare*; the bark of the *Cinnamon zeylanicum* plant; and seeds of plants *Jatropha curcas* and *Syzygium cumini* [1, 3, 7].

ZnONPs are synthesized by the plants *Calotropis gigantean*, *Abrus precatorius*, *Aloe barbadensis*, *Cassia auriculata*, *Acalypha indica*, *Parthenium hysterophorus*, *Camellia sinensis*, *Calotropis procera*, *Musa balbisiana*, *Citrus paradise* and *Medicago sativa* [8, 9].

TiO₂NPs are produced by *Azadirachta indica*, *Murraya koenigii*, *Psidium guajava*, *Syzygium cumini* L., *Nyctanthes arbortristis*, *Eclipta prostrata*, *Jatropha curcas* L., *Solanum trilobatum* L., *Citrus reticulata*, *Aloe vera*, *Trianthema portulacastrum*, *Chenopodium quinoa*, *Curcuma longa*, *Catharanthus roseus*, *Olanum trilobatum* L. and *Medicago sativa* L. [5].

Gold nanoparticles are produced by the leaves of the plants *Murraya koenigii*, *Aloe vera*, *Apiin*, *Camellia sinensis*, *Eucalyptus camaldulensis*, *Pelargonium* and *Azadirachta indica*; fruits of plants *Emblica officinalis* and *Tanacetum vulgare*; flowers of the *Nyctanthes arbortristis* plant; and seeds of the *Cuminum cyminum* plant [7]. In the literature, there is information on the synthesis of AuNPs using such plants as *Crassocephalum rubens*, *Cornus*

mas, *Punica granatum*, *Papaver somniferum*, *Galaxaura elongata*, *Mimosa tenuiflora*, *Anacardium occidentale*, *Aloe vera*, [10, 12] AuNPs are also obtained using *Stenotrophomonas maltophilia* bacteria, *Rhodopseudomonas capsulate*, *Pseudomonas putida*, *Pseudomonas fluorescence*, *Deinococcus radiodurans*, *Actinobacter* spp. [12].

«Green» biotechnologies for the production of metal nanoparticles

Nanoparticles can be gathered by different methods of green synthesis. Frequently, scientists use plant extracts that synthesize nano-metals intracellularly or extracellularly. To produce intracellular NPs, it is necessary to cultivate plants in organic media full of metallic ions. The extracellular production of nanoparticles can be conducted with different plant extracts of leaves, flowers, fruits, *etc.* [10, 11]. Much attention should be paid to the source of the active substances — the extracts of various parts of a plant or different plants contain different biologically active substances. For example, these compounds may have antioxidant properties and reduce gold ions to metallic gold [10]. Nanoparticles can also be gathered by the culture liquid of bacteria. Metallic ions firstly are retained on the surface or inside microbial cells, and after that reduced to nanoparticles with the help of the enzymes [12, 13].

Silver nanoparticles

For example, silver nanoparticles can be synthesized by bacteria, fungi, algae, and plants.

Bacterial cells can produce nano-sized silver in a short period, giving them a certain geometric shape and influencing size. For in-

stance, the bacteria strain *Bacillus* sp. GP-23 from marine soil was inoculated into a flask with LB broth which was incubated at 37 °C for 24 hours. After that, the supernatant from the synthesis was obtained by centrifugation at 6000 rpm for 10 min. Later 100 ml of the resulting solution were moved to a 250 ml Erlenmeyer flask, and the concentration was adjusted to 1 mM AgNO₃. To avoid a photolytic reaction, the reactant was stored in darkness. Silver ions were added to the mixture, and after 24 hours of incubation, the color changed from pale yellow to dark brown and showed an absorption peak at 420 nm, a peak characteristic of AgNPs. The color change took place because of the action of a certain surface plasmon resonance (SPR) of the AgNPs. The particle size was measured by detecting the linear profile of individual spherical particles in the 12–20 nm range, confirmed by HRTEM micrographic images [14].

Fungi have the ability to synthesize metallic nanoparticles thanks to their bioaccumulating forces of metals and their tolerance, high intracellular binding, and absorption capacity [15]. So, *Reishi* mushrooms were used to produce silver nanoparticles in a short period and without great costs. Then 20 ml of *Reishi* mushroom extract are diluted to 100 ml with distilled water. Subsequently, 15 mg of AgNO₃ salt are put into the solution and left on a magnetic stirrer to reduce Ag⁺ ions. The change of a mixture color from transparent to reddish-brown means that the reduction from Ag⁺ to Ag⁰ was successful. The final product has to be washed with ethanol and dried in order to remove unreacted waste. The UV emission spectrum is the observed peak in the absorption band 400–460 nm, corresponding to AgNPs.

