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METAL NANOPARTICLES AND PLANTS

NANOCZĄSTKI METALICZNE I ROŚLINY

Abstract: Metal nanoparticles (MNPs) belong mostly to the engineered type of nanoparticles and have not only unique physical and chemical properties but also different biological actions. In recent years, noble MNPs and their nano-sized agglomerates (collectively referred to as nanoparticles or particles in the subsequent sections) have been the subjects of much focused research due to their unique electronic, optical, mechanical, magnetic and chemical properties that can be significantly different from those of bulk materials. To enhance their use, it is important to understand the generation, transport, deposition, and interaction of such particles. Synthesis of MNPs is based on chemical or physical synthetic procedures and by use of biological material ("green synthesis" as an environmentally benign process) including bacteria, algae and vascular plants (mainly metallophytes). In biological methods for preparation of metal nanoparticles mainly leaf reductants occurring in leaf extracts are used. MNPs can be formed also directly in living plants by reduction of the metal ions absorbed as a soluble salt, indicating that plants are a suitable vehicle for production of MNPs. These methods used for preparation of MNPs are aimed to control their size and shape. Moreover, physicochemical properties of MNPs determine their interaction with living organisms. In general, inside the cells nanoparticles might directly provoke either alterations of membranes and other cell structures or activity of protective mechanisms. Indirect effects of MNPs depend on their physical and chemical properties and may include physical restraints, solubilization of toxic nanoparticle compounds or production of reactive oxygen species. Toxic impacts of MNPs on plants is connected with chemical toxicity based on their chemical composition (*eg* release of toxic metal ions) and with stress or stimuli caused by the surface, size and shape of these nanoparticles. Positive effects of MNPs were observed on the following plant features: seed germination, growth of plant seedlings, stimulation of oxygen evolution rate in chloroplasts, protection of chloroplasts from aging for long-time illumination, increase of the electron transfer and photophosphorylation, biomass accumulation, activity of Rubisco, increase of quantum yield of photosystem II, root elongation, increase of chlorophyll as well as nucleic acid level and increase in the shoot/root ratio. However, it should be stressed that MNPs impact on human and environmental health remains still unclear.

Keywords: environmental and human health, green synthesis, living organisms, metal nanoparticles, positive and negative impacts, vascular plants

Introduction

In the past decade, research efforts in nanoscience and nanotechnology have grown explosively worldwide. While we are just beginning to understand the functionalities that can be accessed through the use of nanostructured materials and surfaces, the tremendous

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potential of “nano” approaches to revolutionize the ways in which matter is fabricated, synthesized and processed is already apparent. Presently atoms, molecules, clusters and nanoparticles can be used as functional building blocks for fabricating advanced and totally new phases of condensed matter on the nanometre length scale. The optimal size of these unit components depends on the particular property to be engineered by altering the dimensions of the building blocks controlling their surface geometry, chemistry, assembly and thus it will be possible to tailor functionalities in unprecedented ways. At the start of the new millennium we are thus confronted with the need and desire to learn more about the atomic scale structure of matter (in detail see [1]).

Since the early 1990s, enormous efforts worldwide have led to the production of many types of nanomaterials. The interest in nanomaterials is a result of the extreme dependence of properties (electronic, magnetic, optical, mechanical, etc.) on particle size and shape in the 1-100 nm regime [2]. Nanoscale materials have received considerable attention because their structure and properties differ significantly from those of atoms and molecules as well as those of bulk materials [1]. Thus, nanotechnology (including metal/nanoparticles) is a major source of innovation with important economic consequences. However, the potential risk of applications and procedures of nanotechnology for health and the environment not only appeared but have raised on national and international levels. Past experience of sanitary, technological, and environmental risks has shown that it is not a good policy to attempt to deal with them after the fact. It is thus crucial to assess the risks as early on as possible [3]. So, new methodical approaches were seeked not only for nanotechnology in general, but especially for nanoparticles including the metal nanoparticles.

Characterization of metal/nanoparticles

In our recent paper [4] we characterized nanoparticles and specially metal nanoparticles in detail. Thus, nanoparticles (NPs) are atomic or molecular aggregates with dimension between 1 and 100 nm that can drastically modify their physico-chemical properties compared to the bulk material. NPs can be made from variety of bulk materials and they can act depending on chemical composition, shape or size of the particles. There are three types of NPs: natural, incidental and engineered. Metal nanoparticles **(**MNPs) belong mainly to the engineered type of NPs and have not only unique physical and chemical properties but also different biological actions. In recent years, noble metal nanoparticles and their nano-sized agglomerates (collectively referred to as nanoparticles or particles in the subsequent sections) have been the subjects of much focused research due to their unique electronic, optical, mechanical, magnetic and chemical properties that can be significantly different from those of bulk materials. To enhance their use, it is important to understand the generation, transport, deposition, and interaction of such particles [5].

