

# RADIATION METHODS AND USES IN NANOTECHNOLOGY

Dagmara Chmielewska

*Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warszawa,  
Poland*

## 1. INTRODUCTION

Nanotechnology is a fast growing area in science and engineering. This multi-disciplinary area has emerged from the convergence of electronics, physics, chemistry, biology, medicine and materials science to generate new functional materials of nanoscale dimensions. Figure 1 illustrates this convergence.

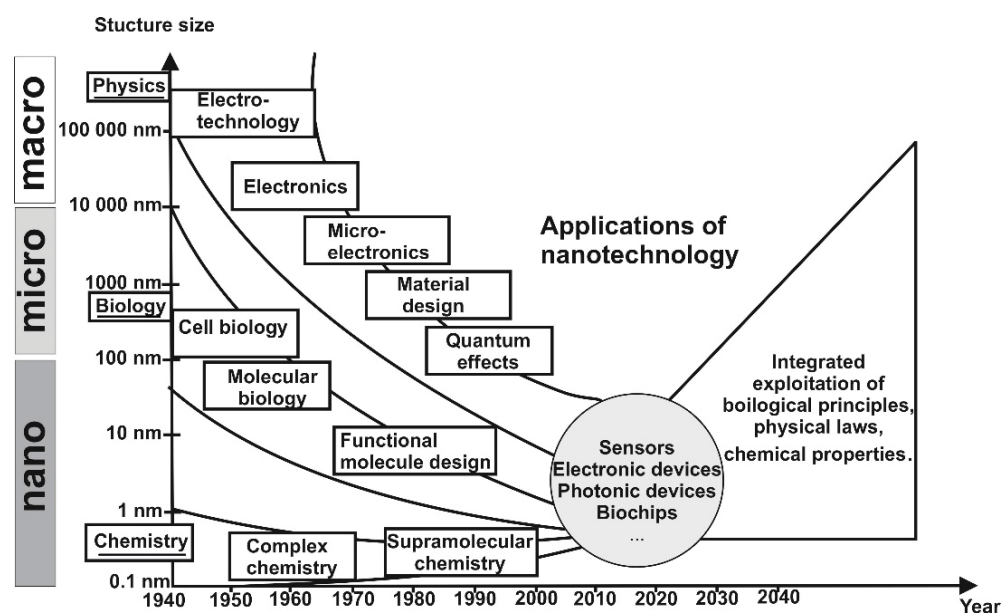


Fig.1. The convergence of the disciplines and multisector applications [1].

Nanotechnology is focused on the design, development, characterization and uses of materials which have at least one dimension that is less than 100 nm. One unique aspect of nanotechnology is that it offers a large increase in

surface area for many nanomaterials, which generates new possibilities in surface-based technologies, such as catalysis and antibacterial applications. The physicochemical properties and functions of nanomaterials may differ significantly from those of the same material in bulk.

The use of radiation techniques in nanotechnology has been known for many years. X-ray, electron beam and ion beam lithography are good examples of such uses. By using electron beams, ion beams or X-rays, structures as small as 10 nm have been made. Ion track membranes with track diameters ranging from 10 to 100 nm are used directly or as templates for the electrodeposition of nanowires of metal, of semiconductors and of magnetic materials. Progress in X-ray, focused ion beam (FIB) and electron beam nanolithography, and in three-dimensional (3D) fabrication has been noted in recent years. Heavy ion beams can be used for the fabrication of nanopores which serve as templates for making nanowires. The use of radiation processing has proved to be an essential technique for the fabrication of nanostructures with high resolution since radiation beams can be focused down to a few nanometers or less. Four groups of nanoscale products are fabricated by radiation techniques: nanoparticles, nanogels, nanotubes and nanocomposites [1].

## 2. FUNDAMENTALS

The prefix “nano-” is derived from the Greek word “νᾶνος” meaning “dwarf”. One nanometer (nm) is a unit of length in the metric system equal to one billionth of a meter or about the width of 6 carbon atoms or 10 water molecules. A human hair is approximately 80 000 nm wide and a red blood cell is approximately 7000 nm wide. Atoms are smaller than 1 nm, whereas many molecules including those of some proteins range between 1 nm and larger [2].

The concept of the nanotechnology was introduced in a presentation entitled “There’s plenty of room at the bottom” at the Annual Meeting of the American Physical Society on 29 December 1959 by Nobel laureate Richard P. Feynman. Feynman described a process for manipulating and controlling matter on a miniature scale, creating nanomaterials atom by atom or molecule by molecule. The term “nanotechnology” was first used in 1974 by Norio Taniguchi, a professor at the Tokyo Science University, and was defined as follows: “Nano-technology mainly consists of the processing of separation, consolidation, and deformation of materials by one atom or one molecule.” [3].

Two complementary approaches to nanomaterial fabrication are used (Fig.2):

- The “top-down” approach – where fabrication starts from the bulk material and reduces it down to the nanoscale.

- The “bottom-up” approach – where fabrication starts from the atomic or molecular level and by building atoms or molecules together complex nanostructures are created.

The term “nanomaterials” describes, in principle, materials that have at least one dimension in the range between 1 and 100 nm.

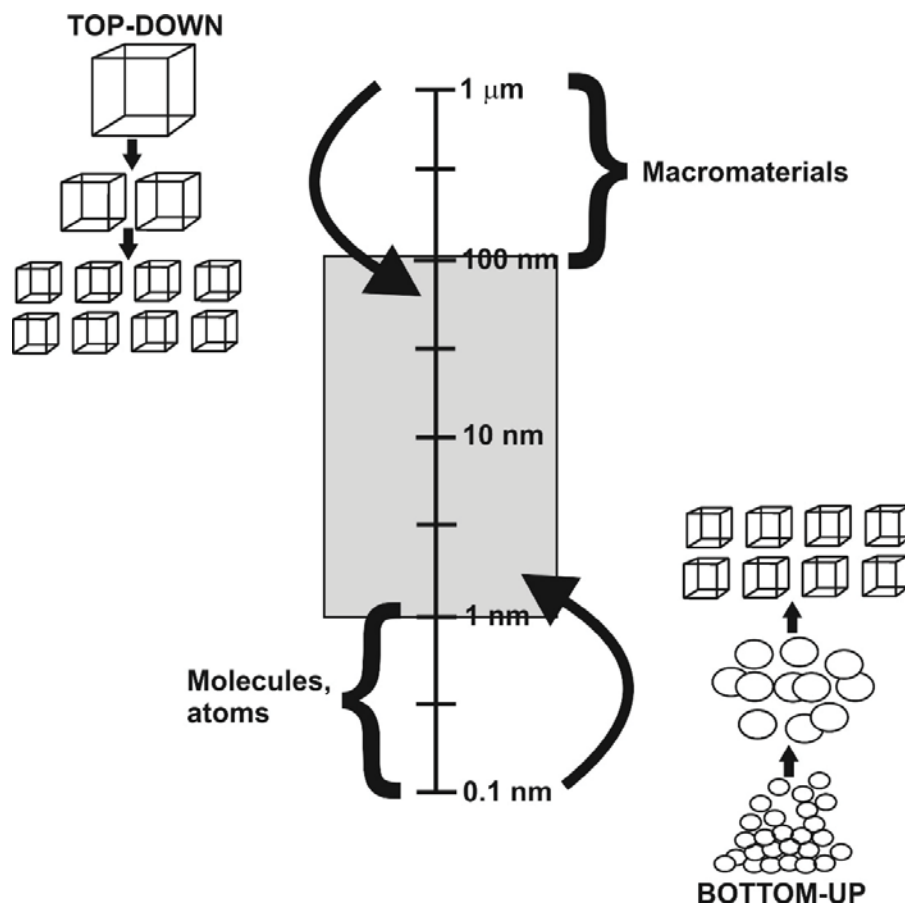


Fig.2. Scheme of the two approaches used in the fabrication of nanomaterials: “top-down” and “bottom-up” [4].

