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OCCURRENCE, CHARACTERIZATION AND ACTION OF METAL NANOPARTICLES

WYSTĘPOWANIE, CHARAKTERYSTYKA I DZIAŁANIE NANOCZĄSTEK METALI

Abstract: Metal nanoparticles (MNPs) are attracting attention for many technological applications as catalysts, in optical materials, medical treatments, sensors, and in energy storage and transmission. The function and use of these materials depend on their composition and structure. A practical route for synthesis of MNPs is by chemical procedure and by use of biological material ("green synthesis" as a dependable, environmentally benign process) including bacteria, algae and vascular plants (mainly metallophytes). Currently, there are various chemical and physical synthetic methods used for preparation of metal nanoparticles and several experimental techniques aimed at controlling the size and shape of MNPs. Toxic effects of MNPs on plants could be 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 the particle. The physicochemical properties of nanoparticles determine their interaction with living organisms. In general, plant cells possess cell walls that constitute a primary site for interaction and a barrier for the entrance of nanoparticles. Inside cells, nanoparticles might directly provoke either alterations of membranes and other cell structures or activity of protective mechanisms. Indirect effects of MNP depend on their chemical and physical properties and may include physical restraints, solubilization of toxic nanoparticle compounds, or production of reactive oxygen species. However, it should be stressed that impact of MNPs on human and environmental health remains still unclear. Thus, evaluation scheme for national nanotechnology policies (that would be used to review the whole national nanotechnology plan) was recommended. The three following criteria for policy evaluation were suggested: appropriateness, efficiency and effectiveness.

Keywords: behaviour, direct and indirect effects, green synthesis, living organisms, metal nanoparticles, plants

Introduction

During the past two decades the nanotechnology field (including nanoparticles) has attracted overwhelming interest not only the scientific community but from business and political representatives, too. Such great attention is connected at least with three reasons. First of all, the nanotechnology achievements and their realization lead to the radical changes in all fields of human activity such as traditional and advanced technique, electronics and information technology, power and chemical engineering, agriculture and environment, medicine and biotechnology, human health and security, defence and transport, etc. Secondly, it is turned out that nanotechnologies really had created many interdisciplinary research directions, where now many specialists of the wide diversity are concentrated. At present, nanotechnology is associated not only with traditional natural sciences (such are physics, chemistry, biology, materials science) but also with lot of technologies and many social and economic sciences. Third reason it is, that this topic has revealed many gaps in fundamental natural-science knowledge, in technology as well as in social sciences (in detail see [1]).

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In general, *nanoparticles* (NPs) - as the main component of nanotechnology - are atomic or molecular aggregates with dimension between 1 and 100 nm that can drastically modify their physico-chemical properties compared with the bulk material. NPs can be made from variety of bulk materials and they can act depending on chemical composition, size or shape of the particles. There were identified three types of NPs: natural, incidental and engineered. The first one has existed from the beginning of the earth´ history and still occurs in the environment (*eg* volcanic or lunar dust, mineral composites). Incidental (waste or anthropogenic) NPs are results of industrial processes (*eg* diesel exhaust, coal combustion, welding fumes) [2]. The last type of NPs can be divided into the following four groups: (1) carbon based materials - single or multiwalled carbon nanotubes; (2) metal based materials - quantum dots, nanogold, nanozinc, nanoaluminium, TiO_2, ZnO and Al_2O_3; (3) nano-sized polymers built from branched units with specific chemical functions; (4) composites nanoparticles which combine nanoparticles with other nanoparticles or with larger bulk-type materials [3]. There is now an extensive discussion about the risks of the anthropogenic or engineered NPs into environment, plants as well as human health. The authors [4] summarized information concerning the current status, knowledge gaps, challenges and future needs of NPs ecotoxicology. These authors concluded that NPs can be toxic to bacteria, algae, invertebrates and fish species, as well as to mammals.

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 extreme dependence of properties, mainly electronic, magnetic, optical, and mechanical. In the field of nanotechnology, the controlled synthesis of NPs size, shape and monodisperdity is essential in order to explore their unique chemical and physical properties. Currently, there are various chemical and physical synthetic methods used for preparation of nanoparticles and several experimental techniques aimed at controlling the size and shape of NPs. However, most of these methods utilise toxic and expensive chemicals, and problems are often experienced with NPs stability, agglomeration of particles and the inability to control crystal growth [5]. *Metal nanoparticles* (MNPs) are attracting attention for many technological applications as catalysts, in optical materials, medical treatments, sensors, and in energy storage and transmission. Thus, this type of nanoparticles is topic of our contribution.

Characterization of metal nanoparticles

In general, nanoparticles (10^{-9} m to be precise) 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 applications. The synthesis and characterization of metal nanoparticles have emerged as an important branch of nanotechnology in the last decade, particularly for nobel metals such are Au, Pd, Pt and Ag (in detail see [6]). 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]. A practical route for synthesis of MNPs is by chemical, physical and biological procedures including bacteria, algae and vascular plants. In recent years, the utilisation of biological systems has emerged as a novel technology for synthesis of various nanoparticles in as attempt to control NPs shape, composition, size and monodispersity [9]. While many studies have looked at metal uptake by plants, particularly with regard to phytoremediation and hyperaccumulation, and a few have distinguished between elemental metal deposition (M^0) and metal salt accumulation (M^+), quantification of the proportion of the salts converted to metal nanoparticles has only rarely been addressed [10].

