International Journal of Engineering Innovation & Research
Volume 3, Issue 5, ISSN: 2277 – 5668

Nanobiomaterials for Environmental Protection: State of the Art, Applications and Modeling

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Abstract – **The environmental protection constitutes one of the pillars of the possible cohabitation between sustainable development and livable community in a modern society. Thanks to their ability to improve some characteristics of the material (such as strength, chemical reactivity and conductivity), nanomaterials are already widely used in a lot of applications, from toothpaste to batteries, from paints to the clothing. These materials are today able to significantly contribute to the industrial development in areas as the energy efficiency, transport and environmental protection. The responsibility for ensuring the safe use of nanomaterials is a primary need for the protection of public health.In this work a state of the art of the current nanobiotechnological applications to the environmental protectionare taken into account and important characteristics of nanomaterials are considered through a new appeared theoretical model, for possible future positive developments.**

Keywords **– Environment, Nano-Bio-Devices, Nano-Bio-Materials, Technologies, Theoretical Modelling.**

I. Introduction

Nanomaterials are materials whose main components have a size between 1 and 100 nanometers, according to a recommendation adopted by the European Commission. This marks an important step towards a great protection for citizens, defining clearly what materials require special treatment through a special legislation.The European Union (EU) proposed for first a unique definition for nanomaterials, to be used for regulatory purposes, and based on scientific contributions and an extensive global consultation. The industry needs a clear and consistent regulatory framework for this important sector of the economy and consumers deserve accurate information about these substances; it is an important step in addressing the potential risks to the environment and the human health, while ensuring that this technology can achieve its full potential [1,2].

Nanomaterials are already used in hundreds of applications and consumer goods; the development of these innovative materials is an important driver of European competitiveness, with a significant potential for progress in areas such as medicine, environmental protection and energy efficiency.

The adopted definition is based on an approach that takes into account the size of the particles that constitute the material, rather than the risk or danger [3]. The statement defines nanomaterials a natural material, accessory or artificial, containing particles, in free state or in the form of aggregate or as an agglomerate and where at least 50% of such particles in the class of numerical distribution has one or more external dimensions in the class size of 1-100 nm.

The focus on nanotechnology in public discussion has increased over the past few years. Nanotechnology is considered to be one of the key future technologies. The aim of this work is to present a broad overview of already applicable and upcoming solutions for environmental protection, so as important theoretical advances for the ideation of new high efficient nanobiodevices. It was checked how the potential benefits and impact on the environment for nanotechnology products and processes are certainly higher if compared with those of conventional solutions [4].

II. Nanomaterials and Environmental Protection

As a result of the current research, a lot of nanotechnology solutions were identified for the sector of environmental protection; among the most interesting, we indicate:

A) Air treatment [5,6]

A_1) Active filters for air conditioners: systems with photocatalytic TiO_2anatase nanoparticles. The main feature consists from photocatalytic activity stimulated by sunlight or lamps. Nanoparticles emit electronegative charges on the surface when they are stimulated by UV rays and direct sunlight. The electronegativity of surface promotes the oxidation (photocatalysis) of organic substances, that are located near the surface, with co-absorption of the dirt after surface redox, purifying the surrounding air. This action remains active.

A_2) Anti-smog cement: photocatalytic active principles for cement products, which can reduce organic and inorganic pollutants present in the air. The researchers calculated that the coating with such products could reduce pollution by about 50%, in particular in the big cities.

A_3) Filtration/separation: in the cars industry filter media lined with nanofibres are frequently used in filters for passenger cabin air. Nanofibre-coated filter media are also applied for air filtration (e.g. dust removal) at industrial plants and for filtration of the inlet air for gas turbines. Research focused also on the development and optimization of nanostructured membranes for CO_2 capture from power plant flue gases.

A_4) Cabin-air filters for passenger cars: in this case cabin-air combination filters for passenger cars, including a coating of nanofibres, were compared with conventional combination filters; product-specific information and test data from the cooperation partners are used.

In terms of fuel savings and CO_2 potential reduction, initial assessments showed interesting advantages for the nano-based filter medium in comparison with the

International Journal of Engineering Innovation & Research
Volume 3, Issue 5, ISSN: 2277 – 5668

conventional one, illustrating the potential benefits for the environment which can result by the use of nanofibres in cabin-air filters. The filter with nanotechnology showed advantages in terms of potential benefits for the environment.