A great variety of nanostructures have been classified in different ways in the literature. Figure 3 shows the most relevant types of nanostructures in nanotechnology, classified according to four nonexclusive criteria [4].

Nanoparticles can be classified as natural, anthropogenic (incidental), or engineered in origin [5]. Taking into account the chemical composition, the dimensions of nanostructures and their distribution within a matrix, they can be homo- or heterogeneous. The chemical composition of nanostructures can be classified as inorganic (noble metal nanoparticles, quantum dots, *etc.*), organic (fullerenes, carbon nanotubes, dendrimers, *etc.*) or hybrid (gold nanoparticles modified with calixarenes, carbon nanotubes functionalized with ferro-

cene, etc.) [5]. The last classification of nanomaterials is based on the dimensions of the nanostructures and on two different approaches for terms used in nanometrology.

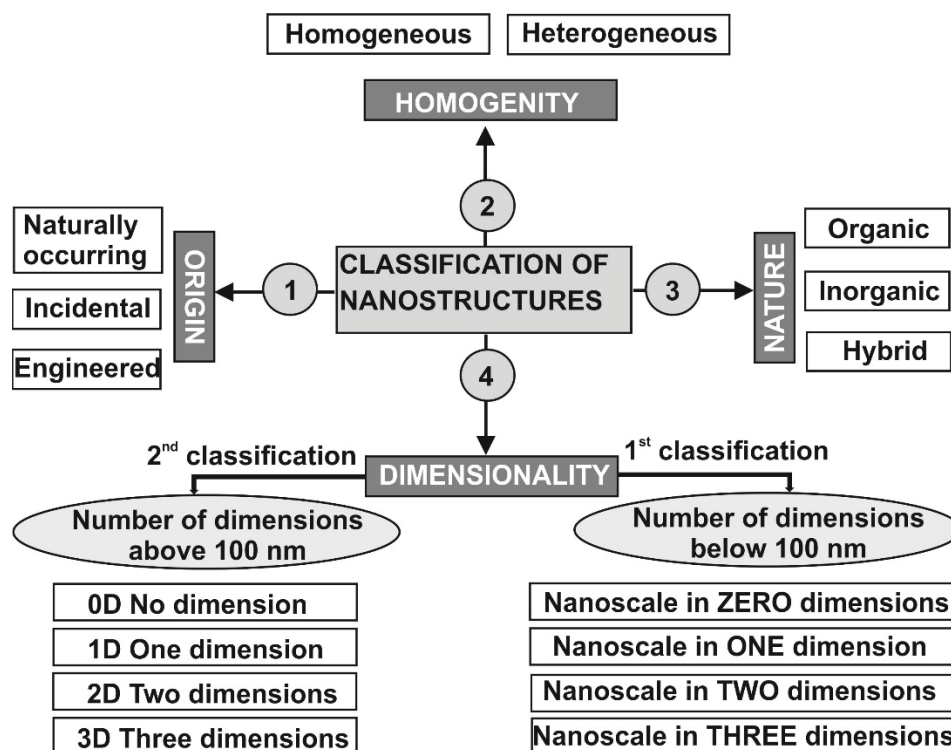


Fig.3. Classification of nanostructures according to the different criteria [4].

The Royal Society of Chemistry and the Royal Academy of Engineering classified nanostructures according to the number of dimensions in the nanoscale [6]. According to this classification three types of nanostructures can be distinguished:

- nanoscale in one dimension, such as surfaces, thin films and layers;
- nanoscale in two dimensions, such as tubes and wires;
- nanoscale in three dimensions, which includes nanoparticles and quantum dots, fullerenes, and dendrimers.

Classification of nanoscale at a zero dimension can also be added, such as materials composed by dispersed nanoparticles [4].

Other classification of nanostructured materials is based on the number of dimensions that are above the nanoscale [7]:

- 0-D nanostructures, such as nanoparticles, quantum dots and nanodots.
- 1-D nanostructures, such as nanowires and nanorods.
- 2-D nanostructures, such as coatings and surface layers. This category includes coatings made of nanocrystalline metals or nanocomposites.
- 3-D nanostructures, which include bulk materials.

The focus below is only on engineered nanostructures, which can be obtained with the use of radiation processing.

### 3. IONIZING RADIATION IN NANOTECHNOLOGY

Radiation-based methods play an important role in the development and modification of nanostructures.

Ion beams are used to fabricate track-etched membranes for ultrafiltration, membranes with electrical and magnetic properties and with potential uses as chemical detectors and biosensors [8]. The junctions between carbon nanotubes can be made by electron beam irradiation at elevated temperatures. Electronic devices require molecular connections between individual nanotubes. Microgels and nanogels produced by radiation techniques are well suited for biomedical applications since they are free of monomers, initiators and any other additives. Thus, they can be used as carriers for enzymes or antibodies used in diagnostics, as drug carriers for therapeutic purposes (controlled drug delivery) and possibly for artificial biological fluids and synthetic vectors for drug delivery.

Ionizing radiation is widely used in industry for the crosslinking of polymers and polymer blends. This technology can be extended to the crosslinking of nanopolymers and nanocomposites. Potential applications involve the irradiation of various types of polymers (natural rubber, polyolefins, polyimides, polystyrene, *etc.*) containing nanosized clays, silica or metal nanoparticles.

Radiation is an important tool in nanotechnology which has already been used (electron beam and X-ray lithography, track-etched membranes) and as results of recent studies indicate will to grow [1].

#### 3.1. RADIATION IN THE PRODUCTION OF NANOMATERIALS

##### 3.1.1. Nanogels

There are at least two definitions of polymeric nanogels and microgels. The first is derived from the definition of polymer gels. A polymer gel is a two-phase system consisting of a stable three-dimensional network of linked polymer chains and of molecules of a solvent filling the pores of this network. The second definition states that a nanogel or a microgel is an internally cross-linked macromolecule. This approach is based on the fact that, in principle, all the chain segments of a nanogel or microgel are linked together and are thus part of one macromolecule. This also reflects the fact that such gels can be made either by intramolecular crosslinking of single linear macromolecules or in a single polymerization event (*e.g.* initiated by one radical) that in the

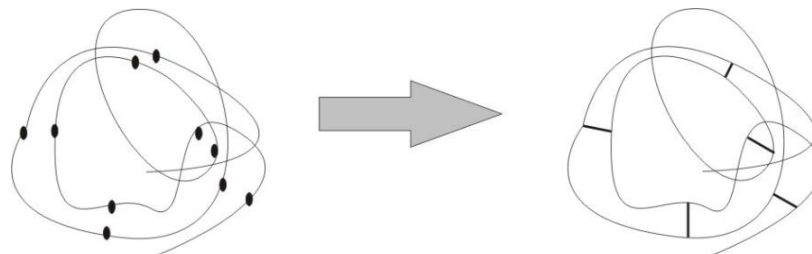


Fig.4. Formation of a nanogel from a single macromolecule by intramolecular recombination of polymer radicals.

absence of crosslinking would lead to the formation of a single linear polymer chain (Fig.4).

### 3.1.2. Metal nanoparticles

Noble metal nanoparticles have attracted interest because of their potential use in areas such as catalysis, nanoelectronics, sensors, health care and medicine [9-12].