As mentioned above, nanoparticles are atomic or molecular aggregates with specific physico-chemical properties compared with the bulk material. Currently, nanoparticles have drawn tremendous attention because of their valuable properties on optical, electronic, medical, sensor, and catalytic application. The synthesis and characterization of metal nanoparticles (MNPs) have emerged as an important branch of nanotechnology in the last decade, particularly for noble metals such are Au, Pd, Pt and Ag (in detail see [6]). Since the function and use of these materials depend on their composition and structure [7]

interest in MNPs currently focuses on control of their size and shape to manipulate their unique optoelectronic, magnetic, catalytic and mechanical properties [8].

Metal/nanoparticles formation

In the field of nanotechnology, the controlled synthesis of nanoparticle size, shape and monodispersity is essential in order to explore their unique chemical and physical properties. Currently, there are various chemical and physical synthetic methods aimed at controlling the size and distribution of NPs. However, most of them utilise toxic and expensive chemicals, and problems are often experiences with nanoparticle stability, agglomeration of particles and the inability to control crystal growth [9]. A practical route for synthesis of MNPs, as an one type of nanoparticles, is by chemical, physical and biological procedures. The utilisation of biological systems has emerged as a novel technology for synthesis of various nanoparticles in attempt to control NPs shape, composition, size and monodispersity [10].

One of the most important route for MNPs formation is above mentioned "green biosynthesis" using not only vascular plants (mainly leaf broth) but also algae, bacteria, yeasts, fungi and actinomycetes. In the field of nanotechnology (including metal/nanoparticles), the controlled synthesis of nanoparticle size, shape and monodispersity is essential in order to explore their unique chemical and physical properties. As it has already been mentioned, there are various chemical and physical methods aimed at controlling the size and distribution of nanoparticles. For example, physical synthetic methods such as inert gas condensation, severe plastic deformation, high-energy ball milling and ultrasonic shot peeling can be used to synthesize Fe(0) nanoparticles with diameters of 10-30 nm [11]. The chemical methods include microemulsion, chemical coprecipitation, chemical vapour condensation, pulse electrodeposition and chemical wet reduction [11]. In biological methods for preparation of metal nanoparticles mainly leaf reductants occurring in leaf extracts are used [12-14]. However, MNPs can be formed also directly in living plants by reduction of the metal ions absorbed as a soluble salt [15-18], indicating that plants are a suitable vehicle for production of MNPs [19].

Experimental methods applied for characterization of metal nanoparticles

For monitoring of formation and characterization of metal nanoparticles several experimental techniques are applied [20-22].

UV-Visible spectroscopy (**UV-VIS**) is a technique used to quantify the light that is absorbed or scattered by a sample. Gold and silver plasmonic nanoparticles have optical properties that are sensitive to size, shape, concentration, agglomeration state, and refractive index near the nanoparticle surface, which makes UV-VIS spectroscopy a valuable tool for identifying, characterizing, and studying nanomaterials. UV-VIS spectrum, known as the surface plasmon absorption band, of the individual nanoparticles differs from that of nanoparticles aggregate and the *surface plasmon resonance* (SPR) of a multi-nanoparticle aggregate will be red-shifted to a longer wavelength compared with SPR of the individual particles. Consequently, aggregation is observable as an intensity increase in the

red/infrared region of the spectrum. Reduction of the metal ions (Ag^+, Au^+, Pd^{2+}) to metal nanoparticles during exposure to the plant leaf extracts was followed by colour change and thus UV-VIS spectrum [23-25].

In **Fourier Transform Infrared Spectroscopy (FTIR)**, a spectrum showing molecular vibrations is obtained, in order to identify or characterize mainly organic materials. From such spectra information about the chemical bonds and molecular structure of a material can be obtained and their comparison with catalogued FTIR spectra enable to identify the material, *eg* the biomolecules responsible for the reduction of metal ions and capping of the bioreduced metal nanoparticles synthesized by using plant extract [26, 27].

Transmission Electron Microscopy (TEM) and **Scanning Transmission Electron Microscopy (STEM)** are closely related techniques that use an electron beam to image a sample and they can also be used to characterize crystallographic phase and crystallographic orientation (by diffraction mode experiments). A scanning tunnelling microscope (STM) is an instrument for imaging surfaces at the atomic level. For an STM, good resolution is considered to be 0.1 nm lateral resolution and 0.01 nm depth resolution [28, 29].