B) Water treatment [7,8]

Advances in nanoscale science and engineering suggest that many of the current problems involving water quality could be resolved or greatly improved using nanosorbents, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes and nanoparticle enhanced filtration among other products and processes resulting from the development of nanotechnology. Innovations in the development of novel technologies to desalinate water are among the most exciting and promising. Additionally, nanotechnology-derived products, which can reduce the concentrations of toxic compounds to sub-ppb levels, are of increasing importance in the attainment of water quality standards and health advisories. We underline recent advances on the development of novel nanoscale materials and processes for treatment of surface water, groundwater and industrial wastewater contaminated by toxic metal ions, radionuclides, organic and inorganic solutes, bacteria and viruses.

B_1) New crystalline highly reactive nanostructured materials, characterized by graphene planes, that assume within the material a particular structure and conformation giving the material unique properties in terms of capacity of contaminant removal and energetic properties. Nanotechnology is applied also for drinking and waste water treatment and for groundwater remediation.

B_2) Filtration/separation (nanomembranes): as membrane materials, organic polymers and inorganic ceramics are used. Applications of nanofiltration can be found, e.g. in drinking water treatment, in the food industry, as well as in the textile and dyestuff industry. A great potential for nanotechnology is expected also in the field of seawater desalination.

B_3) Surface treatment: many developments have the objective of giving nanomaterials functions, such as specific chemical or mechanical properties. Nano-based coatings may minimize fouling processes and deposits on membranes, in heat exchangers and reactors and on ship hulls.

B_4) Sorption: nano-based sorbents may be used for different water treatment purposes; as an example, we remember the arsenic separation from drinking or wastewater.

B_5) Nanocatalysts: nanoscale TiO_2 is used as a catalyst in waste water treatment. During photocatalysis, the illumination of TiO_2 results in water and oxygen from the air being converted into reactive hydroxyl radicals, breaking down organic pollutants resistant to biological degradation in the water. Further development is focused on applying photocatalysis in countries with strong sunlight and for the treatment of small amounts of slightly polluted water.

B_6) Nanoreagents: several kinds of nanoparticles on the basis of zero-valent iron are used for "in-situ" groundwater remediation. Besides pure nanoiron, also bimetallic nanoparticles and iron nanoparticles on activated carbon have been tested and used for groundwater remediation.

B_7) Solar water treatment: it shows that a long-term operation of the solar plant under given boundary conditions results in a considerably higher potential impact on the environment, when nanoscale TiO_2 is used for photocatalysis.

C) Catalysts [9,10]

C_1) It has developed catalytic silencers for cars, which employ nanotechnology, creating a structure of catalytic materials that substantially reduces the amount ofprecious used metals, such as platinum and palladium. These new developments could allow to reduce the amount of these materials from 70 to 90%, without changing the performance as regards the treatment of the exhaust gases, nor the durability with respect to the conventional catalytic silencers.

C_2) Catalytic converters: a three-way catalytic converter has a stainless steel body containing catalytic material as a layer on a substrate (washcoat); the particles of the noble metal catalyst in the washcoat are substituted by nanoparticles. Research is currently in progress also for minimizing the amount of noble metal, but maintaining the same catalytic performance.

C_3) Nanocatalysts for sustainable air purification are under development. For example, the use of nanomaterials in photocatalytic active cement concrete can produce an air purification in towns.

D) Nanosensors - Environmental monitoring [11-13]

D_1) The possibility of "in situ" monitoring of inorganic pollutants such as heavy metals, to be carried out continuously or at discrete intervals, with transmission of data through the computer network in real time. These kind of nanosensors can allow to carry out electrochemical analysis in situ with a limit of detection similar to that used with equipment in the laboratory. Nanostructured electrochemical sensors for the determination of toxic substances, such as arsenic in water, are in evolution, with interesting characteristics, such as improved ratio signal/background, easy and fast, suitable for "in situ" applications, cheap.

D_2) DNA microarray technology: the application of microarray technology to microbial diagnostics is under development, in particular microarrays developed for microbiological applications, known in the literature under the name of MDMs (Microbial Diagnostic Microarrays). Microarray platforms are suitable for microbiological analysis of samples for environmental monitoring. The microarray platform shows a high degree of specificity in hybridization reactions. It is suitable for the identification of different species of pathogens, both bacteria and viruses. Even for parasites specific probes can be present in the platform.

D_3) Study of biological contamination of sewage and aerosol of water treatment plants, using classical and standardized molecular methodologies and DNA microarrays, which will allow the simultaneous analysis of a variety of genres, species, microbial strains, in terms of both quality and quantity. Increased sensitivity is obtainable through the use of luminescent silica nanoparticles as markers for DNA microarray.