During the electron beam or gamma-ray irradiation of liquids, most of the energy is absorbed by the water, so water radiolysis takes place, which results in the formation of reactive species such as the oxidizing hydroxyl radical ( $\cdot\text{OH}$ ) and very powerful reducing radicals as the hydrated electron ( $e_{\text{aq}}^-$ ) and hydrogen atom ( $\text{H}\cdot$ ) [13]. Metal ions in solution are first reduced by these reducing agents to lower valence ions and then into metal atoms. Different parameters, as the initial concentration of metal cations in the solution, the irradiation dose, the dose rate, and the pH, can significantly influence the size of silver nanoparticles [14]. Making metal nanoparticles in an aqueous solution is difficult, because of a tendency for the particles to aggregate. The growth of metal nanoparticles must be controlled by the use of stabilizing (capping) agents, for example polymers with a high affinity for metal atoms, or the use of a solid support for nanoparticle binding. Different metal nanoparticles, Co, Zn, Pd [15], Cu, Hg [16], Ni [17], Ag [18], Au [19], Pt [20] and others [13], can be made with the use of ionizing radiation. Bi- and multimetallic nanoparticles can be also obtained in this way [13].

Metal clusters are generated by radiation-induced reduction either of ion precursors in solution or of ions impregnated in a solid support. The first step is the radiolysis of water which yields reactive free radicals, such as hydrated electrons, hydroxyl radicals and hydrogen atoms, and the molecular products  $\text{H}_2\text{O}_2$  and  $\text{H}_2$ , according to the stoichiometry [21] included in reaction (1):

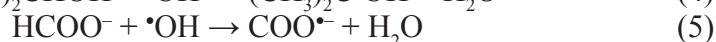
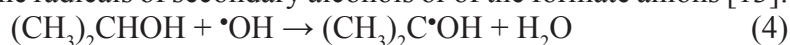


The solvated electron ( $e_{\text{aq}}^-$ ) and hydrogen atom are strong reducing agents (with standard reduction potentials  $E^0(\text{H}_2\text{O}/e_{\text{aq}}^-) = -2.87 \text{V}_{\text{NHE}}$  and  $E^0(\text{H}^+/\text{H}\cdot) = -2.31 \text{V}_{\text{NHE}}$ , respectively [21]), so can easily reduce metal ions down to the zero-valence state:



where  $M^+$  is the symbol for monovalent metal ions and  $M^0$  is the symbol for zero-valent metal.

In the water radiolysis process,  $\bullet\text{OH}$  radicals that are able to oxidize ions or atoms to a higher oxidation state are also generated. To prevent this reaction, a scavenger for  $\bullet\text{OH}$  radicals, such as a secondary alcohol or formate anion, is added to the solution. As the scavenger of  $\bullet\text{OH}$  radicals is added, substances whose oxidation by  $\bullet\text{OH}$  generate radicals that exhibit a strong reducing power, such as the radicals of secondary alcohols or of the formate anions [13]:



The  $(\text{CH}_3)_2\text{C}\bullet\text{OH}$  and  $\text{COO}\bullet^-$  radicals are strong reducing agents too, with standard reduction potentials  $E^0[(\text{CH}_3)_2\text{CO}/(\text{CH}_3)_2\text{C}\bullet\text{OH}] = -1.8 \text{ V}_{\text{NHE}}$  and  $E^0[\text{CO}_2/\text{COO}\bullet^-] = -1.9 \text{ V}_{\text{NHE}}$ , respectively [13].

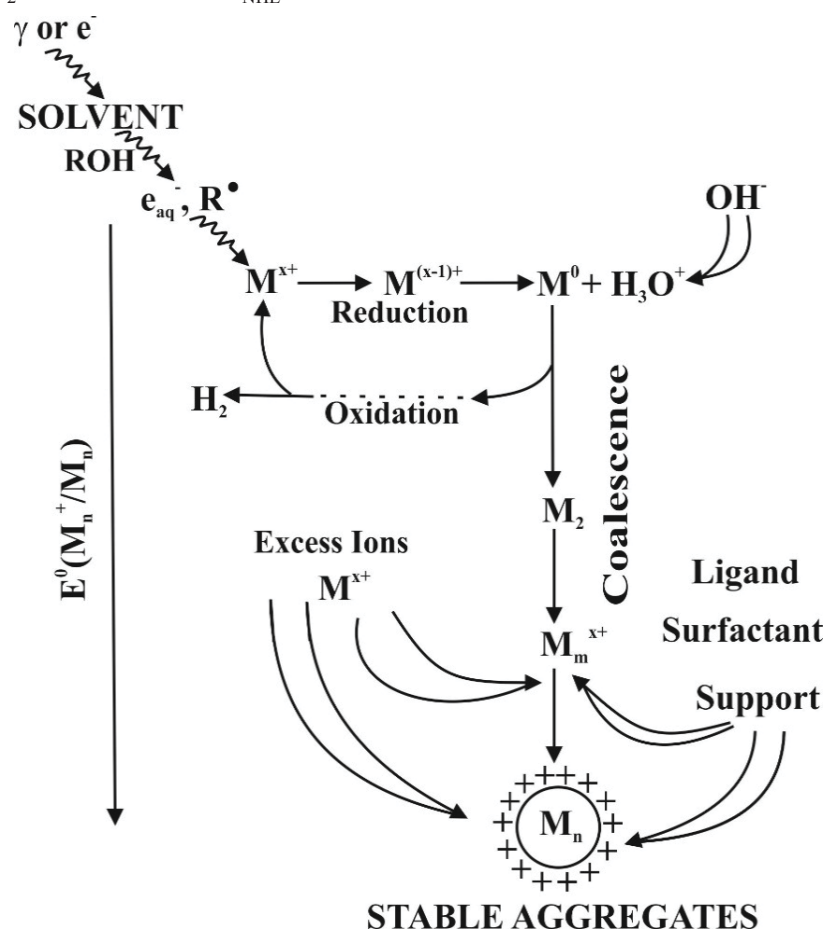
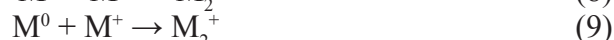


Fig.5. Scheme of metal ion reduction in solution with application of ionizing radiation [13].

In the next step, the generated radicals are able to reduce metal ions:



Metal atoms are formed with a homogeneous distribution throughout the solution. The binding energy between two transition metal atoms is stronger than the atom–solvent or atom–ligand bond energy. As a result, these atoms tend to dimerize when they encounter or associate with an excess of ions [13]:



By a continuation of this process, these species progressively coalesce into clusters following homogeneous kinetics [13]:



where  $m$ ,  $n$  and  $p$  represent the nuclearities (*i.e.* the number of reduced atoms), and  $x$ ,  $y$  and  $z$  are the numbers of associated ions, as illustrated in Fig.5. The redox potential of the clusters increases progressively with the nuclearity.