TEM images indicate that the biosynthesized AgNPs are dispersed, but agglomeration between some particles also occurred. The particles had a spherical shape, and the average particle size ranged from 9 to 21 nm [16].

The plant extracts were obtained to synthesize the metallic silver nanoparticles. They have potential advantages over microorganisms thanks to the ease of scale-up, less biohazard, environmentally friendly, and complex cell culture maintenance process. However, it has a serious drawback, it is necessary to prepare a plant extract. Besides, it matters the place and the time of the plant material collection. For example, plant *S. spinosa* has the ability to obtain silver nanoparticles. The plant material was collected and dried at 37 °C for 48 hours. The dried substance is then crushed in a mortar. 10 ml of distilled water was added to 0.2 g of plant powder and the solution was boiled for 5 minutes and then cooled. The cooled mixture was filtered with the help of filter paper. An aqueous solution of 1 mM silver nitrate was added to the plant extract of *S. spinosa* in a ratio of 9:1. Subsequently, it was constantly rotated in a stirrer at room temperature at 27 ± 2 °C for 6 h. The experiment was repeated three times. At first, the *S. spinosa* extract was yellow, but after interaction with aqueous AgNO₃ solution and being stirred at room temperature, the color changed to red with time, meaning that with time, the color intensity increases confirming the reduction of Ag ion and the formation of AgNPs [17].

The use of microalgae to synthesize nanoparticles is a new approach that considers microalgae as reducing and blocking agents to make NPs. This technology also has many additional stages of extract preparation which

was proven by the research about silver nanoparticles production with the help of algae *C. aeroterrestica* strain BA_Chlo4. Microalgal biomass was centrifuged at 4700 rpm for 10 min after cultivation for 15 days to collect the biomass. Then distilled water was used to wash it four times. After the wash, the resulting product was freeze-dried by a freeze dryer for 2 days. The dried biomass was then mixed with sterilized glass beads and stirred for 5 min to get an algal powder, 500 mg of which were dissolved in 500 mL of distilled water and boiled at 60 °C for 30 min in a water bath. The sample was cooled to room temperature and then filtered. The filtrate was centrifuged at 4700 rpm for 10 minutes to remove residual algae and stored at 4 °C. The AgNPs synthesis was conducted by mixing 90 mL of 10^{-3} M silver nitrate with 10 mL of aqueous algae extract. The mixture was left under fluorescent light for 24 hours at room temperature. The solution first had no color and then turned golden yellow after 24 hours. After the incubation AgNPs were collected by centrifugation at 13000 rpm for 30 minutes and washed three times with distilled water. Some of the washed samples were freeze-dried for 6–8 hours for biological interests. AgNPs were hexagonal with a nanometer diameter of 14.5 ± 0.5 nm and a maximum wavelength of 404.5 nm. FTIR and GC-MS analysis demonstrated that proteins and polysaccharides acted as blocking and reducing agents for AgNPs [18].

Zinc oxide nanoparticles

Green synthesis zinc oxide nanoparticles implement biological substances like plants, fungi, bacteria, and algae to replace chemical reactants to reduce the product and process toxicity.

The process of synthesis of ZnONPs with bacteria proves the diversity of the application of pathogenic strains in the latest technologies for the production of different materials. *S. aureus* strain ATCC 29213 was first cultivated in LB broth and then centrifuged at 10,000 g for 10 minutes to remove the sediment. The supernatant was separated and used for the production of ZnONPs. Then, the culture solution was mixed with 1 mM $\text{Zn}(\text{O}_2\text{CCH}_3)_2$ in an orbital shaker at 250 rpm and 37 °C for the biomimetic synthesis of ZnONPs. The synthesis of nanoparticles was monitored by visual methods of the culture medium color change. After some time, the solution was centrifuged at 3,500 g for 10 minutes to remove any media components, and the nanoparticles were gathered by centrifugation at 25,000 g for 30 minutes. The synthesized ZnONPs were washed several times by centrifugation and dispersed in water to remove residual zinc ions and excess media components. In the end, the obtained nanoparticles were freeze-dried and stored at 0 °C until further experiments. ZnO nanoparticles were irregularly shaped, ranging from 10 to 50 nm. Lyophilized ZnONPs powder ($10 \mu\text{g ml}^{-1}$) was dispersed in acetate buffer by ultrasound and used to measure UV-vis which showed the characteristic absorption peak of ZnO NPs at a wavelength of approximately 373 nm. The absorption spectrum of ZnONPs also indicates a narrow distribution of nanosized particles [19].