E) Thermal insulation - Nanogel[14,15]

With nanotechnology it is possible the creation of panel systems in transparent polycarbonate airgel-filled skylight. The panels are resistant and energy-saving, with multi-wall sheets of glass characterizing a particular surface treatment. The obtained properties provide total resistance to the degrading effects of UV light.

The combination of polycarbonate and nanogel allows a significantly increase in the thermal performance, without affecting the transmission of light, and creates a polycarbonate panel resistant to condensation. This allows also flexibility in both horizontal and vertical wall alignment, added to the overall design freedom.

F) Packaging - Nanofilm barrier [16,17]

It is possible to realize recyclable nanofilm barriers for food packaging with a “mono-material”, which presents the same characteristics of composite films.

G) Photovoltaics - Processes of manufacture “roll-to-roll” [18-20]

Revolutionary photovoltaic panels have low costs thanks to cells based on a mixture of chemical elements known as CIGS (Copper, Indium, Gallium, Selenide), which guarantees a performance comparable to that of silicon cells, but at much lower cost. The CIGS mixture is printed in the form of ink on a flexible material.

H) Cultural heritage - Restauration and maintenance [21-23]

Plasma treatment of cleaning: the use of nano-lime allows to obviate a number of inconvenience, typical of conventional treatments using conventional lime, such as the incompleteness of the “carbonation” process, the low penetration depth reached, the excessive amount of water brought to the stones and the discoloration of surfaces.

I) Energy [24-28]

I_1) Energy storage system

Thanks to nanotechnology, the ideation of electric vehicles is totally opened. Fully electric vehicles, with reduced maintenance costs by an order of magnitude with respect to that of gasoline, can reach autonomies of hundreds of kilometers with speeds of order of 150 km/h or more. They could be reloaded in service stations in ten minutes or with the house power in some hours. With nanotechnology it is possible also the development and production of lithium-ion battery cells and systems for the automotive industry.

I_2) New roof-systems

Construction of buildings with particular panels of modular composite materials, which are new examples of exploitation of renewable solar energy, with a positive energy balance and costs, if compared with current best construction technologies.

III. Confirmations and New Information’s by a Recent Analytical Model

The dynamics of carriers in a nanostructure is well described by the Drude-Lorentz model [29] and its modifications. Recently it has been appeared a new generalization of the Drude-Lorentz model, based on the complete Fourier transform of the frequency-dependent complex conductivity $\sigma(\omega)$ of the system, able to offer analytical expressions for the most important quantities related to transport phenomena, i.e. the velocities correlation function $<\vec{v}(t)\cdot\vec{v}(0)>_T$ at the temperature *T*, the mean squared deviation of position $R^2(t)=\left\langle[\vec{R}(t)-\vec{R}(0)]^2\right\rangle$ and the diffusion coefficient *D* [30], avoiding time-consuming numerical and simulation procedures. The model is useful both for the study of new nano-based devices with desired characteristics and for testing and obtaining new parameters values by existing experimental data. It has been performed the classical and the quantum version of the model [30,31] and the complete relativistic version is in progress [32,33].

The classical version of the model has been tested in last years with very good fitting in relation to experimental data [34,43]; itgives interesting explanations of the ultra-short times and of high mobilities, with which the charges spread in mesoporous systems, of large interest also in photocatalitic and photovoltaic systems. The new model is in agreement with important existing models, such as the Smith model [44] and the EMT theories [45-47].

The quantum version of the model comprehends the oscillator strength weights, related to the discretized energy levels. It demonstrated high generality and is applicable even in the study of ions, like mass transfer, and solutions, so as in nano-bio-systems, allowing significant applications for the diffusion in nanostructured, porous and cellular materials, so as for biological, medical and nanopiezotronic devices.

The relativistic version of the model keeps into account of the possibility of relativistic velocities of carriers travelling in a nanostructure [32,33].

IV. Discussion and Results

The sensitivity is one of the most interesting feature of a nano-bio-device; it is connected to the rapidity of detection, i.e. to the charge transport inside a nanodevice, and therefore to the values and variations of its diffusivity.

Among the most studied promising nanomaterials at today at theoretical and experimental level, we remember Silicon (Si), Zinc Oxide (ZnO), Titanium Dioxide (TiO_2), Gallium Arsenide (GaAs), Carbon Nanotubes (CNTs), Cadmium Telluride (CdTe), Cadmium Sulfide (CdS), Copper Indium Selenide (CIS), Copper Indium Gallium Selenide (CIGS).

Considering a nanowire-based nano-bio-device, the new model permits an interesting analysis related to the diffusion of every nanomaterial. The obtained results confirm experimental existing results and also offer interesting previsions, of great interest in the development and improvement of new high efficiency nano-bio-sensors and nano-bio-devices.