When a high dose rate is used, all of the reducing radicals are produced in a short time, which results in the coalescence of the atoms that were separately formed (Fig.6A). At a low dose rate, atoms dimerization and the coalescence

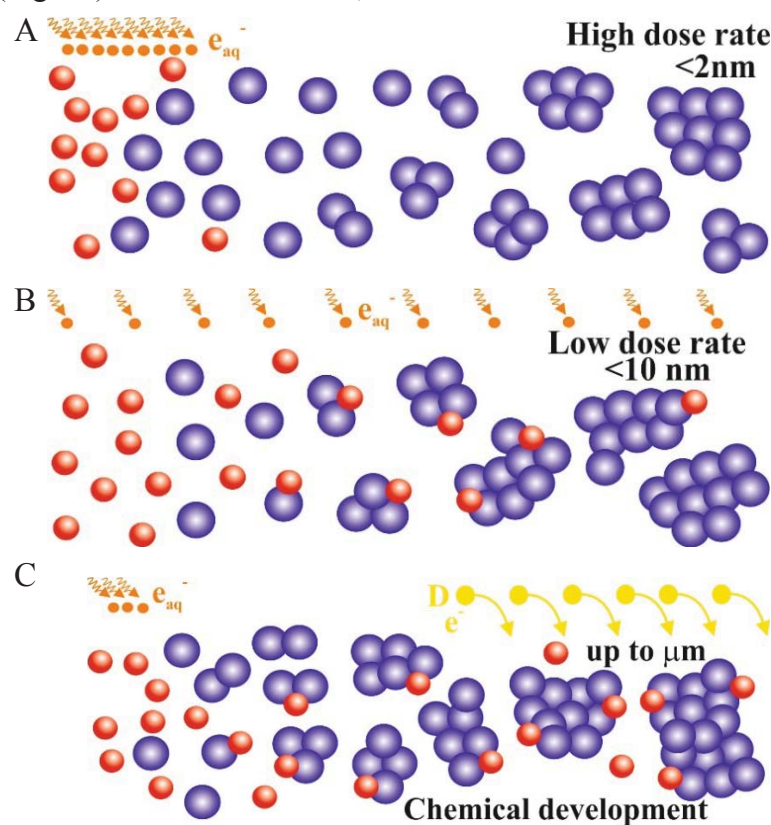


Fig.6. Nucleation and growth of metal clusters generated by radiolytic radicals at high dose rate (A), low dose rate (B) and with an electrons donor D (C).



process are faster than the production rate of the reducing radicals (Fig.6B). When a chemical that can play a role of an electron donor is added, the reduction potential is not negative enough to directly reduce isolated metal ions to atoms. In this case, the reduction of ions adsorbed on the nuclei generated by radiolysis act as seeds. This results in larger clusters being formed (Fig.6C) [22].

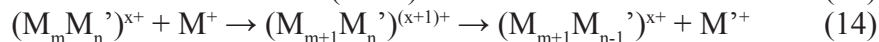
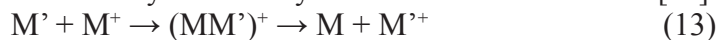
Metal atoms created by irradiation tend to coalesce into oligomers and then continually grow into larger clusters and eventually into precipitates. To prevent this growth, polymers acting as cluster stabilizers (capping agent) are added. Functional groups with a high affinity for the metals (*e.g.*  $-\text{NH}_2$ ,  $-\text{COOH}$  and  $-\text{OH}$ ) ensure the embedding of the molecule at the cluster surface and the polymeric chain protects the cluster from coalescing with a next one through electrostatic repulsion or steric hindrance [22]. Stabilizers should not chemically reduce metals ions bound on the surfaces of clusters. Different polymers, such as poly(vinyl alcohol) (PVA), sodium dodecylsulfate (SDS) [23], sodium polyvinyl sulfate (PVS) [24], polyacrylamide (PAM) or poly(N-methylacrylamide) (PNMAM) [20] and poly(ethylene glycol)s [25] have been used as metal cluster stabilizers. Some ligands (*e.g.*  $\text{CN}^-$ , EDTA – ethylenediaminetetraacetic acid) are also able to stabilize small-sized metal particles, because they are strongly connected with the cluster and prevent their coalescence by electrostatic repulsion. Another possibility for the limitation of the growth of metal nanoparticles is to make them in the presence of a solid support such as silica [14], titanium [26] and alumina. Ionizing radiation is able to penetrate the support and reduce the atoms of the metals to cations embedded on the surface or in the pores or *in situ* everywhere that the ions have diffused.

Bi- and multimetallic nanoparticles, composed of two or more different metal elements, are of greater importance than monometallic ones due to their improved catalytic properties in contrast to single-metal catalysts and to the development of new properties, which may not exist for the monometallic catalysts [27].

The preparation of bimetallic nanoparticles from metal salts can be divided into two groups: co-reduction and successive reduction of two metal salts. These processes yield an alloyed or a core-shell structure. Two ionic precursors of two different metal ions  $\text{M}^+$  and  $\text{M}^{2+}$  can be reduced by radiolytic radicals with equal probabilities:



However a further electron transfer from less noble metal atoms (for example  $\text{M}^0$ ) to more noble metal ions  $\text{M}^+$  systematically favors the reduction into  $\text{M}$  [13].



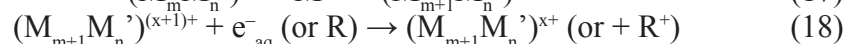
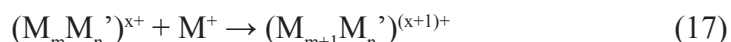
If the ionic precursors are plurivalent, an electron transfer is also possible between the low valences of both metals. This increases the probability of segregation [13]. The less noble metal ions act as an electron relay towards the

noble metal ions. As a result, monometallic clusters,  $M_n$ , are formed first and then, when the  $M^+$  ions are spent,  $M'^+$  ions are reduced at the surface of the  $M_n$ . The result is a core-shell bimetallic cluster where the more noble metal,  $M$ , is covered by the other metal  $M'$ .

Sometimes the inter-metal electron transfer does not occur. Then the initial reduction reactions are followed by mixed coalescence:



and association of atoms and clusters with ions as in reactions (13) and (14) [5]:



Dose rate is a crucial parameter when deciding on the formation of an alloyed cluster or of a core-shell structure since these depend on the kinetic competition between the inter-metal electron transfer and the coalescence process during the radiolytic reduction of mixed metal ion solutions.

### 3.1.3. Carbon nanotubes

A new method using radiation techniques to grow carbon nanotubes was reported in 1996 by Yamamoto *et al.* [28]. In this work, carbon nanotubes were grown using an argon ion beam for the irradiation of an amorphous carbon target under high vacuum condition ( $4 \times 10^{-5}$  Torr) [28]. The incident angle of the ion beam was normal to the target surface and the ion acceleration energy was 3 keV. Nanotubes were produced outside the sputtering region on the target surface after ion irradiation. The tubes had multilayered walls with the distance between carbon layers of 0.34 nm and tube wall thicknesses ranging from 10 to 15 sheets [28].

Single-walled nanotubes (SWNTs) have a diameter that is close to 1 nm, with a tube length that may be many thousands of times longer. The structure of a SWNT can be conceptualized by taking out the one-atom-thick layer from a graphite stack and wrapping it into a seamless cylinder. Single-walled carbon nanotubes have been found to possess the most remarkable electronic and mechanical properties and are used in various nanoscale devices.

Terrones *et al.* demonstrated that single-walled carbon nanotubes can be joined by electron beam irradiation to form molecular junctions [29]. Stable junctions of various geometries have been made *in situ* in a high voltage transmission electron microscope (TEM) with the specimen temperatures at 800°C. After a few minutes of irradiation of two crossing tubes, they consolidate at the point of contact, which results in the formation of a junction with an X shape. The ready-formed X junctions can be manipulated in order to create Y- and T-like molecular connections. The continuous sputtering of carbon atoms from the nanotube body occurs during irradiation, leading to dimensional changes and surface reconstructions [30]. The removal of one of the “arms”

of an X junction generates a Y or T junction by using carefully chosen irradiation conditions. Exposing carbon nanotubes at high temperatures to an electron beam induces structural defects, which promote the joining of tubes *via* the crosslinking of pendant bonds. Junctions can be made *via* vacancies and interstitials, induced by a focused electron beam, to promote the formation of inter-nanotube links. It may now be possible to construct nanotube networks by growing crosslinked SWNTs followed by controlled electron beam irradiation at high temperatures.