The imaging of the crystallographic structure of a sample at an atomic scale is possible by the use of **High Resolution Transmission Electron Microscopy (HRTEM)**. HRTEM is a valuable tool to study nanoscale properties of crystalline material such as semiconductors and metals [30, 31].

Atomic Force Microscopy (AFM) provides images with atomic or near-atomic-resolution surface topography, capable of quantifying surface roughness of samples down to the angstrom-scale. In addition to presenting a surface image, AFM can also provide quantitative measurements of feature sizes, such as step heights and other dimensions [32, 33].

X-Ray Diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. Where a mixture of different phases is present, the resultant diffractogram is formed by addition of the individual patterns [34, 35].

Energy-Dispersive X-Ray Spectroscopy (EDS or EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on the investigation of an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum [36, 37].

X-Ray Absorption Near Edge Structure (XANES) and **Extended X-ray Absorption Fine Structure (EXAFS)** have been used as powerful tools for studying the structures and dynamics of the nanoscale materials. XANES measures the modulation of the absorption coefficient at a particular core level of an atom in a chemical environment and it has been successfully applied to investigate the chemical bonding, electronic structure and surface chemistry. On the other hand, EXAFS has been used extensively in the investigation of local atomic structures such as the number and type of neighbouring atoms, interatomic distances, and disorder and it is well suited for determining the local structures of both non-crystalline and crystalline materials [38-40].

X-ray photoelectron spectroscopy (XPS) uses soft X-rays (with a photon energy of 200-2000 eV) to examine core-levels [41-43].

Toxicity of metal nanoparticles to plants

The physico-chemical properties of nanoparticles (including metal nanoparticles, MNPs) determine their interaction with living organisms. Cells of plants, algae, and fungi possess cell walls that constitute a primary site for interaction and a barrier for the entrance of NPs. Mechanisms allowing NPs to pass through cell walls and membranes are as yet poorly understood. However, inside cells, NPs might directly provoke alterations of membranes and other cell structures and molecules, as well as protective mechanisms. Indirect effects of NPs depend on their chemical and physical properties and may include physical restraints (clogging effects), solubilization of toxic NP compounds, or production of reactive oxygen species [44].

Algae

Toxicity of nano-sized metal oxide particles to algae compared with that of larger-sized bulk particles was found to be higher when dose is expressed as mass and EC_{50} values are generally in the mg/dm^3 range [45, 46]. Growth inhibition test with the green alga *Desmodesmus subspicatus* treated with two different photocatalytic active TiO_2 NPs showed that application of MNPs with particle size of 25 nm (crystalline form: mainly anatase) resulted in inhibition of algal growth with EC_{50} 44 mg/dm^3. It was proven that the toxicity was not caused by accompanying contaminants, since toxicity did not significantly decrease after washing the product. No difference in growth reduction was observed for the tests, regardless of whether preliminary illumination took place or not, indicating that the measured toxic effect was caused by the TiO_2 itself and not by a photocatalytic effect. On the other hand, due to addition of MNPs with particle size of 100 nm (crystalline form: 100% anatase) up to 50 mg/dm^3 no toxic effects were determined and cleaning did not result in a decreased toxicity [47]. Acute algal growth toxicity test of TiO_2 NPs (crystallite size 4.5 nm) and Ag doped TiO_2 NPs (crystallite size 4.6 nm) with *D. subspicatus* showed that after 72 hours of exposure the EC_{50} value was higher for undoped TiO_2 (7.59 mg/ dm^3) than for Ag doped TiO_2 nanoparticles (4.12 mg/dm^3), indicating higher toxic effect for Ag doped nanoparticles [48].

Experiments concerning growth inhibition of *Pseudokirchneriella subcapitata* alga by nanoparticulate and micron size CeO_2 revealed IC_{50} values for reduction in algal growth rate after 72 h (IC_{50}) as 10.3 and 66 mg/dm^3 for the nanoparticles and bulk materials, respectively. The light illumination conditions stimulated photocatalytic activity of CeO_2 nanoparticles, causing the generation of hydroxyl radicals and peroxidation of a model plant fatty acid what resulted in cell-particle interaction causing membrane damage [45]. Also silica (SiO_2) nanoparticles with 12.5 and 27.0 nm diameter were found to inhibit growth rate of *P. subcapitata* and it was found that the particles clearly adhered to the outer cell surface and no evidence was found for particle uptake. The toxicity was attributable to the solid nanospheres, because no aggregation was observed and dissolution of the nanoparticles was negligible [49].

