

Chapter 3

Toxicology of Nano-Objects: Nanoparticles, Nanostructures and Nanophases

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Abstract The present paper discusses classification of nano-objects, which is based on their size, morphology and chemical nature. The subject of nanochemistry includes those nano-objects whose chemical properties depend on size and morphology, such as spheroidal molecules, anisotropic (2D) and isotropic (1D) nanoparticles, nano-clusters and nanophases. Nanophase is a nano-dimensional part of the microphase whose properties depend on its size. The potential health hazards of nano-objects are associated with their capability of penetrating the body through inhalation, digestion or the skin.

Keywords Nanochemistry • Nanotechnology • Nanotoxicology • Nanoparticles • Nanostructures, “micrographene sheet”

3.1 Introduction

At the end of the twentieth century, in the area of physics, and later in the area of chemistry extraordinarily important experimental results were produced, which gave rise to a new concept of nano-world. Development of high resolution electron microscopes allows detection of not only nano-dimensional particles but also large molecules. New types of matter such as spheroidal molecules with a hollow core (fullerenes and nanotubes), nanosized phases formed by a few atoms of metals

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(nanophases) and clusters formed by a few molecules were discovered. The special features and properties of these materials depend on their size and morphology and differ from currently known substances. In the macro-world, properties of macro- and micro-dimensional substances depend on their nature and structure but not on their size. The possibility to manipulate nano-dimensional objects and to create nanorobots at the molecular level is expected to substantially influence technical progress. With appearing of new branches of science and technology, such as nanotechnology and nanomedicine, one can talk about a "nano" era, an era of formation of new science – nanology [1], a science about the nano-world. Nanology has changed the paradigm of all scientific and manufacturing activity. The traditional technology deals with large objects which can be reduced in size whereas nanotechnology constructs its products from individual atoms and molecules "upwards".

3.2 History of Discovery, Classification and Chemistry of Nano-Objects

Before discussing any adverse effects of nano-objects on humans and the environment, it is necessary to classify nano-objects, identify their main sources and understand their chemical properties. Nano-objects certainly existed in nature long before they attracted interest of researchers. Carbon nanoparticles have been continuously generated and released in the atmosphere by forest fires and volcanic eruption. Nature has also designed unique living nano-tools. For instance the gecko – a beautiful lizard, can move easily on a ceiling or a window pane due to adhesive pads on its digits, each of which contains hundreds of spade-like tips of a diameter less than 200 nm.

First scientific research of nano-objects, probably, goes back to the nineteenth century, when Faraday (in 1856) discovered that the colour of highly dispersed colloid gold solutions depends on the particle size of gold. This unique feature of gold solutions was actually known much earlier, in the alchemy era, and even the word "alchemy" probably originates from the Chinese term meaning "gold juice" because of the red colour of some colloid gold solutions.

Other examples of using nano-objects in technology are the unique Lycurgus, King of the Thracian's glass cup, and the legendary Damascus steel made in fourth and eighth century, respectively. Their secrets were unveiled only recently. It appears that a sabre made of Damascus steel is reinforced by anisotropic nanoparticles of carbon nanotubes. Etching of the saber blade by carbon nanotubes creates a superhard surface. The enigmatic change of the Lycurgus cup colour from green to crimson under sunlight is associated with presence of gold and silver nanoparticles in the glass.

Emission of nanoparticles in the atmosphere from anthropogenic sources (machines, aero engines, power stations, smelters, plasma, welding and heat treatment processes) has been continuously increasing ever since the beginning of the industrial revolution.

At present a great variety of nano-objects, which have no analogues in nature, are produced in large quantities. Their potential impact on the environment and