#### 3.1.4. Nanocomposites

Nanocomposite material consists of multiple nanoscale materials or a nanoscale material incorporated into a bulk material. The fabrication of nanocomposites has some challenges to make sure there is compatibility of the different material components in order to obtain desirable properties for the nanocomposite. Virtually all types and classes of nanocomposite materials lead to new and improved properties when compared to their macrocomposite counterparts. Nanocomposites can offer new uses in many fields, such as mechanically reinforced lightweight components, non-linear optics, battery cathodes and ionics, nanowires, sensors and other systems [1].

On the basis of their matrices, nanocomposites can be classified into three major categories:

- polymer matrix nanocomposites,
- metal matrix nanocomposites,
- ceramic matrix nanocomposites.

Polymer nanocomposites consist of a polymer or copolymer having nanoparticles or nanofillers dispersed in the polymer matrix. Since many monomers can polymerize upon exposure to gamma rays, monomer polymerization has been used to make nanocrystalline materials [31, 32]. A novel strategy is to synthesize semiconductor/polymer nano-assemblies in a single step at room temperature by gamma irradiation. In general, a metal ion source, chalcogen salt and an organic monomer are mixed homogeneously as a deaerated aqueous solution with an appropriate amount of alcohol, as hydroxyl radical scavenger. The resulting mixture is then subjected to gamma irradiation (irradiation dose –  $10^4$  Gy) leads to the simultaneous formation of nanocrystalline metal chalcogenide particles and the polymerization of the monomers. The metal ion attached onto the surface or inside the polymer microspheres and the chalcogen ion, which is released by decomposition of the salt upon gamma irradiation, a homogeneous dispersion of nanocrystalline metal chalcogenide particles in microsphere polymer matrixes can be precipitated. Nanocomposites are thus formed at room temperature and under ambient pressure without the use of chemical initiators. By appropriate control of the reaction conditions, the gamma irradiation method may be extended to the preparation of a variety of spherical assemblies of metals and of semiconductors/polymer nanocomposites

in aqueous systems. Analogously, several kinds of semiconductor/polymer nanowires have been made in a heterogeneous solution system. In this system, an organic monomer with polar groups can self-organize into amphiphilic supramolecules (micelles, microemulsions, vesicles and monolayers on surfaces), using the difference in the solubility of different fragments in the monomer. Under gamma irradiation, such supramolecules can polymerize to a pre-organized polymer tubule with a hydrophilic core and a hydrophobic sheath. The polymer tubule acts as both a template and a nanoreactor for the following growth of inorganic semiconductor nanowires in the hydrophilic cores from various water soluble systems [33].

Another example of the use of ionizing radiation in making polymer matrix composites is that of producing silver nanostructures in a cotton matrix using electron beam irradiation [12]. Ag-cotton nanocomposites exhibit antibacterial activity against gram-negative and gram-positive bacteria. Cotton samples were placed in silver nitrate solutions of different concentrations and then exposed to the electron beam irradiation using a 10 MeV, 8 kW linear accelerator. Water radiolysis generated very powerful reducing radicals that were able to overcome of the thermodynamic barrier of reducing the single metal ion while in solution. In this way, silver nanoparticles were embedded in the cotton fibers, as shown in Fig.7.

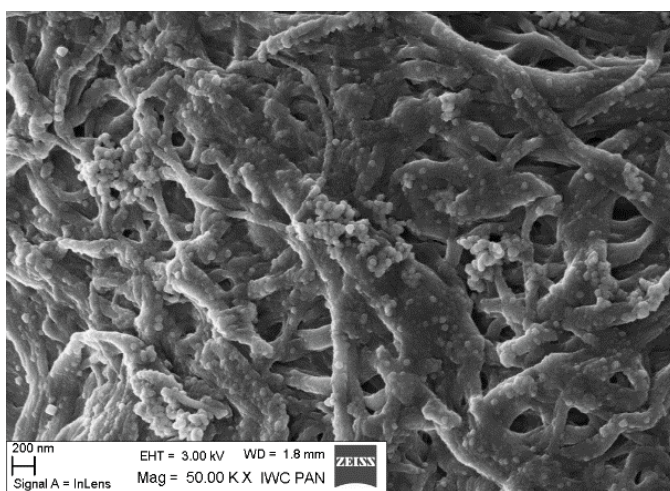


Fig.7. Silver nanoparticles embedded in a cotton matrix.

Among the large number of inorganic layered materials that exhibit intercalation capabilities, layered silicates are one of the most typical because of the versatility of their reactions. In particular, the smectite group of clay minerals, such as montmorillonite, saponite and hectorite, has been used since they have excellent intercalation ability. The combination of clay silicate layers and polymer matrices at the nanoscale level constitutes the basis for preparing an important class of inorganic-organic nanostructured materials.

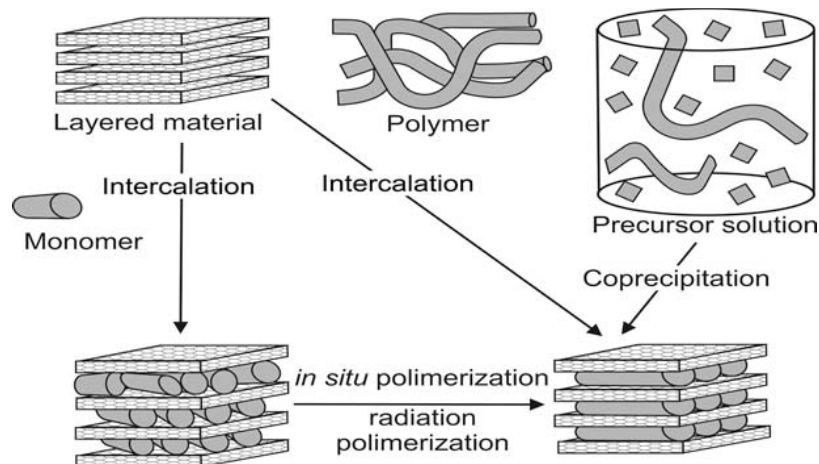


Fig.8. The overall process of preparing nanocomposites based on clay and polymer/monomers.

Clay such as montmorillonite consists of a dioctahedral aluminum sheet sandwiched between two silica tetrahedral sheets in a layered structure that is  $\sim 1$  nm thick (Fig.8). Stacking layers lead to a regular Van der Waal's space between the layers called the interlayer. Clay has the ability to undergo extensive interlayer expansion or swelling, exposing a large active surface area, permitting guest molecules to enter into the interlayer. Interlayer cations such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{K}^+$  exist on the internal surfaces but can be exchanged with alkyl ammonium cations to give surfaces that are less ionic or polar. Such interlayers can be organically modified since they are more easily penetrated by polymers (either in the molten state or in solution) or by monomers which can be subsequently crosslinked or polymerized chemically or by using radiation [34]. In the process of making polymer-clay nanocomposites, it is important to ensure the compatibility of the entering polymer/monomer (hydrophobic) with the clay surface interlayer (ionic) by using intermediates, such as exchangeable organic based cations, intercalation agents or compatibilizers.