Fungi are used as an alternative to bacteria because of their tolerance, and better capacity to bioaccumulate metals, as they produce enzymes, facilitate the growth process, economic viability, and easy management of the biomass.

Therefore, *A. niger* mushrooms are the raw material used for the zinc oxide nanoparticles synthesis. *A. niger* is grown on a liquid medium at 200 rpm and a temperature of 37 °C. The mycelium is then separated and 5 mM zinc nitrate is added and cultivated at 200 rpm at 32 °C for 2 days. A color change from yellowish to a colorless liquid is noticed after 48 hours. A white precipitate forms at the bottom of the flask, showing the recovery process. The white sediment is precipitated by centrifugation at 10,000 rpm for 10 min. The biosynthesized ZnONPs have a peak at 320 nm and size from 84 to 91 nm and are spherical in shape, which is proved by SEM analysis [20].

Seaweeds can as well be used as biofactories for nanoparticle synthesis. Thus, *S. muticum* was taken as the example for the formation of ZnONPs due to the polysaccharides that they produce. Dried seaweed powder was added to 100 ml of distilled water, heated to 100 °C, and filtered. 50 ml of the aqueous solution was mixed with a 2 mM solution of zinc acetate dihydrate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$) and kept for 3–4 hours in a water bath while stirring at 70°C. The white solid was collected using centrifugation at 4000 rpm for 10 min and thoroughly washed with distilled water and then dried at 100 °C. ZnONPs were obtained by heating ZnO *S. muticum* at 450 C for 4 hours. The ZnONPs formation was observed by the color change of the solution from dark brown to white. ZnONPs have a hexagonal structure with particle sizes ranging from 3 nm to 57 nm [21].

Zinc oxide nanoparticles can be synthesized by plant extracts. For instance, the leaf extract of *G. pentaphylla* was used to produce ZnO

nanoparticles. 0.2 M zinc acetate dihydrate was added to 50 ml of the extract of the leaves using a magnetic stirrer at 60 °C for 1 hour. When the reaction was done, the light-yellow solution was cooled to room temperature. The yellow extract was subjected to centrifugation at 8000 rpm for 20 min, then washed with distilled water and methanol to remove impurities, and at the end dried at 80 °C. The powder was dried in a muffle at 350 °C for 3 hours. ZnONPs synthesized by *G. pentaphylla* leaf extract showed a high absorption peak at 351 nm with an average size of 36 nm and a hexagonal structure [22].

Gold nanoparticles

The production of gold nanoparticles is a fairly simple process that does not require an increase in temperature and pressure. Biosynthesis occurs when the HAuCl_4 salt solution is combined with the prepared plant extract and mixed to initiate the AuNPs synthesis process. A change in the color of the resulting solution indicates the formation of nanoparticles [12]. It is known from the literature that a solution of Au (III) (1 mM HAuCl_4) was used for the synthesis of gold nanoparticles and cultivated at different temperatures (25–37 °C) and pH (2.5–8.5). Observe the change in color of the suspension, the absorption spectrum of the suspension, and the size and shape of the particles [12].

For instance, *D. radiodurans* obtained from cell culture were washed three times with deionized water followed by incubation with 1 mM Au(III) solution at 32 °C and pH 7.0 for 8 hours. The resulting purple solution was centrifuged at $8000 \times g$ for 10 min to separate and collect the cell pellet and supernatant,

respectively. The cell pellet was washed with deionized water until the supernatant became colorless. Supernatants were combined, filtered using 0.22 μm syringe filters, and then dialyzed against ultrapure water for 48 hours with agitation. Bacterial pellets and dialyzed supernatant were frozen at $-20\text{ }^{\circ}\text{C}$ for 12 h, respectively, and then transferred to $-80\text{ }^{\circ}\text{C}$ for 12 h and lyophilized. Purified purple powders from the supernatant were used to characterize AuNPs [23].

A solution of gold chloride (1 mM HAuCl_4) was added to the suspension of the cell mass of *Stenotrophomonas maltophilia* and cultivated at $25\text{ }^{\circ}\text{C}$ for 24 hours, while a color change from light yellow to cherry red was observed, which indicates the accumulation of gold nanoparticles. The spectra thus obtained revealed a strong absorption at almost 530 nm after 8 hours of incubation. Spherical gold nanoparticles approximately 40 nm in diameter were formed [24].