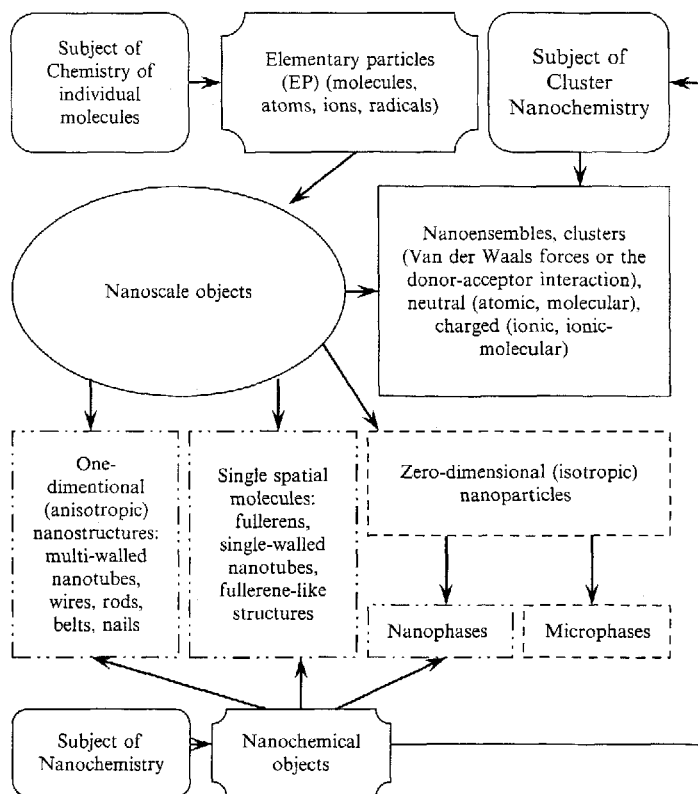


Fig. 3.1 Classification of nano-objects based on their dimension, morphology, structure and chemistry

humans is unknown. Thus studying possible adverse effects of these nano-objects is an extraordinarily important task. On the other hand, because nano-dimensional objects are extremely various in their chemical nature, composition, structure and morphology, it is necessary to classify them (Fig. 3.1). Such a classification would be a logical starting point for a systematic approach to assessing environmental and health effects of nano-objects.

It is especially important to create and develop terminology of nanochemistry as a part of a new area of science – nanology, or the “science of the nanoworld” (nanologists prefer this term to a more widely used word nanoscience). Figures 3.2–3.8, show the diversity of the morphology of nanostructures of carbon, silicon and boron carbides, which were synthesised via hydrocarbon pyrolysis [2–5] or from elemental substances [6–10]. Morphologies of carbon nanotubes thus obtained are very unusual (Fig. 3.2).

Carbon nanotubes with armchair shape present a special interest because it is possible to see that the metal catalyst is not always located at the top of nanotube. Therefore it is evident that the growth of graphene layers may occur not only from a surface of a metal nanoparticle, as it is usually understood. Among the products

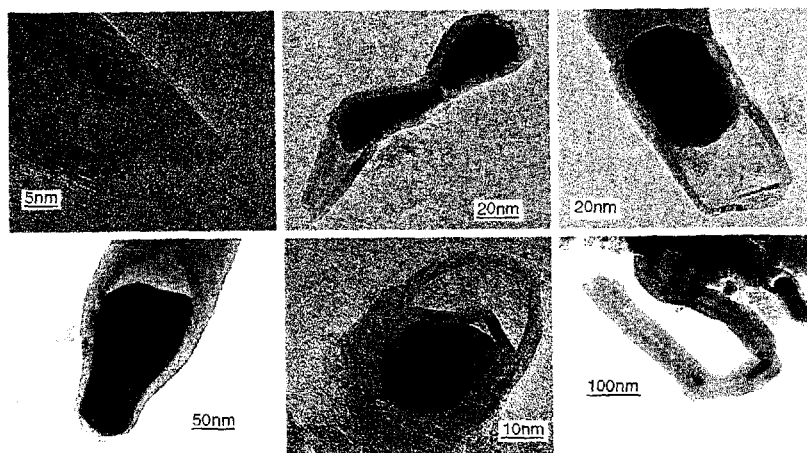


Fig. 3.2 Unusual morphologies of carbon nanotubes containing metallic nanoparticles inside

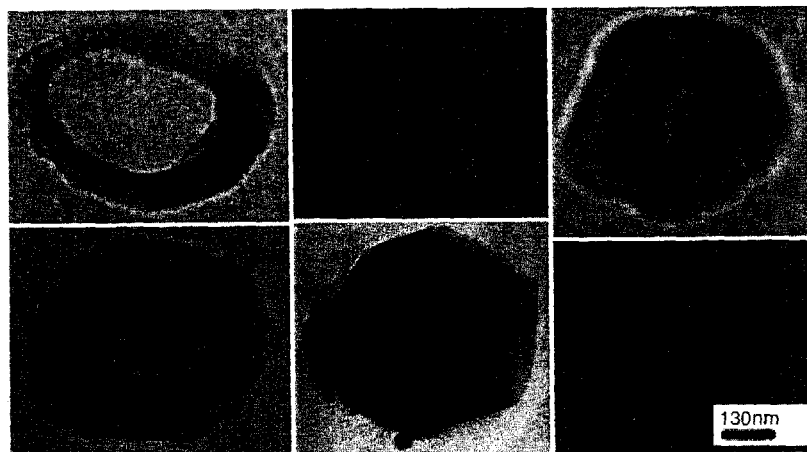


Fig. 3.3 Carbon toroids formed simultaneously with the growth of carbon nanotubes and carbon onions

of pyrolysis other unique carbon nanostructures such as various polygons, a ring with a hollow core and onion structures were found (Figs. 3.3 and 3.4).