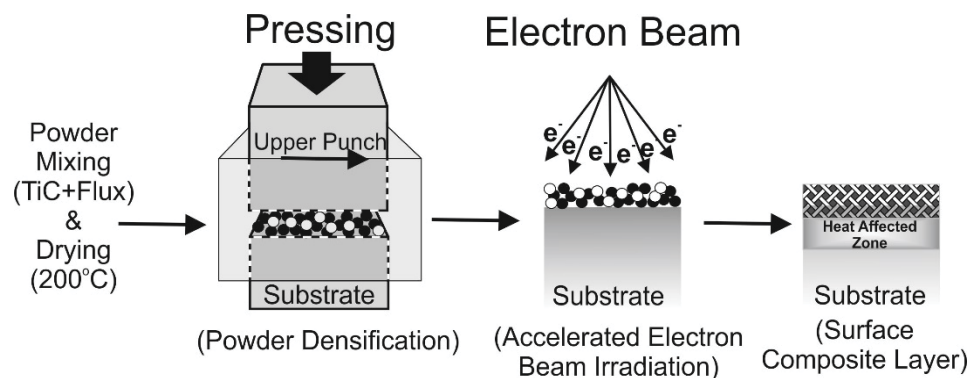


Fig.9. Scheme of the fabrication of TiC-reinforced surface composites [35].

Metal matrix composites reinforced with titanium carbide (TiC) particulates can be fabricated by high energy electron beam irradiation (Fig.9) [34].

A mixture of magnesium oxide (MgO) and calcium oxide (CaO) powders were used as a flux in order to obtain uniform TiC dispersion on a composite surface. Upon electron beam irradiation of a metal surface on which ceramic powders were evenly deposited, the metal surface melts, while the ceramic powders are either partially or completely melted and then precipitated again during solidification, thereby forming a surface composite [35]. Ferrous composites reinforced with TiC show high strength, high elastic modulus, and improved resistance to wear and oxidation.

### 3.2. LITHOGRAPHY

Lithography is the transfer of a pattern from a master slide/plate/mask to another surface. Nanolithography is suitable for use in the nanofabrication of electrical devices, data storage drives, sensors, drug delivery systems, *etc.* The two fundamental characteristics of an imaging system are its resolution (RES) and its depth of focus (DOF). The equations which define these are known as the Rayleigh criterion and are usually expressed as:

$$RES = K_1 \lambda / NA \quad (19)$$

$$DOF = K_2 \lambda / (NA)^2 \quad (20)$$

where  $\lambda$  is the wavelength of the radiation used to carry out the imaging, and NA is the numerical aperture of the imaging system (or camera). These equations show that better resolution can be achieved by reducing  $\lambda$  and/or by increasing NA.

Ultraviolet radiation has been used to create patterns in lithography. The move of semiconductor technology towards the miniaturization of integrated circuits pointed out the limits of photolithography as technique for the fabrication of structures with dimensions on the submicron to nanometer scale. Due to diffraction effects, the resolution of the photolithography process is limited

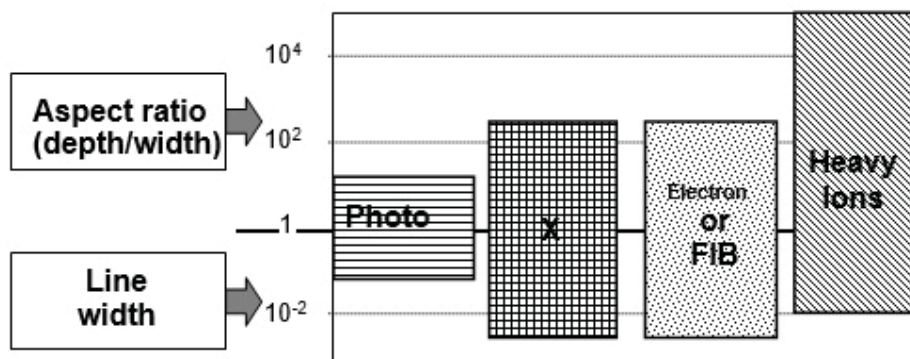


Fig.10. Optical and radiation sources for nanotechnology [36].

to a few microns. To obtain smaller and more precise chips, it was necessary to go to radiation-based technology using X-rays, electron beams and ion beams in order to approach submicron patterning (Fig.10) [36].

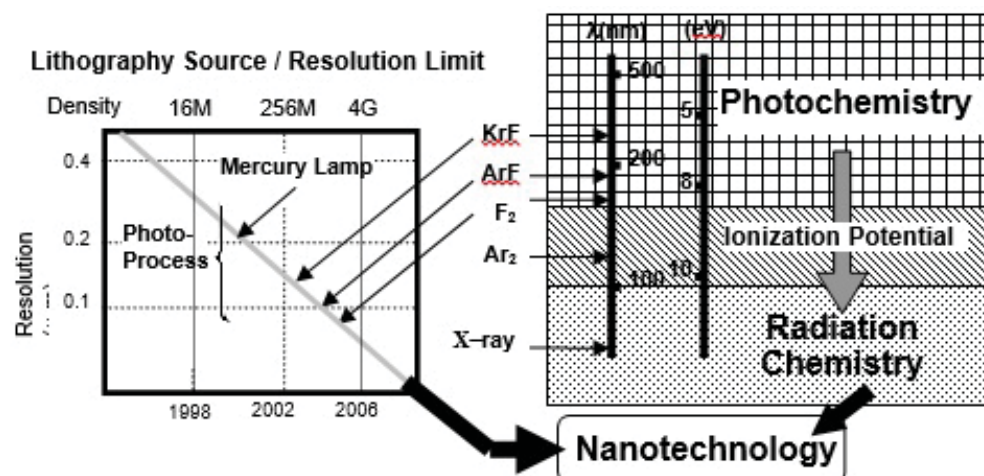


Fig.11. Aspect ratio and resolution limit of various lithographic methods [36].

Figure 11 [36] shows the aspect ratios and resolution limits (line width) of optical and radiation processes. Radiation methods are essential to nanotechnology because of their high resolution and high aspect ratios. Especially, nanofabrication requires electron beam and X-ray processes to attain resolutions lower than 10 nm. X-rays, electron beams, and low energy ion beams, such as electron beam scanning devices and focused ion beam, are useful in nanolithography, and in 3D nanofabrication. Heavy ion beam processes can be used for the fabrication of nanopores and nanowires since they too give high aspect ratio patterns.

### 3.2.1. Electron beam lithography

The concept of electron beam lithography (EBL) is to write patterns on thin films of electron sensitive material using a finely focused (submicrometer diameter) electron beam. The technology is capable of making very complex patterns with very high resolution, almost to the atomic level. EBL is a flexible technique that can work with a variety of materials and an almost infinite number of patterns, but it has some disadvantages, since it is one or more orders of magnitude slower than optical lithography.

Electron beam lithography was originally developed using an electron beam from a scanning or transmission electron microscope (SEM or TEM, respectively) to expose an electron-sensitive resist. A silicon substrate was first oxidized to form a layer of silicon dioxide ( $\text{SiO}_2$ ) several nanometers thick, which was then spin-coated with a uniform layer of polymer (the resist) that was sensitive to ionizing radiation. The beam was controlled by a computer through

a position generator interface which allowed writing any computer-defined patterns on the resist. Films with the desired geometry are made by covering areas where exposure is not wanted with a metallic pattern. Pattern transfer from the resist to the unpatterned SiO<sub>2</sub> film is done by wet or dry etching. Wet etching uses chemical or electrochemical processes to dissolve and remove the exposed areas of SiO<sub>2</sub>. In dry etching, either ion bombardment (sputter etching) or plasma etching with activate species (ions, atoms, free radicals) is used to remove the unwanted materials. These dry etching processes can produce straight and sharp pattern edges with a better resolution. Thus, dry etching is more useful for patterning ultrafine nanostructures.

