

NANO-TECHNOLOGIES FROM THE ASPECT OF HUMAN ENVIRONMENT AND SAFETY AND HEALTH AT WORK

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Received 30.09.2009.

Accepted 22.12.2009.

Abstract

In the last couple of years the term "nano-technology" is very often used to describe process technologies and analytical techniques used during synthesis of materials in ultra fine range of magnitude of the millionth fraction of a millimeter. Considering that they will have a significant impact on human activities in the 21st century it is right to consider they represent a flywheel of the following industrial revolution.

On the other side, an exceptional surface activity of nano-particles can cause different effects, which do not always have a positive influence on work, as well as on human environment.

An analysis of inter-relation of nano-technologies and human environment is carried out in this paper taking into account the origin of particles, i.e. the route of their processing. The influence of nano-technologies on internal environment, i.e. work surroundings is analyzed from the aspect of safety and health at work. Apart from that, a particular attention is paid to prevent nano-particles releasing, whereas a survey of the developed techniques of nano-particles separation is presented.

Key words: nano-technologies, human environment, safety and health at work

Introduction

Nano-technologies are a quite wide and interdisciplinary notion which covers building of structures and mechanisms at atomic and molecular level of particles in the range from 1 to 100 nm.

Depending on the set properties of the finished products, the original powders particles have to satisfy different demands. There upon, physical properties (particle

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size, particle size distribution and shape, surface, morphology), chemical (basic metal contents, admixtures contents, gas pollution in chemical connections, adsorbed or dissolved condition) and technological properties (pouring density, flowability, compressibility) [1].

During studying particles and powder technology, the key task is decreasing particle size in order to increase their functional properties, whereas new applications would be found and new product would be obtained with superior properties. Great interest, first of all, is shown in submicron and even finer particles, whereas more research efforts in the area of nano-dimensions have been conducted in recent years. Research and development have progressed at high rate due to cooperation of science and industry in many fields, starting from synthesis of particles and their size analysis with direction in designing and processing of particles in the range of nano-metric size [2-4].

The dimensions below 100nm are specific wherein the phenomena of quantum physics become dominant over the phenomena of classical physics. This is primarily related to the changes in the electronic system, which leads to new electronic properties. In addition, nano-dimensions have much larger ratio between the number of atoms located on the surface and atoms in the interior than the micro-dimensions. It apparently can affect the structure, stability and reactivity of the system, resulting in formation of new materials. The nano-structural particles and powders have many different properties in comparison to the materials of large volume which they originate from. Specific surface increases with the reduction of particle size. The increase of the specific surface of particles directly affects many properties, e.g. the degree of solubility and reactivity of the particles, which is one of the main factors for the unique properties of nano-particles [5].

Since nano-particles have excellent surface activity and can be used for the production of new materials with different functions and specific properties, further research with application of sophisticated technologies is extremely important. Such materials may have application in the field of catalysis, membrane technology, optoelectronics, in the systems for the conversion and conservation of energy etc. Also, the great expectations are present with the nano-structural materials in the field of medicine, biology, information and communication technologies, metrology etc. The most attractive fields in which the nano-technological inventions will be mostly used are: production, storage and conversion of energy, improving agricultural production, processing and purifying the water, detection and examining the diseases, treating the ill people, the medical monitoring, the food processing and storage, refining the air pollution, detection and destroying the pests.

On the other side, an exceptional surface activity of nano-particles can cause different negative effects, therefore nano-particles may not always impose a positive influence on human environment. An attention has to be paid to their influence on safety and health of people as well. Overcoming of indicated problems will enable application of extraordinary properties of nano-particles in the entire spectrum of practical areas, such as, among other, processing of materials based on micron size or sub-micron particles. In order to achieve this goal, an overall analysis is necessary on the influence of nano-technologies on human environment and relevant safety and health parameters [1].

Internal relations between nano-technologies and human environment should be clarified from the aspect of their influence on the human environment depending whether nano-particles are generated artificially or naturally. Apart from that, the influence of nano-technologies is not less important in internal surroundings, i.e. where nano-particles are produced. Therefore, the interrelation between nano-particles and work surroundings from the aspect of safety and health at work has to be considered.

Nano-particles and human environment

Nano-particles can be voluntarily taken into the body from medical purposes (during administrating drugs) or unwillingly absorbed from the environment (dust inhaling from air, which contains nano-particles). Apart from this, a difference should be made between the nano-particles produced for industrial application and those particles unintentionally generated and released into the human environment.