The growth of such structures is possible only from a gas phase and probably occurs as a result of dehydropolymerisation (polycondensation) [4,11]. Under more harsh reaction conditions multi-walled nanotubes grow as a loop on ceramic reactor walls (Fig. 3.4). We suggest that the benzene molecule could be the main fragment in the graphene network formation. At temperatures $>600^{\circ}\text{C}$ benzene rapidly undergoes dehydrogenation followed by diphenyl formation that can be considered

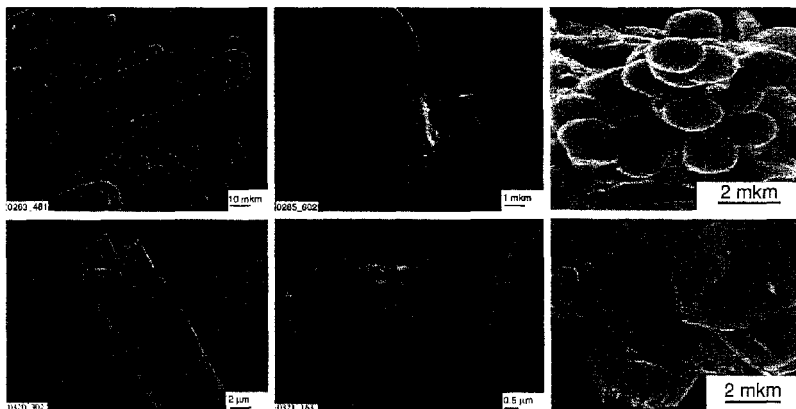


Fig. 3.4 SEM images of multi-walled carbon nanotubes and carbon onions

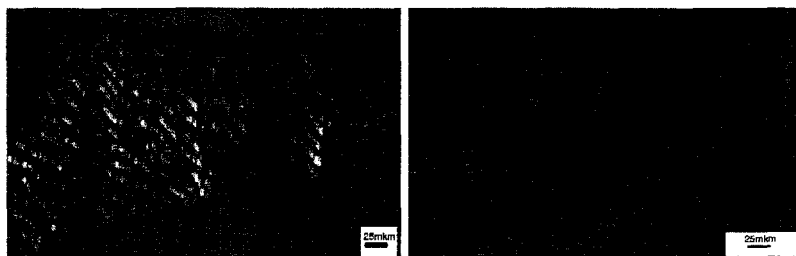


Fig. 3.5 Optical microscopy images of “micrographene sheet” and “carbon microclusters”

as the first stage of a graphene network formation. Further condensation of benzene and diphenyl expands the number of condensed carbon hexagons leading to formation of the graphene network. The network is formed from planar molecules but because of sp^3 - hybridisation of peripheral carbon atoms, convolution of the formed carbon structure occurs. This mechanism has been confirmed by discovery of unique structures in the shape of “micrographene” sheet and “carbon microclusters” (Fig. 3.5), which we have found in hydrocarbon pyrolysis products.

For the first time we have discovered transparent (painted in various colours) thread-like crystals of carbon among the products of hydrocarbon pyrolysis and during synthesis of silicon and boron carbides (Fig. 3.6) [12]. The X-ray spectral analysis has shown that the transparent threads consist of carbon (Fig. 3.7).

Growth of anisotropic silicon and boron carbide nanoparticles from powdered reagents was performed using a process of exothermic nanosynthesis [6,7] (Fig. 3.8).

Such nanostructures are formed as a result of fast growth at temperatures, at which the equilibrium pressure of silicon, boron and especially carbon vapour is