Three key parameters of the source are: (i) the virtual source size, (ii) its brightness (expressed in A·cm<sup>-2</sup>·sr<sup>-1</sup>), and (iii) the energy spread of the emitted electrons (measured in eV). As electrons penetrate the resist, they undergo a series of low energy elastic collisions, which deflect the electrons slightly. This results in beam broadening that increases with thickness. This effect is more significant at low incident energies [37]. Most of the electrons pass entirely through the resist and penetrate into the depth of the substrate. However part of those electrons will eventually undergo large angle scattering (backscattering). At higher energies, backscattered electrons can cause exposure microns away [38] from where the beam entered. This is related with the so-called proximity effect [39] where electrons writing a feature at one location increase the exposure at a nearby feature, causing pattern distortion and overexposure [40].

Backscattering can be minimized by exposing a thin membrane substrate. With sufficient exposure, the polymer chains in the resist are either broken (positive resist) or become crosslinked (negative resist), thus forming a positive or a negative image of the mask. After irradiation, the resist is developed to form the desired pattern, which, through an etching process, is then transferred onto the substrate.

The 3D nanopatterning and nanofabrication, called also stereolithography (SL), can be conducted by exposing a three-dimensional object to an electron beam. A special drive is needed to rotate the sample and the use of electron beam nanolithography, which has resolution 100 times higher than that which can be obtained using optical or X-ray sources. This results in reasonably fast 3D fabrication and patterning. One key technique is to rotate a 3D sample in such a way that any of its faces can be exposed to the electron beam. Another key technique is focusing the beam on a 3D sample. The height (Z coordinate) and horizontal position (X and Y coordinates) of any point on a sample must be determined. To measure the height, a confocal laser microscope has been used. A height map of the sample enables the height of any point on the sample to be determined, even if the sample is rotated [36].



### 3.2.2. X-ray and ion beam lithography

X-ray lithography uses X-rays from a synchrotron radiation facility or rays from a laser-induced plasma. Similar to electron beam lithography, the sample is covered with a resist layer of high sensitivity to X-rays and then exposed to the synchrotron X-radiation. Between the radiation source and the sample, at a few micrometers above the resist layer, a mask, having the same feature sizes as what will be made, is placed to define the pattern. X-ray masks are usually made of very thin (about 2  $\mu\text{m}$ ) films of silicon carbide, covered by a metal pattern having the desired geometry that is made of high-Z absorber material to prevent unwanted X-ray exposure of the sample. After irradiation, the resist is developed to yield the desired pattern, which, through an etching process, is then transferred onto the substrate. Both electron beam and X-ray lithography are capable of patterning down to lines and spaces well under 70 nm.

As with electron beams, ion beams can be used for the direct writing of nanostructure patterns on a surface being processed. Both electron and ion beams can be easily focused down to a narrow size, as small as a few nanometers, using electromagnetic lenses. Once focused, they can also be scanned across a surface with great precision. Focused beams can be computer controlled to reproduce a digitally stored image by rastering across the substrate without the need of resists or masks. This is useful in producing nanostructures which have high feature fidelity.

## 4. CONCLUSIONS

The ability to produce materials and structures with very high, nanometric precision is basic to the development of nanotechnology. Ionizing radiation is very powerful tool that can be used in this field. Radiation-based techniques using X-rays, electron beams and ion beams play important role in micropatterning. Another use of radiation in nanotechnology is making different nanostructures and nanocomposites. The use of ionizing radiation in nanotechnology has led to the development of new materials and advanced products for different branches of industry.

## REFERENCES

- [1]. Chmielewski, A.G., Chmielewska, D.K., Michalik, J., & Sampa, M.H. (2007). Prospects and challenges in application of gamma, electron and ion beams in processing of nanomaterials. *Nucl. Instrum. Meth. Phys. Res. B*, 265, 339-346. DOI: 10.1016/j.nimb.2007.08.069.

- [2]. Whitesides, G.M. (2003). The ‘right’ size in nanobiotechnology. *Nat. Biotechnol.*, *21*, 1161-1165. DOI: 10.1038/nbt872.
- [3]. Nimesh, S. (2013). *Gene therapy. Potential applications of nanotechnology*. UK: Woodhead Publishing Limited.
- [4]. Valcárcel, M., & López-Lorente, A.I. (2014). Gold nanoparticles in analytical chemistry. In D. Barcelo (Ed.), *Comprehensive analytical chemistry* (pp. 3-35). Amsterdam: Elsevier.
- [5]. Lopez-Lorente, A.I., Simonet, B.M., & Valcarcel, M. (2012). Determination of nanoparticles in biological matrices. *Front. Biosci.*, *4*(3), 1024-1042. DOI: 10.2741/438.
- [6]. The Royal Society & The Royal Academy of Engineering. (2004, July). *Nano-science and nanotechnologies*. Retrieved October 21, 2015, from <http://www.nanotec.org.uk/report/chapter3.pdf>.
- [7]. Daniszewska, A., Lojkowski, W., Fecht, H., Kurzydłowski, K.J., Narkiewicz, U., Salishchev, G.A., Zehetbauer, M.J., Kulczyk, M., Chmielecka, M., & Kuzmenko, D. (2006). Metallic nano-materials and nanostructures: Development of technology roadmap. *Solid State Phenom.*, *114*, 345-391. DOI: 10.4028/www.scientific.net/SSP.114.345.
- [8]. Maekawa, Y., Koshikawa, H., & Yoshida, M. (2004). Anisotropically conducting films consisting of sub-micron copper wires in the ion track membranes of poly(ethylene terephthalate). *Polymer*, *45*, 2291-2295. DOI: 10.1016/j.polymer.2003.11.011.
- [9]. Arabatzis, I.M., Stergiopoulos, T., Bernard, M.C., Labou, D., Neophytides, S.G., & Falaras, P. (2003). Silver-modified titanium dioxide thin films for efficient photodegradation of methyl orange. *Appl. Catal. B-Environ.*, *42*(2), 187-201. DOI: 10.1016/S0926-3373(02)00233-3.
- [10]. Shipway, N.A., Katz, E., & Willner, I. (2000). Nanoparticle array on surfaces for electronic, optical and sensor applications. *Chem. Phys. Chem.*, *1*(1), 18-52. DOI: 10.1002/1439-7641(20000804)1:1<18::AID-CPHC18>3.0.CO;2-L.
- [11]. Haes, A.J., Zou, S., Schatz, G.C., & Van Duyne, R.P. (2004). Nanoscale optical biosensor: short range distance dependence of the localized surface plasmon resonance of noble metal nanoparticles. *J. Phys. Chem. B*, *108*(22), 6961-6968. DOI: 10.1021/jp036261n.
- [12]. Chmielewska, D., & Sartowska, B. (2012). Radiation synthesis of silver nanostructures in cotton matrix. *Radiat. Phys. Chem.*, *81*, 1244-1248. DOI: 10.1016/j.radphyschem.2011.11.067.
- [13]. Belloni, J., Mostafavi, M., Remita, H., Marignier, J.L., & Delcourt, M.O. (1998). Radiation-induced synthesis of mono- and multi-metallic nanocolloids and clusters. *New J. Chem.*, *22*, 1239-1255.
- [14]. Ramnani, S.P., Biswal, J., & Sabharwal, S. (2007). Synthesis of silver nanoparticles supported on silica aerogel using gamma radiolysis. *Radiat. Phys. Chem.*, *76*, 1290-1294. DOI: 10.1016/j.radphyschem.2007.02.074.
- [15]. Marignier, J.L. (1987). *Synthesis of metal nanoaggregates induced by ionizing radiations, structure and thermodynamical properties*. Thesis of “Doctorat d’Etat”, Paris-Sud University, Orsay.