People and animals come into the contact with nano-particles through different situations: nano-particles can be inhaled with air, swallowed with water, eaten with food, as well as, absorbed through skin from cosmetic. It should be emphasized that apart from the workers who participate in production where the danger of emission of nano-particles exists, consumers of nano-based materials can also be exposed to certain risks. Therefore, attention has to be directed not only to work, but also to human environment, i.e. ecosystems where there is a danger of nano-particles and nano-materials release.

In our atmosphere surroundings, the particles are suspended size of about tenth parts of a micron and they are emitted into the atmosphere in the quantity of 2.5 billion tons on the annual basic. The emission sources are classified into natural and artificial ones. Natural particles include 60% of total particles quantity which mainly consist of sea salts particles (about 1 billion tones) and soil particles (about 0.5 billion tone). In the same time particles of other origin are also generated as a consequence of human activities. Although they include only 16% of totally emitted particles, their size is mainly of submicron order and since they contain hazardous chemical components, such as nitrates, sulfates, hydro-carbonates, heavy metals and other in high concentration, their influences on ecosystems is serious and demands a detailed analysis. Fig. 1 shows an overview of the size and concentration ranges of various aerosol particles. As it can be seen, the number concentration of atmospheric aerosol which we inhale every day ranges from several thousand particles per cm^3 in clean area to several hundred thousands in dusty areas, and the size range lies between 10nm and several tens of micrometer [1].

Emission sources of the unwanted nano-particles are also exhausting gases, whereas a difference should be made between the exhausting gases originating from combustion processes in stationary reactors of different capacities, and exhausting gasses from diesel engines for stationary and transportation use. For combustion processes in stationary reactors fuels are used, such as: coal, crude oil and gas. Lighter fuels have lower degree of certain emission, but they have higher contents of ultra fine and nano-sized particles. It is believed that majority of particles, contained in exhausting gases of combustion processes, where coal is used a driving fuel, are formed directly from ashes, primarily contained in coal. Also, the presence of unburned carbon should

not be neglected. Depending on the formation mechanism there is a difference between the ultra fine and nano-size particles. One type of particles is formed during evaporation of elements with low boiling point contained in coal ashes, whereas ultra fine and nano-sized particles are generated during cooling of exhausting gasses. The other type comprises soot, i.e. carbon particles formed in gas stage [6].