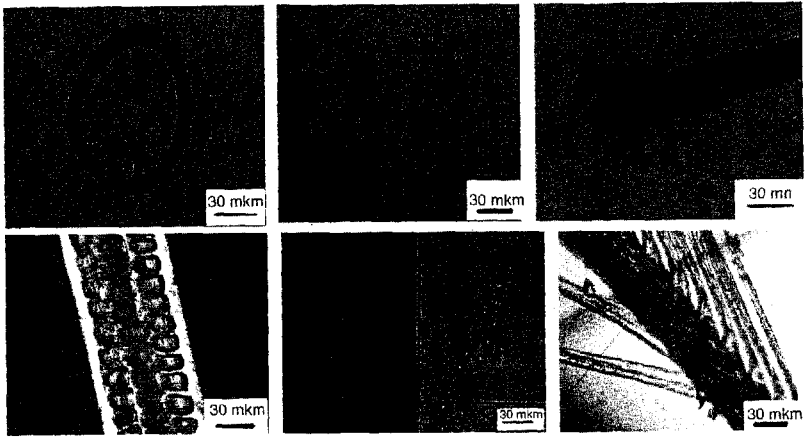


Fig. 3.6 Optical microscopy images of transparent carbon crystalline threads obtained in polarised light

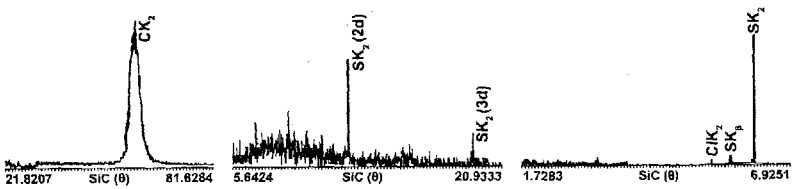


Fig. 3.7 The X-ray spectral analysis of carbon threads shown in Fig. 3.6

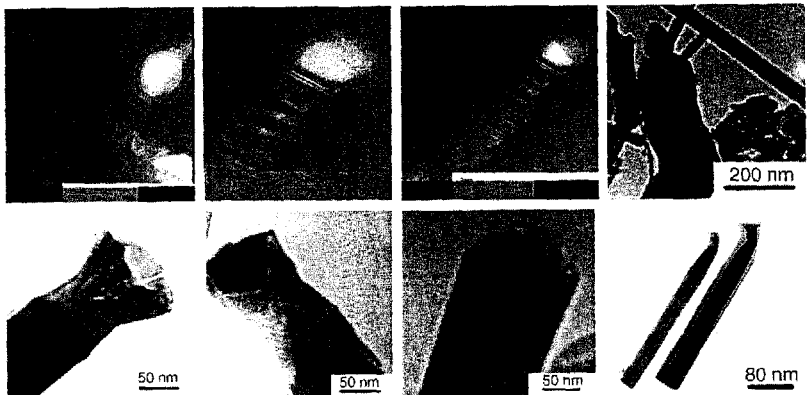


Fig. 3.8 TEM images of the tips of silicon carbide nanothreads

negligible. The reaction occurs because the local temperature and respective vapour pressure in the vicinity of the reactive zone is much higher than the temperature and vapour pressure across the reactor creating a nanocentre of growth of an isotropic particle. Melting of the nanocentre and sublimation of the reagents in its vicinity is facilitated by the heat of the exothermic reaction. The evaporating atoms are mainly transported in the direction of the molten nanocentre forming a carbide product.

Nanostructures of various morphologies and nanoparticles can be considered as objects of nanochemistry, as their properties are mainly determined by their "nano" dimensions. Thus nanoparticles, being a nano-dimensional part of a microphase, have essentially different physical, chemical and electronic properties, and sometimes even a different crystal structure. They should therefore be described as a nanophase, as opposed to a microphase. For example, the melting temperature (T_m) of nanoparticles (5–10 nm) of gold is hundreds of degrees lower than T_m of the gold microphase [13]. Moreover gold nanoparticles of such dimensions have a crystal structure completely different from that of the gold microphase. Contrary to microphases, nanophases are limited in their size to nano-dimensions. The geometrical dimensions of a nanophase are strictly individual and determined by other characteristics of the object. Each characteristic of a nanophase such as its electronic, optical and magnetic properties, or melting temperature could have a different limiting size which distinguishes it from a microphase.

Nano-clusters are also nano-dimensional objects. They can be neutral (atomic or molecular) or charged (ionic or ionic-molecular) complexes or ensembles of molecules, atoms and ions.

Chemical properties of nano-objects are related to their:

- (a) nano-dimensions, which are comparable to the size of individual molecules;
- (b) dependence of nanophase properties on particle size;
- (c) unusual shape (tubes, tapes, rods, spheres);
- (d) large surface area, etc.

3.3 Toxicity of Nano-Objects

At present nanotechnology is often perceived as a panacea for solving many global problems. However few systematic studies have been carried out to elucidate effects of nano-objects on health and the environment. Even specialists are practically unaware of the possible impact of nano-objects they are dealing with. However some of the results of studying toxicity of nanoparticles are alarming [14]. Penetration of nanoparticles into biosphere can cause many problems. The unique feature of nano-objects is that they are capable of easily overcoming biological barriers of the living organism, and can interfere with normal physiological and biochemical processes causing various pathologies (Fig. 3.9). It seems that the nature does not have natural protection mechanisms against damaging effects of novel nano-objects already produced in substantial quantities.