The examination of short-term toxicity of AgNP**s** and ionic silver (Ag^+) to photosynthesis in *Chlamydomonas reinhardtii* revealed that based on total Ag

concentration, toxicity was 18 times higher for $AgNO_3$ than for AgNPs (in terms of EC_{50}). However, when compared as a function of the Ag^+ concentration, toxicity of AgNPs appeared to be much higher than that of $AgNO_3$. The results indicated that the interaction of these particles with algae influences the toxicity of AgNPs, which is mediated by Ag^+ and that particles contributed to the toxicity as a source of Ag^+ which is formed in presence of algae [44]. Miao et al [50] demonstrated that silver engineered nanoparticles can be taken in and accumulated inside the algal cells of mixotrophic freshwater alga *Ochromonas danica*, where they exerted toxic effects. This indicates that nanoparticle internalization may be an alternative pathway through which algal growth can be influenced. Exposure of *Chlorella vulgaris* and *Dunaliella tertiolecta* to 50 nm AgNPs (0-10 mg/dm^3) for 24 h resulted in strong decrease in chlorophyll content, viable algal cells, increased ROS formation and lipids peroxidation [51].

Nanoparticulate Al_2O_3, SiO_2, and TiO_2 (DJ3, rutile) had no significant toxicity, nano-ZnO and nano-TiO_2 (HR3, anatase) greatly inhibited the growth of *C. vulgaris* with 6 d EC_{30} of about 20 and 30 mg/dm^3, respectively [52]. While at the concentration lower than 50 mg/dm^3 the algal toxicities decreased in the following order: Zn^{2+} > nano-ZnO > bulk-ZnO, at concentrations > 50 mg/dm^3 nano-ZnO had higher algal toxicity than Zn^{2+} ions and released less Zn^{2+} ions into the culture media than bulk-ZnO. This suggests that dissolved Zn^{2+} ions from nano-ZnO were not the dominant mechanism for the algal growth inhibition. The comparison of the nanotoxicities in the presence and absence of illumination excluded shading effects of nano-ZnO and nano-TiO_2 (HR3) from the main mechanism of the nanotoxicity. However, observed large aggregates of nano-ZnO and nano-TiO_2 (HR3) entrapping and wrapping the algal cells may contribute to the nanotoxicity. The growth inhibitory effect of alumina nanoparticles was observed for both *Chlorella* sp. and *Scenedesmus* sp. (72 h EC_{50} values were 45.4 and 39.35 mg/dm^3, respectively). Bulk alumina was toxic to a lesser extent (72 h EC_{50} value, 110.2 mg/dm^3 for *Chlorella* sp.; 100.4 mg/dm^3 for *Scenedesmus* sp.). Moreover, a clear decrease in chlorophyll content was observed in the treated cells compared with the untreated ones, more effect being notable in the case of nanoparticles [53].

Response of vascular (higher) plants to MNPs

Toxic effects of metal nanoparticles on plants could be connected with chemical toxicity based on the chemical composition (*eg* release of toxic metal ions) and with stress or stimuli caused by the surface, size and/or shape of the particle [54]. It is well known that at nanosize range, the properties of materials differ substantially from bulk materials of the same composition, mostly due to the increased specific surface area and reactivity, which may lead to increased bioavailability and toxicity [55]. Moreover, toxicity of metal NPs may involve production of hydroxyl radicals due to visible light generating extracellular reactive oxygen species (ROS) that may damage cell membranes resulting in the change of the membrane permeability and consequently, the probability of entry of NPs into the cell increases [56]. On the other hand, several studies confirmed also positive effects of metal and metal oxide nanoparticles on growth of higher plants.

Negative effects of MNPs on plants

According to Navarro et al [44] NPs may induce the formation of new and large-size pores and routes for the internalization of large NPs through cell walls. The investigation of cytotoxic and genotoxic impacts of AgNPs (below 100 nm size) using root tip cells of *Allium cepa* as an indicator organism showed that with increasing concentration of the NPs (25, 50, 75, and 100 ppm, respectively) decrease in the mitotic index from 60.30% (control) to 27.62% (100 ppm Ag NPs) was noticed. The AgNPs impaired stages of cell division causing chromatin bridge, stickiness, disturbed metaphase, multiple chromosomal breaks and cell disintegration [57]. It was reported by Mushtaq [58] that Fe_3O_4, TiO_2, and carbon NPs caused negative effect to seed germination rate, root elongation, and germination index of cucumber plants.