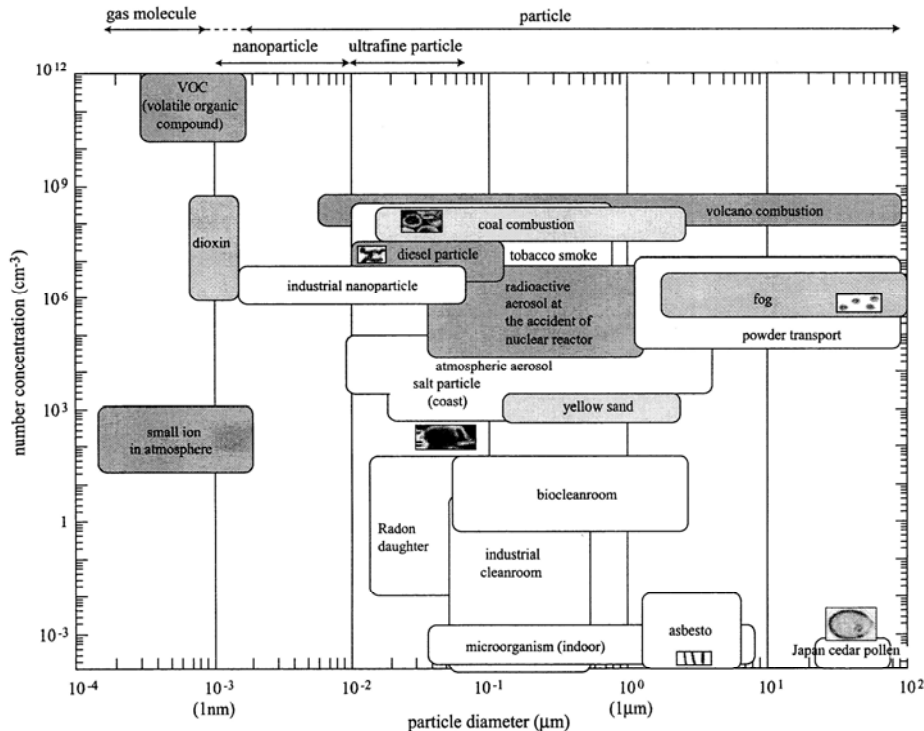


Figure 1. Particle size and concentration of various aerosols

In accordance with life style changes, based on mass production and mass sale, bringing along a drastic development of economy and industry, the quantity of industrial and communal waste waters is significantly increased every year. Having in mind that the waste waters, depending on their origin, contain different ingredients, such as particles of different origin, organic materials and emulsions, it is necessary to develop adequate effective methods of waste waters treatment. In general, waste waters may contain inorganic and organic nano-particles. For a repeated usage of the waste waters containing inorganic nano-particles, treatments such as membrane filtration, preceded by a biological pre-treatment are applied.

In the procedure of chemical-mechanical polishing, as a process applied in the semiconductor industry, waste waters may contain significant quantities of ultra fine and nano-particles SiO_2 , Al_2O_3 or CeO_2 , depending on the procedure. The treatment of these waste waters comprise chemical pre-treatment, i.e. the process of chemical coagulation-sedimentation as well as the membrane filtration when great quantities of mud are produced [7].

In different production branches, such as metal-processing industry, electronic components industry, pigments and cellulose production industry, generate waste waters contain metal colloids of nano-size, which are difficult to be separated by the coagulation-sedimentation process [8]. In copper wire production for the needs of electric industry a worn-out emulsions are released from the system, containing nano-sized copper colloid. Treatment of these industrial waters is carried out by means of the integrated membrane system based on ultra-filtration and nano-filtration. In glass industry, generated waste waters contain ultra fine and nano-particles of clay and glass generated in the surface grinding process during glass production for TV sets and monitors. Separation of these particles is also carried out through application of ultra- and nano-filters [1].

Waste waters from dye industry have a rather complex composition since apart from dye they contain auxiliary and finishing dye additives. In principle, dyes cannot be subject to a standard biological treatment due to exceptionally low bio-decomposition, therefore the treatment is carried out by the coagulation-sedimentation procedure, whereas nano-particles produced during the treatment are released into the human environment.

Waste waters from food industry contain organic substances in different concentration degree. In dairy industry, in cheese production, only 10% of the original milk quantity becomes a product-cheese and remaining 90% is turned into a byproduct - cheese whey, rich in proteins and lactose. Development of technology of membrane systems production based on ultra and nano-filtration enables a successful treatment of waste waters containing cheese whey [9].

Pesticides, with particle size at nano-metric level are used in enormous quantities for agricultural purposes, so the treatment of waste waters which contain pesticides is extremely significant. The recent results in this field point out to very effective pesticide separation by using nano-filter based membranes [10].

Communal waste waters contain different components, such as viruses, pharmaceutical substances, endocrine destroying compounds originated from animal secrete substances, etc. In this case a development of new procedures and technologies of waste waters treatment is necessary with a particular attention paid to nano-particle behaviour.

Finally, removing nano-particles contained in waste waters from the wide range of industrial branches, such as chemical, textile, cellulose industry and paper production, food industry and industry of dairy products, pharmaceutical industry has become an essential need, having in mind all possible negative consequences which these particles can have on working and human environment.

With the actual urbanized life style, people tend to spend more and more time indoors thus being exposed to so called "internal" nano-particles, originated from several sources, such as products from chemical reactions, unevaporable sediments of liquid drops, printers, photocopying machines, bioaerosols and air infiltration. Bearing this in mind, with the aim of estimating influence of the quality of air in closed premises on human health, a necessity of a detailed characterization of the particles contained in closed premises is imposed. Also, a correlation between these particles and those originating from human environment must be considered.

The main sources of generating "internal" nano-particles are as follows:

- chemical reaction by means of ozone,

- terpens (α -pinene, limonene) – ozone reaction, formation of irritating products,
- unevaporable sediments of drops, humidifiers and air cleaners
- printers and photocopying machine,
 - particles from ink-jet printers, substances originating from toners of laser and photocopying machines,
- burning,
 - cooking on gas stoves, smoking, burning of candles and incense,
- bioaerosols,
 - viruses,
- external sources,
 - penetration of external nano-particles through windows and other house openings.

Nano-technologies from the aspect of safety and health at work

Considering that nano-particles can be synthesized by different procedures, it is necessary to thoroughly analyze the influence of nano-particles production on work as well as on human environment.