Titanium dioxide nanoparticles

Chemical methods for the synthesis of TiO_2 nanoparticles have been found as environmentally toxic because the synthesis involves high temperature and pressure, leading to limitations in the mass production of TiO_2 . Thus, green nanotechnology has been explored as an alternative and environmentally friendly approach for the synthesis of TiO_2 nanoparticles because it uses reducing agents obtained from biological sources and the same reducing agent can be used to synthesize many metal compounds. In addition, the use of plants, their waste, fruit extract, and microorganisms used in the synthesis reduces the use of toxic and expensive chemicals [25]. Thus, environmen-

tally friendly synthesis methods are vital to obtaining stable nanoparticles of suitable size and able to disperse with low energy consumption [26].

Titanium dioxide nanoparticles (TiO_2 NPs) are obtained from *Carica papaya* Shell extracts. 65 ml of 0.2 M titanium isopropoxide were placed in triple distilled water. 15 ml of *Carica papaya* Shell extracts were gradually added dropwise to the solutions at $85\text{ }^{\circ}\text{C}$ using a magnetic stirrer for 5 hours at pH 11. The resulting mixtures were centrifuged at 15,000 rpm for 15 minutes. It was then dehydrated at $55\text{ }^{\circ}\text{C}$ for 5 hours and calcined at $455\text{ }^{\circ}\text{C}$ to obtain TiO_2 nanoparticles. The absorption spectrum was recorded at 350 nm [27].

There is also information on environmentally friendly biosynthesis of TiO_2 by isolated halophilic marine bacteria *Halomonas* sp. RAM2. The seed culture of *Halomonas* sp. was prepared under optimal conditions ($\text{NaCl} = 5\%$, $\text{pH} = 8.30$, $30\text{ }^{\circ}\text{C}$) at 120 rpm for 48 hours. 20 ml of 0.025 M TiO_2 were added to the culture supernatant obtained after centrifugation of the culture liquid at 6000 rpm for 15 min, stirred at room temperature for 1 hour, and then heated at $60\text{ }^{\circ}\text{C}$ for 30 minutes. Biosynthesized TiO_2 nanoparticles were centrifuged, washed several times with methanol and distilled water, and then dried [28].

Titanium oxide nanoparticles are also produced with the help of *Trigonella foenum* leaf extract. 15 ml of leaf extract were added to a 0.5 M solution of titanium oxysulfate and stirred for 15 min. Next, 1M sodium hydroxide was added dropwise until the pH reached 8. The precipitate was washed with deionized water to remove excess sodium hydroxide scale, and then the washed precipitate was

filtered and dried at 700 °C for 3 h. High temperature ensures the formation of well-crystalline nanoTiO₂ with a resolution of about 100 nm [29].

Silver nanoparticles and their use

Silver nanoparticles (AgNPs) are clusters of silver atoms with a diameter of 1 to 100 nm and are of great interest to scientists as antimicrobial agents in the medical field.

Silver nanoparticles are obtained by various methods, namely chemical, physical and biological. In particular, chemical methods of production are more popular, although they are more dangerous from the point of view of ecology [30]. Moreover, obtaining metal nanoparticles by conventional methods is associated with the toxic substances that pollute the environment [30–32]. The safest method of obtaining metal nanoparticles remains the biological method with the help of various biological agents.

Silver nanoparticles are often used in various fields of biomedicine due to the manifestation of antimicrobial properties since there is a problem of resistance of various microorganisms to antibiotics. Silver nanoparticles have antimicrobial properties against a variety of gram-negative and gram-positive bacteria [33]. In addition, elemental silver has also been shown to exhibit antifungal, antibacterial, and antiviral effects [34].

Biomedical applications of silver nanoparticles can be effective due to the use of nanoparticles synthesized by biological methods that minimize toxicity and maintain stability. However, the application of silver nanoparticles is not limited to their antimicrobial potential but also promotes the obtaining

and development of new biomedical products. For example, AgNPs are used to deliver medicinal substances, optical probes, orthopedic materials, as well as disinfectant sprays, bandages, catheters, *etc.* [30, 35].

It has been found that changing the size, surface, and shape of AgNPs affects the cell membrane and cell organelles, so it can be used to reduce pathogenicity and increase drug sensitivity [30, 36].

There is a lot of information that AgNPs-based nanosystems have been tested as additional nanocarriers of various anti-inflammatory, antioxidant, antimicrobial and antitumor agents for effective drug delivery [4, 30].

There are also literary data that many cytotoxic agents are used to treat cancer, but their effectiveness has not yet been fully proven and studied [37, 38]. Therefore, it is very important to create innovative, affordable and safe alternative methods of cancer treatment. There is an opinion that AgNPs can be effective in cancer therapy [37, 38].

Silver nanoparticles, due to their shape and properties, are considered very potential for the possible treatment of leukemia and cancerous tumors of the mammary glands, lungs, liver, prostate, skin, *etc.* Many sources claim that AgNPs can be used as antitumor agents due to their antiproliferative and apoptosis-inducing properties [37, 38]. It has been demonstrated that properly selected silver nanoparticles can integrate inside target cells and reprogram them to trigger apoptosis [37, 38].