Lee et al [59] investigated the effects of four metal oxide nanoparticles (nano-Al_2O_3, nano-SiO_2, nano-Fe_3O_4 and nano-ZnO) applied at three different concentrations (400, 2000, and 4000 mg/dm^3) on seed germination, root elongation, and number of leaves of *Arabidopsis thaliana* and found that the phytotoxicty of nanoparticles decreased in the following order: nano-ZnO > nano-Fe_3O_4 > nano-SiO_2 > nano-Al_2O_3, which was not toxic. Inhibition of seed germination by ZnO depended on particle size, with nanoparticles exerting higher toxicity than larger (micron-sized) particles at equivalent concentrations. Significant inhibition observed by the smaller, monodisperse nano-ZnO particles (44.4 nm) could be connected with the fact that intracellular spaces (< 10 mm) in seed coat parenchyma may be filled with aqueous media facilitating the transport of soluble nutrients as well as small particles to the embryo. Because complete (100%) inhibition of seed germination was obtained only with application of 500 mg/dm^3 of soluble Zn, *ie* at concentration, which was one order of magnitude higher than the amount released by toxic levels of nano-ZnO, phytotoxicity of nano-scale metal oxides cannot be explained solely by the dissolved metal species, and that the particles themselves also contribute to phytotoxicity.

The 50% inhibition of growth of duckweeds, *Landoltia punctata*, treated with CuO-NPs and comparable doses of soluble Cu was observed at 0.6 mg/dm^3 soluble copper or 1.0 mg/dm^3 CuO-NPs that released only 0.16 mg/dm^3 soluble Cu into growth medium [60]. Application of 1.0 mg/dm^3 CuO-NP resulted in significant decrease of chlorophyll in plants, while treatment with comparable 0.2 mg/dm^3 soluble Cu did not affect the level of this assimilation pigment. This could be connected with the fact that the Cu content of fronds exposed to CuO-NPs was four times higher than in fronds exposed to an equivalent dose of soluble copper. The 2-d median effective concentrations for *Phaseolus radiatus* and *Triticum aestivum* exposed to Cu nanoparticles was found to be 335 and 570 mg/dm^3, respectively, indicating higher sensitivity of *Phaseolus radiatus* to Cu nanoparticles. Cupric ions released from Cu nanoparticles had negligible effects and the apparent toxicity clearly resulted from Cu nanoparticles. Bioaccumulation increased with increasing concentration of Cu nanoparticles, and agglomeration of particles was observed in the cells using transmission-electron microscopy-energy-dispersive spectroscopy [61].

Transformation of copper into metallic nanoparticles in and near roots with evidence of assistance by endomycorrhizal fungi when common wetlands plants *Phragmites australis* and *Iris pseudoacorus* were grown in contaminated soil in the natural environment was reported by Manceau et al [62]. The researchers stated that this mode of copper

biomineralization by plant roots under copper stress may be common in oxygenated environments because the transformation occurs likely due to biomolecular responses to oxidative stress, similar to reactions used to abiotically synthesize Cu^0 nanostructures of controlled size and shape.

Nekrasova et al [63] observed that in *Elodea densa* Planch plants treated with copper ions and Cu nanoparticles enhanced lipid peroxidation (to 120 and 180% of the control level, respectively) was induced. While the nanoparticles were more actively accumulated by plants, catalase and superoxide dismutase activities in plants treated with nanoparticles increased by a factor of 1.5-2.0 and photosynthesis was suppressed at a concentration of 1.0 mg/dm^3. On the other hand, Cu ions reduced photosynthesis already at a concentration of 0.5 mg/dm^3. Atha et al [64] reported for the first time that copper oxide nanoparticles induce DNA damage in agricultural and grassland plants. Significant accumulation of oxidatively modified, mutagenic DNA lesions (7,8-dihydro-8-oxoguanine; 2,6-diamino-4-hydroxy-5-formamidopyrimidine; 4,6-diamino-5-formamidopyrimidine) and strong plant growth inhibition were observed for radish (*Raphanus sativus*), perennial ryegrass (*Lolium perenne*), and annual ryegrass (*Lolium rigidum*) under controlled laboratory conditions. Exposure of hydroponically cultivated *Cucumis sativus* seedlings to Cu^{2+} and Zn^{2+} as well as to four kind of nanoparticles (size of 50 nm) resulted in plant biomass reduction and the corresponding IC_{50} values were as follows: 333 mg/dm^3 (Cu NPs), 376 mg/dm^3 (CuO NPs), 14 mg/dm^3 (Cu^{2+}), 1700 mg/dm^3 (Zn NPs), 629 mg/dm^3 (ZnO NPs), and 262 mg/dm^3 (Zn^{2+}), respectively [65]. All nanoparticles more greatly aggregated in the nutrient solutions than in the deionized water and the size of the aggregated Zn and ZnO NPs was found to be 500 nm. Treatment with both NPs increased the Cu and Zn concentrations in *C. sativus* tissues and it seems that NPs crossed the cell membrane and formed agglomerates, either with themselves or with other cellular materials within the cells. Due to the presence of NPs or NP aggregates within the cell toxic effects of NPs occur. Zn accumulation in *C. sativus* following ZnO NP treatments was higher than those of other NP treatments indicating highly defense mechanism of this plant to ZnO NP treatments. Increased metal uptake by plants is probably connected with the ability of root exudates to change the properties and behavior of ZnO nanoparticles in solution. Increased antioxidant enzyme (SOD, CAT, and POD) activities in plant root tissues exposed to CuO and ZnO NPs were observed, as well.