The production of nano-particles can be generally divided into the methods of the approach "from the bottom-to the top" ("bottom-up approach") and methods of the approach "from the top-to the bottom" ("top-down approach"). In the "bottom-up approach" the nano-particles are generated either atom by atom or molecule by molecule. The production by this process is carried out mostly by chemical synthesis, self-assembling and positioning of the single nano-particles. Chemical synthesis is well known and allows the production of nano-particles in large quantities, while the positioning of single nano-particles requires application of microscopy techniques, which are considered as a low productive. Self-assembling refers to the techniques of production in which the atoms and molecules organize by themselves up to the regular structure on the nano-scale. In the "top-down approach" a large volume gradually decreases until the proportion not achieves nano-metric dimensions, which may be attained by mechanical treatment. The current search of nano-technologies is aimed to optimizing the relevant parameters of technological processes in order to obtain the determined specific properties. Four main approaches are currently being considered regarding the extensive production of nano-particles. They are based on the different mechanisms responsible for the formation of nano-particles: deposition from the gas phase ("bottom-up approach"), deposition from the liquid phase ("bottom-up approach"), evaporation-condensation ("bottom-up approach") and the processes of mechanical grinding ("top-down approach"). Recently, very successfully developed methods of recycling and valorization of useful components from secondary raw materials while the end product obtained ultra fine and nano-powders provide obtaining final products with pre-defined enhanced properties compared to the same obtained by conventional procedures [11].

Most of these processes are performed in a closed chamber installed in the clean room or controlled environment. The humans are not exposed to nano-particles during the synthesis, unless there is an unexpected leakage of a system (e.g. inadequate

hermeticity). After the production process is fulfilled when the reaction chamber is open, at the process of the product drying or at post-processing handling, human exposure to nano-particles may occur.

The release of nano-particles during the cleaning operation in the reaction chamber is the second critical moment, which involves the use of clean water or some other solvent. Brushes, sponge or cloth used for cleaning can become carriers of nano-particles. Finally, the stored waste and waste water from the cleaning process can become sources of the nano-particle release in the environment.

In addition, further processing of nano-particles, such as pressing, sintering and coating, in order to get the final product, can lead to the release of nano-particles in the work environment.

Techniques of the nano-particle separation

In order to prevent the release of nano-particles from the system and maintain the ecological safety, a special attention has been paid to the development of techniques of nano-particle separation.

In general, to prevent the nano-particle release three basic forms of the separator have been used (Fig. 2):

- the nano-particle separation of using a field force (electrostatic, centrifugal, gravitational etc.), where representative separator is the electrostatic settling tank (depositor),
- the separation of nano-particles using the induced obstacles placed in the loaded course of the particles, typical separators of this type are air filters,
- the nano-particle separation by the procedure of sifting, where the geometric size of the openings in the separator must be less than the size of the particles, typical representatives of this group of the separators are membrane filters and fibrous filters [7].

Elementary cause	Force field	Force field and abstacle	Obstacle
Form			
Collection efficiency	low	middle	high
Separator	- Electrostatic precipitator (ESP) - Cyclone	- Venturi scrubber - Fibrous filter - Granular bed	- Filter press - Bag filter - Membrane filter

Figure 2. Types of separators

Considering the types of separators, the main mechanisms of particle separation from the exhaust or suspended gas are Brownin's diffusion and electrostatic force, while

the effects of sifting and force of interception/adhesion are characteristic of the nano-particle separation in liquids.

Pan et al. [7] give an overview of the performed analysis of the efficiency of the nano-particle removal due to different forces such as gravity, centrifugal force, electrostatic force, inertia, Brownin's diffusion-force. They concluded that the rates of the nano-particle removal dependant on gravity, centrifugal force and inertia decrease with the particle size reduction, while the rates generated as a result of this Brownin-diffusion and electrostatic force increases with the decrease of particle diameter. This indicates that Brownin's diffusion and electrostatic force are the most effective for the nano-particle separation.

Fig. 3 presents an overview of the typical conventional particle separators [7].