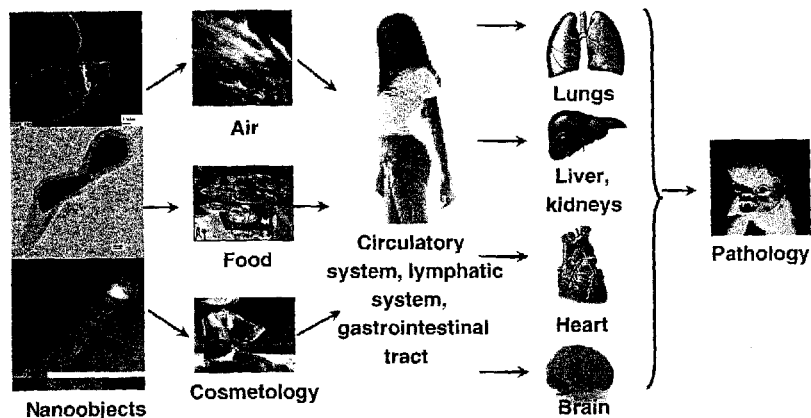


Fig. 3.9 The main routes of nano-object penetration into the human organism

The main routes of nano-objects penetration into the organism are (Fig. 3.9):

- Through inhalation (adsorbed by the huge surface of the lungs and thence transfer into the blood stream);
- By digestion (easily transferred into the blood via intestines, and passing into the liver as a protecting barrier);
- Through the skin (especially if it is damaged).

Experiments on animals and fish have demonstrated a big danger of uncontrolled distribution of nanoparticles in the environment: nanoparticles can get directly into brain tissue from the circulatory system. Inhalation of polystyrene nanoparticles causes an inflammation of the pulmonary tissue and initiates thrombosis of blood vessels. Impact of carbon nanotubes on the lungs is comparable with toxicity of asbestos and benzpyrene; it has been suggested that carbon nanotubes can suppress the immune response of the body. Through the respiratory pathway nanoparticles can influence the nervous system [15]. The experiments on dogs and aquarium fish have shown that fullerenes penetrate the brain. Having a large surface area, carbon nanoparticles, especially those partially destroyed or with imperfect morphology (Fig. 3.4), can become containers/carriers for the adsorbed carcinogenic substances - products of hydrocarbon pyrolysis. Thus both morphology and structure of nanoparticles and the chemical nature of the adsorbed chemicals can have an adverse effect on human health.

Environmental behaviour of carbon nanostructures is extremely difficult to predict because they contain on their surface a number of adsorbed substances such as polyaromatic hydrocarbons (PAH), which are known carcinogenic substances. Carbon nanoparticles generated by combustion processes, in particular from cigarette smoke contain thousands of different chemicals, which may be toxic to living species [16].

The number of studies on the health effects of fullerenes and carbon nanotubes is rapidly increasing. However, the data on their toxicity are often mutually contradictory. For example, the researchers from universities of Rice and Georgia (USA) found that in aqueous fullerene solutions colloidal "nano-C₆₀" particles were formed, which even at low concentration (approximately 2 molecules of fullerene per 108 molecules of water) negatively influence the liver and skin cells [17–19]. The toxicity of this "nano-C₆₀" aqueous dispersion was comparable to that of dioxins. In another study, however, it was shown that fullerene C₆₀ had no adverse effects and, on the contrary, had anti-oxidant activity [20]. Solutions of C₆₀ prepared by a variety of methods up to 200 mg/mL were not cytotoxic to a number of cell types [21]. The contradiction between the data of different authors could be explained by different "nano-C₆₀" particles composition and dispersion used in research.

In other publications single-walled carbon nanotubes were shown to promote neoplasm formation in kidneys [22, 23]. Contrary to [20], other authors found that carbon nanostructures were capable of inducing reactive oxygen species (oxygen radicals) that could damage cellular structures [24–26].

3.4 Conclusions

Our current state of knowledge is insufficient to fully assess potential health hazards associated with the use of nano-objects and relate health effects to their chemical, structural and morphological properties. The main danger of nano-objects is that they are capable of easily penetrating the blood stream and internal organs via inhalation, ingestion and through the skin. Further systematic research of "structure-properties" of nano-objects is required.

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