There is also a problem of contamination with biofilms and various bacteria in the water lines of dental facilities, which leads to environmental pollution [19]. The authors [39] investigated the possibility of disinfecting such

systems using a disinfectant with nanosilver, which had a spherical shape and dimensions from 3 to 5 nm and were connected to a stabilizing polymer. After treatment, there was no stabilizing polymer, and the AgNPs particle size varied from 50 to 200 nm. The surface transformation of the dominant particles of silver nanoparticles before disinfection from AgO to AgCl was also observed. AgNPs are found to adsorbed on the surface of biofilms and are toxic to bacteria. It is also shown that AgNPs are transformed depending on the conditions in which they are [39].

There are studies using AgNPs as an antibacterial additive to bone cement made of polymethyl methacrylate [40, 41]. Bone cement is used to attach joint prostheses during joint replacements [40, 41].

Bandages with silver nanoparticles significantly shorten the healing time of wounds to 3 days and increase the rate of cleaning of infected wounds. It is also interesting that side effects of dressings with AgNPs were not observed [40, 42, 43]. Thus, these results clearly show the advantages of dressings with nanosilver in healing the surface of burn wounds.

Zinc nanoparticles and their use

Zinc nanoparticles are often used in various fields like electronic, textile, rubber, pharmaceutical, and cosmetic industries, and these nanoparticles can also be a part of photocatalysis [44]. ZnO was approved for safe (GRAS) material so that these nanoparticles can be a part of a component for food packaging [45, 46]. Zinc ions have antimicrobial activity since these nanoparticles can have an effect on the integrity of the bacterial cell, especially the development of reactive oxygen

species (ROS) by accumulating them and blocking important metabolic pathways in microbial cells [47].

Zinc nanoparticles are highly toxic to certain bacteria, but almost do not affect human cells [48]. There are also data that showed a wide antibacterial effect against major food pathogens, such as *E. coli* O157:H7, *Salmonella*, *Listeria monocytogenes*, and *Staphylococcus aureus*, especially when they reduce the particle size [49].

Also, ZnO nanoparticles showed a great tendency to deactivate cancerous T cells (approximately 28–35×) in comparison to healthy cells. What's more, the cell's activation state has been observed to contribute to nanoparticle toxicity, when resting T cells demonstrate corresponding resistance, whilst cells stimulated via the T cell receptor and CD28 costimulatory pathway indicate greater toxicity which provokes a direct connection with the level of activation. The toxicity occurrence is reported relating to the involvement of generated ROS, as cancer T cells generate higher induced levels than regular T cells. Besides, ZnONPs activate apoptosis in Jurkat T cells [50].

Elemental zinc may be seized by various biological, chemical, or physical methods. The most universally used mode is the application of biological agents such as stabilizers or reducers to produce nanoparticles.

ZnONPs are also effective in the generation of elements for solar panels in the shape of nanowires, they are also part of field and light resistors and photodiodes [44, 51].

ZnO nanoparticles have an impressive antibacterial effect and also can absorb electromagnetic radiation (ultraviolet, microwave, infrared, and radio frequency). By giving this

characteristic to glass, plastics, synthetic fibers, and paint, it is possible to obtain new, more functional materials with improved properties, such as protection from ultraviolet rays in sunglasses, creams, ointments, *etc.* Some components consisting of ZnO nanoparticles can be a part of infrared sensors [52].

Nanoparticles of ZnO have exceptional compatibility with tissues and living cells, although it takes some time for them to dissolve, attach to bioligands, and reach the target. The depot of highly dispersed zinc powder created in the body can ensure the slow entry of the trace elements into the body in doses close to physiological, which can be one of the ways to obtain a long-term therapeutic effect, for instance, in ethanol addiction, since chronic alcohol intoxication is one of the main factors of the development zinc deficiency [53].

It is seen from the studies that the ZnO nanoparticles' properties are extremely effective in case of UV radiation arising from a typical band gap or visible radiation due to ZnO defects in metal and organic molecule detection methods. A luminescence method for dopamine detection — one of the important catecholamine neurotransmitters obtained from the amino acid tyrosine and is crucially important in homeostasis and clinical diagnosis — is based on (3-aminopropyl) triethoxysilane (APTES) capped with luminescent ZnONPs [54]. Cu^{2+} is known as a common environmental toxin, but it is used as a trace component in biological systems. Luminescent ZnO nanoparticles are used as Cu^{2+} sensors thanks to their luminescence quenching [55].