Metal nanoparticle formation and determination

Nanoparticles can be made from variety of bulk materials and they can act depending on chemical composition, size or shape of the particles. Metal nanoparticles are specific type of NPs with unique physical and chemical properties and with different biological effects. One of the most important route for MNPs formation is “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. Most of these methods, however, utilize toxic and expensive chemicals, and problems are often experiences with nanoparticle stability, agglomeration of particles and the inability to control crystal growth [5]. For example, physical synthetic methods such as inert gas condensation, severe plastic deformation, high-energy ball milling and ultrasonic shot peening 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]. On the other hand, in biological methods for preparation of metal nanoparticles mainly leaf reductants occurring in leaf extracts are used (*eg* [12-14]). However, MNPs can be formed also directly in living plants by reduction of the metal ions absorbed as a soluble salt (*eg* [15-18]), indicating that plants are a suitable vehicle for production of MNPs ([19]).

For monitoring of formation and characterization of metal nanoparticles several experimental techniques are applied, such as *UV-Visible spectroscopy* (UV-Vis), *Fourier transform infrared spectroscopy* (FTIR), *transmission electron microscopy* (TEM), *high-resolution transmission electron microscopy* (HRTEM) and *scanning transmission electron microscopy* (STEM), *atomic force microscopy* (AFM), *X-ray diffraction* (XRD), *X-ray absorption near edge structure* (XANES) and *extended X-ray absorption fine structure* (EXAFS) and as well as *X-ray photoelectron spectroscopy* (XPS) (*cf* [20-22]).

Action of metal nanoparticles to living organisms

The toxicity of nanoparticles observed in living organisms can be intrinsic (direct - due to the nanoparticle alone) or indirect (nanoparticle as potential carrier) owing to their proven adsorption potential, which means that there may be pollutants at their surface or within their structure whose toxic potential may be induced, repressed, or limited. Indeed, when they come into contact with the environment, the nanoparticles will be in permanent interaction with the other components of the medium, and in particular, the contaminants.

In some cases, the nanoparticles may play role of collector, *eg* adsorption, for certain molecules, or a masking role wherein they immobilise a non-negligable fraction of the compounds that are potentially reactive for living matter (in detail see [23]).

Papers concerning plant-nanoparticle interactions showed that plants (both vascular and non-vascular) strongly interact with their atmospheric and terrestrial environments and are expected to be affected as a results of their exposure to nanoparticles, including the MNPs. Studies on the toxicity of nanomaterials are still emerging and basically evidence several negative effects on growth and development of plantlets [2]. Toxic effects of MNPs 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 shape of the particle. The physico-chemical properties of nanoparticles determine their interaction with living organisms. In general, plant cells possess cell walls that constitute a primary site for interaction and a barrier for the entrance of nanoparticles. Inside 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 chemical and physical properties and may include physical restraints, solubilization of toxic nanoparticle compounds, or production of reactive oxygen species. However, it should be stressed that potential risks for health and environment have raised questions on national, European 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 as possible [24] and thus to avoid serious negative impact of MNPs to environment.

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WYSTĘPOWANIE, CHARAKTERYSTYKA I DZIAŁANIE NANOCZĄSTEK METALI

Abstrakt: Nanocząstki metali (MNPS) przyciągają uwagę ze względu na ich wykorzystanie w wielu zastosowaniach jako katalizatory, materiały optyczne, czujniki, w zabiegach medycznych, w przechowywaniu i transmisji energii. Funkcja i zastosowanie tych materiałów zależą od ich składu i struktury. Praktycznymi drogami syntezy MNPS są metody chemiczne i wykorzystanie materiałów biologicznych („zielona synteza" niezawodna, przyjazna środowisku), w tym bakterii, glonów i roślin naczyniowych (głównie metalofitów). Obecnie stosowane są różne fizyczne i chemiczne metody wytwarzania nanocząstek metali i kilka technik eksperymentalnych, mających na celu kontrolę wielkości i kształtu MNPS. Toksyczny wpływ MNPS na rośliny może być związany z toksycznością chemiczną ze względu na ich skład chemiczny (np. uwalnianie jonów metali) oraz stresem lub stymulacją spowodowanymi przez powierzchnię, wielkość i kształt cząstek. Interakcje z organizmami żywymi są określane przez fizykochemiczne właściwości nanocząstek. Ogólnie rzecz biorąc, ściany komórkowe roślin stanowią podstawowy element interakcji i barierę wejścia nanocząstek. Wewnątrz komórek nanocząstki mogą bezpośrednio wywoływać zarówno zmiany błon komórkowych, jak i innych struktur lub spowodować aktywizację mechanizmów ochronnych. Pośrednie skutki MNP zależą od ich właściwości chemicznych i fizycznych, mogących prowadzić do tworzenia pewnych ograniczeń fizycznych, rozpuszczania związków toksycznych czy wytwarzania reaktywnych form tlenu. Jednak należy podkreślić, że wpływ MNPS na zdrowie ludzi i stan środowiska jest nadal niejasny. Z tego względu konieczne jest stworzenie schematu systemu oceny polityki w dziedzinie nanotechnologii (które zostaną wykorzystane do przeglądu całości krajowego planu nanotechnologicznego). Zaproponowano trzy następujące kryteria oceny polityki: adekwatność, efektywność i skuteczność.

Słowa kluczowe: zachowania, skutki bezpośrednie i pośrednie, zielona synteza, organizmy żywe, nanocząstki metali, rośliny