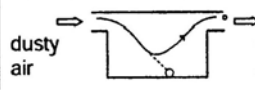
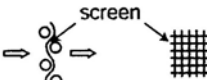
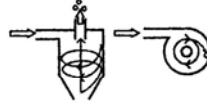
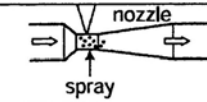

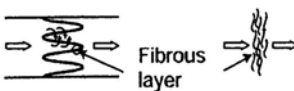
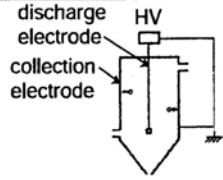
type	typical collector	shape of collector	particle size
gravity	settling chamber		>20 μm
inertia	mist separator		>10 μm
centrifugal force	cyclone		>2 μm
scrubbing	venturi scrubber		>0.5 μm
filtration	bag filter		all size range (high conc.)
	air filter		all size range (low conc.)
electrostatic force	electrostatic precipitator (EPS)		>50 nm

Figure 3. Typical conventional particle separators

To separate nano-particles in liquids two main methods are used: membrane filtration and ultra-centrifugal sedimentation. Membrane filtration collects particles by a membrane as the liquid flows freely through it. At the ultracentrifugal sedimentation, nano-particles from the liquid retained in the rotary vessel are settled due to the ultracentrifugal force of several tens of thousands of rpm.

Biological effects of nano-materials

Investigations on impact of nano-technology and nano-particles on the safety and health of humans in the working environment have started relatively recently. This is the reason why there are not enough available systematized results. Also, there are no regulations or standards for the assessment of biological effects of nano-materials, and there are rather insufficient toxicological data related to nano-materials. According to some studies, most of the ultra-fine particles and nano-particles are breathed out without deposition in the respiratory system, and therefore cannot cause negative effects on human health, especially the appearance of the lung diseases.

However, it is known that the properties of nano-particles differ from bulk properties of materials, which originate from, so that the known biological effects of bulk material cannot be applied to nano-materials. Actually, it may be expected that the nano-particles of the same material will have much stronger reaction along with more distinctive impact on human health.

Inhalation is the main way of exposure to nano-particles. The particles inhaled with the air through the mouth and nose. They penetrate through throat (nasopharyngeal and oropharynx) and tracheo-bronchial tree to the alveolar region where the oxygen goes from the alveoli to the blood and carbon dioxide from the blood to the alveoli. Penetration and deposition in any of the respiratory passages, such as the nose cavity, tracheo-bronchial tree and alveoli depend on the size of particles and mechanism of deposition.

The evidence from numerous studies [12, 13] on the insoluble particles (which are mainly aqueous) refers that the primary influence of the particle impact on health depends on the surface area of particles. Large surface coupled with large surface energy and the effect of attractive force between particles lead to the formation of agglomerates. In the working environment, the concentration of nano-particles is extremely high, with most of the nano-particles forming agglomerates, while only a few appear in the form of an individual. This phenomenon is the subject of discussion of many studies, which are related to the problem whether agglomerates of particles or individual nano-particles react in lungs and other human organs.

If the indissoluble nano-particles are retained in the human body for a longer without the possibility for their release, they may lead to health disorders, such as, for example, pneumonia. Also, it should be emphasized that aqueous nano-particles in the lungs through the alveolar epithelium may penetrate to blood vessels. In this situation they can damage or produce the blood clots. Aqueous nano-particles from nose can go directly to the brain through olfactory tubule [14].

Regarding that humans come into the contact with nano-particles of different materials and in different ways, the subject of the recent numerous studies is the analysis of biological effects of nano-particles of different materials.

Namely, nano-particles of iron and nickel used as catalysts in the process of formation carbon nano-tubes, show the negative biological effects [15]. In the same time, Oberdörster et al. [12, 13] states that the carbon nano-tubes are extremely toxic. It is considered that TiO₂ particles of a micron size have almost none toxicity. However, the results [9, 10] derived from the submicron TiO₂ particles and TiO₂ nano-particles indicate that the reduction in the particle size intensifies certain inflammatory reactions in the human body. According to International Agency for Research on cancer (IARC) the nickel compounds are categorized as the carcinogenic matters of the group 1. The nano-particles of nickel oxide have higher toxicity than the particles on the micron level [1]. Also, nano-particles of cobalt induce certain lung inflammatory reactions, more intensive than those caused by the particles of micron size [16]. The development of the materials based on indium attracts increasing attention of researchers in these days, since these materials applied in the preparation of electrodes for flat panel displays. However, in Japan have been registered the cases of pulmonary interstitial pneumonia and pulmonary fibrosis in workers employed in the work of cutting and grinding the sintered indium-tin oxide as a result of inhalation the nano-particles of this oxide [17].

Conclusion

An exceptional surface activity of nano-particles can cause different negative effects, therefore the influence of nano-technologies on human environment and work surroundings, i.e. on safety and health of people, must not be neglected. Having this in mind, it is necessary to insist on carrying out the whole sequence of activities and measure for preserving and improving safety and health, preventing, stopping and timely detecting incidents, as well as prompt and effective eliminating consequences contributing to risks of diseases caused by nano-technologies.