Furthermore, an important aspect of these nanoparticles is their antibacterial and antifungal activity, which proves the antimicrobial

properties of the substance. Steady and concentration-dependent antioxidant activity was recorded for ZnNPs-Alt [56].

Scientists have reported that the ZnO quantum dots (QDs) can be carriers for plasmid DNA delivery. This polycation-modified ZnO QDs-DNA nano-complex may facilitate the adequate transmission of plasmid DNA into COS-7 cells [57].

ZnO is valuable as a treatment for different skin problems, in cosmetics such as diaper rash powder or barrier creams, hemimorphite cream, shampoos with anti-dandruff effect, and antiseptic ointments. In addition, it is part of a tape with zinc used by athletes to avoid injuries of soft tissue while training [58, 59].

TiO₂ nanoparticles and their use

The green synthesis of titanium oxide nanoparticles is an economical, non-toxic, and harmless technique. TiO_2 NPs themselves can be used in cosmetic products as UV filters. Since TiO_2 is not only a UVA filter but also an extremely effective UVB filter, it exhibits the highest versatility among all sunscreen products [60, 61]. *Calendula* (MG), a strong antioxidant, protects the skin and acts as an anti-aging agent. Scientists confirmed that biosynthesized MG-mediated TiO_2 nanoparticles (NPs) produce bioactive compounds that have reducing and blocking effects. Remedial plants showed their antibacterial activity against 24 mm *Salmonella gallinarum* for MG- TiO_2 NPs of methanol (MGM) and ethanol extract of *calendula* (MGE), showing moderate inhibition but no zones against *Paeruginosa aeruginosa* [9, 62].

Today, domestic and industrial debris have a lot of risky and unsafe substances, like toxic

dyes and nitroarene compounds polluting the environment. These dyes and other harmful substances hardly soluble in water and are highly stable, which justifies the threat to marine life [63]. Some scientists declare that green-synthesized TiO₂ nanoparticles are commonly used to reduce dyes and compounds by photocatalytic reaction [64–67]. The TiO₂ oxide photocatalysts are really impressive photocatalysts to purify water. The G-TiO₂ nanoparticles were studied for their catalytic potential against the process of the photocatalytic degradation of the dye. Degradation of methylene blue under UV light in 120 minutes showed 96 % success.

Green TiO₂ nanoparticles were also tested for their antibacterial properties to inhibit gram-positive and gram-negative bacteria, although gram-positive ones are less reactive because of their structure.

The antibacterial effects of G-TiO₂ nanoparticles were investigated for gram-positive *Staphylococcus aureus* (ATCC 6538) and gram-negative bacteria *Escherichia coli* (ATCC 8739) and were compared with the gentamicin and mulberry extract. Thus, the bactericidal effect of G-TiO₂ is 29 % less than the same results of gentamicin, but 40 % more than the effect from the mulberry extract. Therefore, the catalytic and microbial properties of G-TiO₂ nanoparticles make them a promising solution for water reclamation and biomedical treatment [68].

Numerous studies have shown how TiO₂ nanoparticles can be implemented for antibacterial objectives to kill pathogens like *E. coli*, *Pseudomonas aeruginosa*, *S. Aureus*, *A. hydrophila*, *S. pyogenes*, *E. faecalis*, *S. faecalis*, *Y. enterocolitica*, *B. subtilis*, *Enterococcus hi-*

rae and *Bacteroides fragilis* under the ultraviolet light [69–71]. While TiO₂NPs contact bacterial cells, ROS are generated which reduce adhesion causing the death of bacteria, disintegration of cell walls, and gene expression.

The antiviral properties of TiO₂ nanocolloids were investigated against Newcastle virus (NDV), which showed viral inhibition at a minimum dose of 6.25 µg/ml. TiO₂-NCs break up the lipids in the viral envelope by G-Sol, damaging the glycoprotein spikes and blocking the adhesion, terminating infection. This can be stated as a promising clue of titanium nanoparticles as the active component of NDV infections treatment. Titanium nanoparticles may become a good contestant for the creation of novel antiviral medications [72].

Germes may be neutralized by TiO₂ under illumination with the help of its photocatalytic properties. Hydroxyl radicals and ROS formed on the illuminated TiO₂ surface oxidize polyunsaturated phospholipid components of the cell membrane of the microbe [73]. An impressive TiO₂NPs antimicrobial film maintains the quality and ensures the protection of food on food packaging which makes the ability to use nanoparticles of TiO₂ in the food industry [74].