- [16]. Ershov, B.G., & Sukhov, N.L. (1990). A pulse radiolysis study of the process of the colloidal metal formation in aqueous solutions. *Radiat. Phys. Chem.*, *36*(2), 93-97. DOI: 10.1016/1359-0197(90)90220-C.
- [17]. Marignier, J.L. Belloni, J., Delcourt, M.O., & Chevalier, J.P. (1985). Microaggregates of non-noble metals and bimetallic alloys prepared by radiation-induced reduction. *Nature*, *317*, 344-345. DOI: 10.1038/317344a0.
- [18]. Liu, Y., Chen, S., Zhong, L., & Wu, G. (2009). Preparation of high-stable silver nanoparticle dispersion by using sodium alginate as a stabilizer under gamma radiation. *Radiat. Phys. Chem.*, *78*, 251-255. DOI: 10.1016/j.radphyschem.2009.01.003.
- [19]. Mosseri, S., Henglein, A., & Janata, E. (1989). Reduction of dicyanoaurate (I) in aqueous solution: formation of nonmetallic clusters and colloidal gold. *J. Phys. Chem.*, *93*(18), 6791-6795. DOI: 10.1021/j100355a042.
- [20]. Rafaeloff, R., Haruvy, Y., Binenboym, J., Baruch, G., & Rajbenbach, L.A. (1983). Radiolytic method of preparation of colloidal redox catalysts and their application in light-induced hydrogen generation from water. *J. Mol. Catal.*, *22*(20), 219-233. DOI: 10.1016/0304-5102(83)83028-4.
- [21]. Buxton, G.V. (2008). An overview of the radiation chemistry of liquids. In M. Spothem-Maurizot, M. Mostafavi, T. Douki & J. Belloni (Eds.), *Radiation chemistry: From basics to applications in material and life science* (pp. 3-16). France: EDP Science.
- [22]. Belloni, J., & Remita, H. (2008). Metal clusters and nanomaterials. In M. Spothem-Maurizot, M. Mostafavi, T. Douki & J. Belloni (Eds.), *Radiation chemistry: From basics to applications in material and life science* (pp. 97-116). France: EDP Science.
- [23]. Henglein, A. (1979). Reactions of organic free radicals at colloidal silver in aqueous solution. Electron pool effect and water decomposition. *J. Phys. Chem.*, *83*(17), 2209-2216. DOI: 10.1021/j100480a006.
- [24]. Jonah, C.D., Matheson, M.S., & Meisel, D. (1977). Polyelectrolyte effects on rates of hydrated electrons. *J. Phys. Chem.*, *81*(19), 1805-1810. DOI: 10.1021/j100534a003.
- [25]. Graetzel, M. (1981). Artificial photosynthesis: water cleavage into hydrogen and oxygen by visible light. *Acc. Chem. Res.*, *14*(12), 376-384. DOI: 10.1021/ar00072a003.
- [26]. Hou, X.-G., & Liu, A.-D. (2008). Modification of photocatalytic TiO<sub>2</sub> thin films by electron beam irradiation. *Radiat. Phys. Chem.*, *77*, 345-351. DOI: 10.1016/j.radphyschem.2007.04.003.
- [27]. Toshima, N., & Yonezawa, T. (1998). Bimetallic nanoparticles—novel materials for chemical and physical applications. *New J. Chem.*, *22*, 1179-1201. DOI: 10.1039/A805753B.
- [28]. Yamamoto, K., Koga, Y., Fujiwara, S., & Kubota, M. (1996). New method of carbon nanotube growth by ion beam irradiation. *Appl. Phys. Lett.*, *69*(27), 4174-4175. DOI: 10.1063/1.116976.
- [29]. Terrones, M., Banhart, F., Grobert, N., Charlier, J.-C., Terrones, H., & Ajayan, P.M. (2002). Molecular junctions by joining single-walled carbon nanotubes. *Phys. Rev. Lett.*, *89*(7), 075505-1-075505-4. DOI: 10.1103/PhysRevLett.89.075505.

- [30]. Ajayan, P.M., Ravikumar, V., & Charlier, J.-C. (1998). Surface reconstructions and dimensional changes in single-walled carbon nanotubes. *Phys. Rev. Lett.*, *81*(7), 1437-1440. DOI: 10.1103/PhysRevLett.81.1437.
- [31]. Zhu, Y.J., Qian, Y.T., Zhang, M.W., Chen, Z.Y., & Xu, D.F. (1994). Preparation and characterization of nanocrystalline powders of cuprous oxide by using C-radiation. *Mater. Res. Bull.*, *29*, 377-383. DOI: 10.1016/0025-5408(94)90070-1.
- [32]. Zhu, Y.J., Qian, Y.T., Li, X.J., & Zhang, M.W. (1997).  $\gamma$ -radiation synthesis and characterization of polyacrylamide-silver nanocomposites. *Chem. Commun.*, *12*, 1081-1082. DOI: 10.1039/A702946B.
- [33]. Liu, H.R., Ge, X.W., Zhu, Y.J., Xu, X.L., Zhang, Z.C., & Zhang, M.W. (2000). Synthesis and characterization of polyacrylamide-nickel amorphous nanocomposites by  $\gamma$ -irradiation. *Mater. Lett.*, *46*(4), 205-208. DOI: 10.1016/S0167-577X(00)00170-1.
- [34]. Komori, Y., & Kuroda, K. (2000). Layered silicate-polymer interlocation composites. In T.J. Pinnavia & G.W. Bell (Eds.), *Polymer-clay nanocomposites* (pp. 3-18). New York: J. Wiley & Sons.
- [35]. Choo, S.-H., Lee, S., & Kwon, S.-J. (1999). Effect of flux addition on the microstructure and hardness of TiC-reinforced ferrous surface composite layers fabricated by high-energy electron beam irradiation. *Metall. Mater. Trans. A*, *30*(12), 3131-3141. DOI: 10.1007/s11661-999-0224-4.
- [36]. Maekawa, Y. (2004). Nanotechnology and nanolithography using radiation technique in Japan. In *Emerging applications of radiation in nanotechnology, Proceedings of a consultants meeting held in Bologna, 22-25 March 2004* (pp. 221-232). Vienna: IAEA. (IAEA-TECDOC-1438).
- [37]. Lee, Y.H., Browning, R., Maluf, N., Owen, G., & Pease, R.F.W. (1992). Low voltage alternative for electron beam lithography. *J. Vac. Sci. Technol. B*, *10*, 3094-3098. DOI: 10.1116/1.585935.
- [38]. Kamp, M., Emmerling, M., Kuhn, S., & Forchel, A. (1999). Nanolithography using a 100 kV electron beam lithography system with a Schottky emitter. *J. Vac. Sci. Technol. B*, *17*, 86-89. DOI: 10.1116/1.590520.
- [39]. Chang, T.H.P. (1975). Proximity effect in electron-beam lithography. *J. Vac. Sci. Technol.*, *12*, 1271-1275. DOI: 10.1116/1.568515.
- [40]. Mohammad, M.A., Muhammad, M., Dew, S.K., & Stepanova, M. (2012). Fundamentals of electron beam exposure and development. In M. Stepanova & S.K. Dew (Eds.), *Nanofabrication* (pp. 11-41). Wien: Springer-Verlag.