Therefore, it is necessary to insist on the implementation of the whole set of activities and measures for the preservation and improvement of safety and health, prevention, early detection and suppression of negative phenomena, as well as timely and efficient removal of the consequences in order to reduce the risks caused by nano-technologies.

The properties of nano-particles are quite different from those of bulk material which they originate from. From these reasons the known biological effects of bulk material cannot be applied to nano-materials. Nano-particles of the same bulk materials possess much higher impact on human health. The behavior causes the development of new modern methods and procedures for the purpose of preserving and improving the conditions of working environment. In accordance with this, special attention, through the definition of appropriate standards, should be paid to: determining of the limiting values, i.e. the lowest and the highest allowable concentration of nano-materials in the working environment; the definition of methods of testing and measuring the concentration of nano/materials in the working environment; standardization of appropriate measures and protection norms; standardization of appropriate preventive measures to reduce risk in the working environment, in order to improve the safety and health of all those who are in the direct contact with nano-particles; the definition of action with materials having properties of nano-materials.

In addition, in order to prevent release nano-particles in human surroundings and maintain ecological safety, a particular attention should be paid to development of techniques of nano-particles separation, i.e. in defining techniques of eliminating nano-particles from work, as well as from all segments of human environment (water, air and soil).

References

- [1] M. Hosokawa, K. Nogi, M. Naito, T. Yokoyama, *Nanoparticle Technology Handbook*, 385-417 (2007)
- [2] Z. Andić, M. Korać, Ž. Kamberović, A. Vujović, M. Tasić, Analysis of the properties of Cu-Al₂O₃ sintered system on the basis of ultra fine and nanocomposite powders, *Science of Sintering*, Vol. 39, No. 2, 2007
- [3] Z. Andić, M. Korać, M. Tasić, K. Raić, Ž. Kamberović, The synthesis of ultra fine and nanocomposite powders based on copper, silver and alumina, *Kovove materialy*, 3, Vol. 44, (2006), 145-150
- [4] M. Korać, Ž. Kamberović, M. Filipović, Determination of Al₂O₃ particle size in Cu-Al₂O₃ nanocomposite materials using UV spectrofotometry, *Metalurgija – Journal of Metallurgy*, Vol. 14(4), 2008, 279-284
- [5] M. Milun, *Nanoznanosti i nanotehnologije, Izazovi i poticaji*, *Kem. Ind.* 53 (12), 545-547 (2004)
- [6] K. Saito, *J. Soc. Powder Technol., Jpn.*, 38 (7), 493–502 (2001)
- [7] J. R. Pan, C. Huang, W. Jiang, C. Chen: *Desalination*, 179, 31-40 (2005)
- [8] M. Moriya, *J. Jpn. Soc. Water Environ.*, 22, 346–351 (1999)
- [9] A. Rektor, G. Vatai: *Desalination*, 162, 279-286 (2004)
- [10] Y. Kiso, H.-D. Li, T. Kitao: *J. Jpn. Soc. Water Environ.*, 19, 648-656 (1996)
- [11] R.W. Siegel, E. Hu, M.C. Roco, *Nanostructure Science and Technology*, WTEC, Loyola College in Maryland, 15-34 (1999)
- [12] G. Oberdörster, J. Ferin, R. Gelein, S. C. Soderholm, J. Finkelstein: *Environ. Health Perspect.*, 97, 193-197 (1992)
- [13] G. Oberdörster, E. Oberdörster, J. Oberdörster: *Nano-toxicology: Environ. Health Perspect.*, 113, 823-840 (2005)
- [14] A. Nemmar, M. F. Hoylayerts, P. N. M. Hoet, J. Vermeylen, B. Nemery: *Toxicol. Appl. Pharmacol.*, 186, 38-45 (2003)
- [15] C. W. Lam, J. T. James, R. McCluskey, R. L. Hunter, *Toxicol. Sci.*, 77, 126-134 (2004)
- [16] Q. Zhang, Y. Kusaka, X. Zhu, K. Sato, Y. Mo, T. Klutz, K. Donaldson: *J. Occup. Health*, 45, 23-30 (2003)
- [17] A. Tanaka, M. Hirata, M. Omura, N. Inoue, T. Ueno, T. Homma, K. Sekizawa: *J. Occup. Health*, 44, 99-102 (2002)