Ghodake et al [66] investigated the phytotoxicity of cobalt and zinc oxide NPs using the roots of hydroponically cultivated *Allium cepa* (onion bulbs) as an indicator organism. With increasing concentrations of the NPs (from 5 to 20 μg/cm^3) the elongation of the roots was severely inhibited by both the cobalt and the zinc oxide NPs with respect to control plants. Cobalt oxide NPs were found to be of spherical, truncated, and uneven nature with an average size of approximately 60-10 nm, while most of zinc oxide NPs was rod shaped, spherical, or hexagonal with sizes ranging between approximately 50 and 100 nm, and the particles were found to be clustered. During the exposure of the *A. cepa* roots to both metal oxide NPs these aggregated and precipitated, probably due to the interaction of the oxide NPs with unknown extracellular biomolecules. The phytotoxicity of cobalt oxide NPs was connected with their massive adsorption into the root system, while zinc oxide NPs caused damage because of their severe accumulation in both the cellular and the chromosomal modules. It could be supposed that the cobalt oxide NPs could block the water channels

through adsorption and the zinc oxide NPs possibly penetrate radically into onion roots and spoil the whole cellular metabolism and stages of cell division.

Recently, action of nanoparticles of unusual metals, such are ytterbium (Yb) or lanthanum (La), were investigated. For example, Zhang et al [67] studied the phytotoxicity of nanoparticulate Yb_2O_3, bulk Yb_2O_3, and $YbCl_3 \cdot 6H_2O$ to cucumber plants and found that the decrease of biomass was evident at the lowest concentration (0.32 mg/dm^3) when exposed to nano-Yb_2O_3, while at the highest concentration, the most severe inhibition was from $YbCl_3$. The inhibition was dependent on the actual amount of toxic Yb uptake by the cucumber plants and in the intercellular regions of the roots, Yb_2O_3 particles and $YbCl_3$ were all transformed to $YbPO_4$. Similar results were obtained in assessing of the phytotoxicity of lanthanum oxide (La_2O_3) NPs to cucumber plant in which $LaCl_3$ was also studied as a reference toxicant [68]. La_2O_3 NPs and $LaCl_3$ were both transformed to needle-like $LaPO_4$ nanoclusters in the intercellular regions of the cucumber roots. Because *in vitro* experiments demonstrated that the dissolution of La_2O_3 NPs was significantly enhanced by acetic acid, the researchers proposed that the dissolution of NPs at the root surface induced by the organic acids extruded from root cells played an important role in the phytotoxicity of La_2O_3 NPs.

Positive effects of MNPs on plants

Positive effects on germination of aged spinach seeds and on the growth of seedlings were obtained if the seeds were soaked in high-strength TiO_2-nanoparticles-solution (0.25 to 4‰) and the best results provided application of 2500 mg/dm^3 nano-TiO_2 The TiO_2 NPs were found to promote growth of spinach and accelerate nitrogen assimilation [69]. Addition of 0.25% nano-TiO_2 (rutile) stimulated oxygen evolution rate in spinach chloroplasts, improved chloroplast coupling and enhanced activities of Mg^{2+}-ATPase and chloroplast coupling factor I CF_1-ATPase on the thylakoid membranes [70] and nano-TiO_2 (rutile) protected chloroplasts from aging for long-time illumination [71]. Great increase of the electron transfer, oxygen evolution, and photophosphorylation was observed also in chloroplasts from nanoanatase-TiO_2-treated spinach under visible light and ultraviolet light illumination [72]. Biomass accumulation of spinach (*Spinacia oleracea*) by TiO_2 NPs (by 60%) was also observed by Gao et al [73]. The activity of Rubisco in the nano-anatase-treated spinach was significantly higher than the control, by up to 2.33 times, and bulk TiO_2 treatment had no such significant effects. Together, one of the molecular mechanisms of carbon reaction promoted by nano-anatase is that the nano-anatase treatment results in the enhancement of Rubisco mRNA amounts, the protein levels, and activity of Rubisco, thereby leading to the improvement of Rubisco carboxylation and the high rate of photosynthetic carbon reaction [74].