Innovative porous titanium dioxide (TiO₂) nanoparticles improved by polyethyleneimine (PEI) can be created to analyze the titanium dioxide photocatalytic properties to get ultraviolet (UV) radiation-induced drug delivery. Paclitaxel, a poorly water-soluble anticancer drug, was covered with those porous TiO₂NPs. PEI on the surface of this complex can close off the way to stop the hasty drug release maintaining tolerable circulation time to target cancer cells. Above all, UV irradiation time

can adjust the amount of drug released from the multifunctional porous TiO₂ nanoparticles to further control the anticancer effect. This porous TiO₂ nanoparticle shows a sequence of stimulated drug release and cancer cell targeting [75].

Titanium dioxide nanoparticles (TiO₂NPs) have proven to be effective and can be widely used in agriculture, in particular for the treatment of soils contaminated with heavy metals among other known NPs. According to previous reports, NPs have both antagonistic and synergistic effects on heavy metal accumulation and plant growth under different environmental conditions [76].

However, the impact of TiO₂ nanoparticles can also harm crops. For example, a large number of these nanoparticles can cause a decrease in leaf growth, the amount of carbon absorption by the stem and leaves, and the presence of TiO₂NPs can lead to lipid peroxidation and a decrease in overall plant development. But at the same time, in some plant species, the presence of TiO₂ nanoparticles increases the content of thymoquinone due to the genetic increase of metabolic pathways in the plant and triggers enzyme activity. Therefore, depending on the plant's specific perception of titanium dioxide nanoparticles, the effect of treatment and the subsequent course of using the solution or additives may change [77].

Nanoparticles have several novel and attractive properties that can be used for the sorption of heavy metals from domestic, sewage, or industrial wastewater in treatment technologies. Nanomaterials are effective due to their small size, high specific surface area, and morphological features that have made

these materials suitable for use in separation technology. TiO₂ nanoparticles have attracted a lot of attention due to their unique chemical and physical properties, such as strong oxidation and reduction ability, good permeability, and special optical/electrical properties. It is a good semiconductor that is mainly known in the world in various fields of application. In addition, TiO₂ nanoparticles have various applications in the food industry, personal care products, pathogen inactivation in wastewater treatment, and many construction materials such as tiles, paints, and plasters [78].

Gold nanoparticles and their use

Gold nanoparticles are impressively stable *in vivo*, efficiently uptaken by cells, and generally used to deliver chemical components. According to scientists, gold nanoparticles (GNPs or AuNPs) have great efficiency and low toxicity. Gold nanostructures have a great variety such as gold nanoparticles, nanoclusters (AuNCs), nanocages, nanorods (AuNRs), nanostars, nanoshells, and even nanoplates. AuNPs controlled geometrical and optical properties, as well as chemical interaction, give them a prioritizing position for biomedical purposes [79].

Some studies reported that gold nanoparticles tend to penetrate through the blood-brain barrier. Earlier the scientists proved the inhibition of nanogold (AuNPs) of the β -amyloid peptides accumulation and the β -amyloid aggregates reduction. AuNPs also demonstrated blockage of acetylcholinesterase and butyrylcholinesterase, so they strengthen the anti-Alzheimer effect. Gold nanoparticles diminish neuroinflammation and enhance motor dynamics in Parkinson's-induced mice [80–83].

Quantum Gold (QG) acts like an endotoxin antagonist by decreasing inflammation and stopping (re)initiation of chronic disease, and as a result, the wound bed turns from an inflammatory to a proliferative phase [84]. A similar gold nanocomposite may be modified into bifunctional quantized gold (QG) to attach to LPS without affecting the catalysis of the inner core.

Lesion healing after hemostasis can be problematic due to sickness. Thus, platelet-like particles (PLPs) are usually aggregated with antibacterial gold to create nanogold composites (NGCs) to stimulate the curing. These NGC PLPs imitate the platelets' shape, induce thrombus contraction, demonstrate some antibacterial capability, and have all chances to stop post-traumatic blood loss and infection [85].

The use of gold nanoparticles as new antimicrobial agents was revealed to become a viable alternative to current techniques of limiting or preventing the spread of many pathogenic species. These nanoparticles can strongly prohibit the growth of pathogenic gram-positive or gram-negative bacteria such as *Staphylococcus saprophyticus* and *Bacillus subtilis* or *Escherichia coli* and *Pseudomonas aeruginosa* relatively [86], it is also known about the inhibition of the growth of pathogenic *Klebsiella pneumonia* by green synthesized AuNPs [87]. The antibacterial effect was stronger in the case of *P. aeruginosa*, which may be a consequence of the electrostatic interaction between positively charged nanoparticles and negatively charged surfaces of microbial cells [88].