Substantial increase of *L. minor* biomass accumulation accompanied with increased root length and number of fronds per colony as well as by increased photosynthetic efficiency, was observed due to alumina NPs (average nominal size of 20 nm) application. This enhancement of biomass accumulation was associated with increased efficiencies in the light reactions of photosynthesis [75]. Alumina nanoparticles increased the quantum yield of photosystem II, but not the maximal quantum yield of photosystem II (Fv/Fm), perhaps suggesting that the alumina nanoparticle effect is not directly on PS II. Also aluminium nanoparticles were found to enhance root elongation growth of radish and rape

(76]. According to Lee et al [59] who observed positive influence of nano-Al_2O_3 (applied at 400, 2000, and 4000 mg/dm^3) on root elongation of *Arabidopsis thaliana,* enhanced root elongation could be connected with the fact that inert nano-Al_2O_3 could serve similar functions as nano-sized perlite, which enhances gas transfer, prevents water loss, and hinders soil compaction. On the other hand, the presence of nanoscale aluminum (Al) particles did not have a negative effect on the growth of *Phaseolus vulgaris* and *Lolium perenne* in the tested concentration range, but while *P. vulgaris* did not show uptake of aluminum, for rye grass a 2.5-fold increase in Al concentration in the leaves was observed as compared with control tests [77].

Sheykhbaglou et al [78] tested the effects of nano-iron oxide particles applied in the form of spray on agronomic traits of soybean in field experiments and found that nano-iron oxide at the concentration of 0.75 g/dm^3 increased leaf + pod dry weight and pod dry weight. Application of 0.5 g/dm^3 nano-iron oxide particles resulted in the highest grain yield showing 48% increase in comparison with control. Nano-iron oxide was also found to facilitate the photosynthate and iron transferring to the leaves of peanut [79]. Analysis of the influence of magnetic nanoparticles coated with tetramethylammonium hydroxide on the growth of *Zea mays* plant in early ontogenetic stages showed that application of small ferrofluid concentrations (10-50 mm^3/dm^3) induced plant length stimulation, the increase of chlorophyll *a* **(**up to 13%) as well that the nucleic acid level (up to 10%) in maize plantlets during their first days of life, while higher ferrofluid concentration (100-250 mm^3/dm^3) led to marked drop in chlorophyll *a* level and the ratio chlorophyll *a*/chlorophyll *b* (about 35% decreasing in both cases) [80]. Even though water based ferrofluid addition in culture medium represents a source of iron, it could be supposed that ferrophase nanoparticles may have also a magnetic influence on the enzymatic structures implied in the different stages of the photosynthesis reactions. Treatment of *Zea mays* plantlets with an aqueous dispersion of water based magnetic fluid constituted by coating the small magnetic nanoparticles with perchloric acid resulted in slight inhibition of plant growth and on the leaf surface of plants treated with an enhanced volume fraction of aqueous magnetic fluid solution brown spots occurred [81]. It could be supposed that the iron oxides provided by the magnetite from magnetic fluid ferrophase could interfere with the complex redox reactions involved in the photosynthesis phenomenon. According to Gonzalez-Melendi et al [82], the biocompatible magnetic fluids can be uptaken into whole living plants and further can move inside using the vascular system being concentrated in specific areas by application of magnetic gradients. In an another experiment maize plants grown from the seeds germinated in the magnetic fluid presence and then exposed to electromagnetic field during the germination process (LM-EMF samples) as well as plants grown from the seeds germinated in the magnetic fluid presence but in the lack of electromagnetic exposure (LM samples) were tested for the content of assimilatory pigments and nucleic acids [83]. Because for the LM-EMF samples a decrease of pigment contents was observed, the researchers assumed that the electromagnetic field exposure moment could produce a process like that of hyperthermia, a local heating occurring due to the electromagnetic field energy absorbed by the magnetic nanoparticles internalized in vegetal tissue and this local heating of the vegetal tissue could affect the redox reactions implicated in the photosynthesis process. A twice higher level of nucleic acids in the LM-EMF experimental samples than in the control samples is probably connected with regeneration reactions of the plant metabolism processes against the putative local heating of the vegetal tissue produced by the

electromagnetic field energy absorbed by the magnetic nanoparticles internalized in vegetal tissue.

Application of MNPs such are silica, palladium, gold and copper nanoparticles significantly influenced the growth of lettuce plants after 15 days of incubation which was reflected in an increase in the shoot/root ratio (compared to that of the control) [84].

Conclusion

It was stated that nanoparticles have drawn tremendous attention because of their valuable properties on optical, electronic, medical, sensor, and catalytic application. The synthesis and characterization of MNPs have emerged as an important branch of nanotechnology in the last decade, particularly for noble metals such are Au, Pd, Pt and Ag. Function and use of these materials depend on their composition and structure and thus interest in MNPs currently focuses on control of their size and shape to manipulate their unique optoelectronic, magnetic, catalytic and mechanical properties. There were found various chemical and physical synthetic methods aimed at controlling the size and distribution of MNPs. Recently, utilisation of biological systems (including bacteria, algae and vascular plants) has also emerged as a novel technology for synthesis of various nanoparticles in attempt to control MNPs shape, composition, size and monodispersity. It was found that physico-chemical properties of MNPs determine their interaction with living organisms. Cells of plants, algae, and fungi possess cell walls that constitute a primary site for interaction and a barrier for the entrance of MNPs into the cells. However, mechanisms allowing MNPs to pass through cell walls and membranes are still poorly understood. Similarly, impact of MNPs on environmental and human health remains still unclear.

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NANOCZĄSTKI METALICZNE I ROŚLINY

Abstrakt: Ze względu na unikalne właściwości fizyczne i chemiczne, ale także różne działanie biologiczne nanocząstek metali (MNPS) są obiektem zainteresowania nowo powstałej inżynierii tych materiałów. W ostatnich latach MNPS metali szlachetnych (zbiorowo określane w dalszej części tekstu jako nanocząstki lub cząstki) były poddawane wielu badaniom ze względu na ich unikalne właściwości elektroniczne, optyczne, mechaniczne, magnetyczne i chemiczne, które mogą być znacząco różne od właściwości materiałów litych. Synteza MNPS polega na procesach chemicznych lub fizycznych oraz na wykorzystaniu materiału biologicznego („zielona synteza" - proces przyjazny środowisku), w tym bakterii, glonów i roślin naczyniowych (głównie metalofitów). W biologicznych metodach wytwarzania nanocząstek metali używane są głównie substancje redukujące, występujące w ekstraktach z liści. MNPS również mogą być utworzone bezpośrednio w żywych roślinach przez redukcję jonów metali absorbowanych w postaci rozpuszczalnych soli, co wskazuje, że rośliny są odpowiednim środkiem produkcji MNPS. Metody te pozwalają na kontrolę rozmiarów i kształtu cząstek. Jest to ważne, ponieważ właściwości fizykochemiczne MNPS określają ich oddziaływanie z żywymi organizmami. Zwykle w komórkach nanocząstki mogą bezpośrednio wywoływać zmiany w błonach komórkowych albo w innych strukturach oraz mogą wpływać na aktywność komórek lub na ich mechanizmy ochronne. Pośrednio skutki działania MNPS zależą od ich właściwości fizycznych i chemicznych. Skutki te mogą obejmować ograniczenia fizyczne, rozpuszczanie toksycznych MNPS lub wytwarzanie reaktywnych form tlenu. Toksyczny wpływ MNPS na rośliny jest związany z toksycznością chemiczną, uzależnioną od składu chemicznego (np. uwalnianie toksycznych jonów metali) oraz ze stymulacją lub napięciami wywołanymi przez kontakt z powierzchnią. Istotne są także rozmiary i kształt nanocząstek. Pozytywne wpływy MNPS obserwowano na: kiełkowanie nasion, wzrost siewek roślin, stymulację tempa przemiany tlenu w chloroplastach, ochronę przed starzeniem chloroplastów wywołanym przez długotrwałe oświetlanie, zwiększenie transferu elektronów i fotofosforylacji, gromadzenie biomasy, aktywność RuBisCO, wzrost wydajności kwantowej fotosystemu II, wzrost korzeni, wzrost chlorofilu, jak również poziomu kwasów nukleinowych i stosunku długości pędów i korzeni. Jednak należy podkreślić, że wpływ MNPS na zdrowie ludzi i na środowisko jest nadal niejasny.

Słowa kluczowe: środowisko i zdrowie ludzi, zielone syntezy, organizmy żywe, nanocząstki metali, wpływ pozytywny i negatywny, rośliny naczyniowe