Scientists stated that gold nanoparticles have a great effect on curing rheumatoid ar-

thritis. Results have revealed that AuNPs (15 nM, 25 µg/kg) improves the inflammatory mediators shaping and oxidative stress formation in collagen-induced arthritis (CIA) rats [89]. What causes rheumatoid arthritis (RA) is yet unexplained, but inflammatory mediators like TNF- α , IL-1 β , COX-2, and nitric oxide (NO) are in charge of the destruction of articular cartilage.

Last studies proved the potential of the combination of curcumin particles and glucose nanogold (20 µl per 1 ml medium) to lessen tumor hypoxia and enhance the radiosensitivity of breast cancer stem cells, which can provide a chance for the development of new highly active cells that have high efficiency and low toxicity of radiosensitizers [90]. Besides, there is a possibility of the use of AuNPs in alternative phytochemical delivery vehicles for the treatment of cancerous diseases to decrease the side effects of radiation and chemotherapy [91].

Molecules/structures on the outer cell layer can be labeled with Au nanoparticles connected to specific antibodies against these molecules/structures. In contrast to immunostaining, only particular antibody-conjugated Au nanoparticles are meant to track individual particles, so after attaching to the cell, the particle labels that are on the cell membrane can be diluted [92].

AuNPs present great biocompatibility and exhibit unique structural, electronic, magnetic, optical, and catalytic properties that have brought attention to this topic for the creation of biosensors, chemosensors, and electrocatalysts [93, 94]. Thus, NPs in general, and AuNPs, in particular, offer attractive properties in the role of DNA hybridization labels [95]

with interest in the emergence of sensitive electrochemical gene sensors.

AuNPs can greatly adsorb DNA due to their broad surface area and high surface free energy. The negative charges from citrate adsorption (used in most manufacturing processes) enhance the electrostatic adsorption between AuNPs and DNA strands. DNA can also be immobilized on AuNPs with special functional groups like thiols that can strongly interact with AuNPs [96].

The colorimetric use of AuNPs in detection can be a really promising analytical approach to the recognition and determination of biomolecules like enzymes, amino acids, peptides and proteins, nucleic acids, and inorganic ions. The key procedure is based on the interparticle lengths being shorter than the diameter of the average AuNPs, so the color turns from red to blue, which is clear to see with the naked eye. The label combined with the sensors usually is split into two strategies: red-shift and blue-shift of absorption, resulting in aggregation and disaggregation of AuNPs. To record the results, you can use a UV spectrophotometer [97].

Conclusions

Metal nanoparticles currently play a fundamental role in various fields of production and human activity. The question of their safe receipt and disposal after use is especially acute. Thanks to the latest research, metal nanoparticles are implemented even in the everyday life of people, and we encounter them more often than we imagine. Nanoparticles of zinc, titanium, silver, and gold are used in the fields such as medicine and biomedicine, virology and microbiology, optics, chemical industry,

cosmetic industry, agriculture, electronics, textile, rubber, pharmaceutical industry, and waste disposal. In the current realities, when the economic use of resources is reasonable, there should be economically profitable and «green» types of production of nanoparticles for the above industries. However, this wide spectrum of application of nanoparticles is not fully examined and requires further studies to use metal nanoparticles appropriately with the desired result and their further utilization.

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«Зелений» синтез металевих наночастинок.

Застосування і майбутні перспективи

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Наночастки металів наразі є одними з найбільш досліджуваних матеріалів в галузі науки і техніки. Ці метали мають розміри до ста нанометрів і відрізняються від звичайних металів своїми унікальними фізичними та хімічними властивостями.

Використання наночасток металів у біомедицині є одним із найперспективніших напрямів їх застосування. Так, наприклад, наночастки золота можна використовувати для діагностики та лікуванні раку. Наночастки золота можуть бути покриті різними молекулами, які можуть націлюватися на ракові клітини та взаємодіяти з ними, дозволяючи виявляти рак і діагностувати його. Наночастки срібла можна використовувати як антимікробні засоби, оскільки срібло має високу активність проти бактерій і грибків. Також наночастки срібла можна використовувати для лікування ран, оскільки вони сприяють швидкому загоєнню та запобігають інфекціям.

Металеві наночастки також використовуються в інших галузях промисловості. Так, з них можна виготовляти електроніку, покращувати властивості матеріалів, виготовляти каталізatori та багато іншого, що використовується як у побуті, так і у виробництві та вдосконаленні технологічних процесів. У цій статті обговорюється використання металевих наночасток срібла (AgNPs), цинку (ZnNPs), оксиду титану (TiO₂NPs) і золота (AuNPs) у біомедицині та інших галузях.

Ключові слова: «зелений» біосинтез, наночастинки, нанометали, мікроорганізми.

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