The diffusion coefficient D related to the new model in the classical version has the following analytical expression [30]:

$$D = \left(\frac{KT}{m^*}\right)(\tau)\left(\frac{1}{\alpha_I}\right)\left(\exp\left(-\frac{1-\alpha_I}{2}\frac{t}{\tau}\right) - \exp\left(-\frac{1+\alpha_I}{2}\frac{t}{\tau}\right)\right), \quad (1)$$

with K the Boltzmann's constant, T the temperature of the system, m^* the effective mass and τ the relaxation time. The parameter of the model α_I is a real number, varying in the interval $[0,1]$, and with the following definition:

$$\alpha_I = \sqrt{1-4\tau^2\omega_0^2} \quad (2)$$

Considering Eq. (1), we note that many variables can influence the diffusion and therefore the sensitivity of a nano-bio-device:

a) the temperature T of the system, directly proportional to D;

b) the parameter $\alpha_I = \alpha_I(\tau, \omega_0)$, i.e. the values of τ and ω_0; $\alpha_I(\tau, \omega_0)$ appears also in the arguments of the exponentials in Eq. (1), affecting therefore also the form of the curve of diffusion;

c) the variation of the effective mass m^* [48], related to the physical and chemical treatments on materials, like the doping. The opto-electronic, photo-electro-chemical, photocatalytic and photoexcited properties can be tuned towards the desired directions by doping different elements; the materials can be engineered towards specific applications, through accurate dopants selection [49,50];

d) the variation of the chiral vector inscribed in (n,m) indices, reflecting in a variation of m^*;

e) at quantum level, the possibility to consider the weights of each mode and to vary the carrier density$N$, in consideration to the relation:

$$\omega_{p_i}^{\ 2} = \frac{4\pi N e^2}{m} f_i, \quad (3)$$

with ω_{p_i} plasma frequencies [31];

f) at relativistic level, the possibility to vary, through a modulation of the carriers velocity [32,33], the initial peak in diffusion and the value of diffusion in time.

As examples of application, it has been considered the behaviour of D in relation to two of the previously indicated nanomaterials, for two different values of τ and α_I. Figs 1 and 2 represent the behaviour of the diffusion in time for CdS and GaAs respectively. The values $\alpha_{I1} = 0.1$, $\alpha_{I2} = 0.9$, $\tau_1 = 10^{-12}\,s$, $\tau_2 = 10^{-13}\,s$ were considered, with the respective effective mass value [51,52].

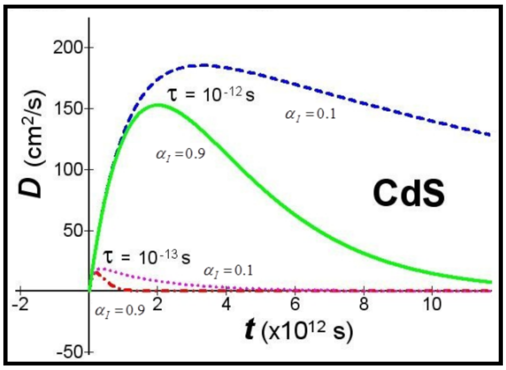

Fig.1. Dvs$t$ for CdS at T = 300 K considering two different values of τ and of α_I (see text); $m^*_{CdS} = 0.22\, m_e$.

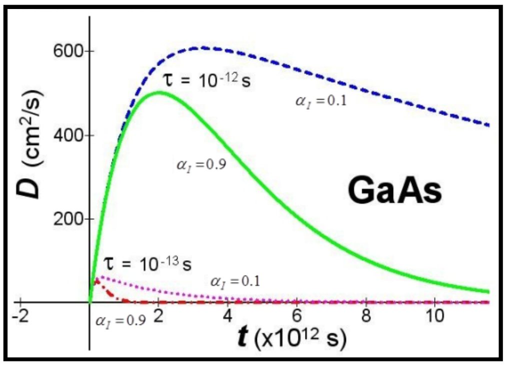

Fig.2. Dvs$t$ for GaAs at T = 300 K considering two different values of τ and of α_I (see text); $m^*_{GaAs} = 0.067\, m_e$.

The parameter α_I changes the form of the curves too, reflecting in a variation of the D-curve aspect.

V. Conclusion

A clean environment is an essential element and a critical resource for the human health. We assist to a rising demands of clean water in the world, in consideration to extended droughts, population growth and stringent health-based regulations. Nanomaterials have a great number of physical and chemical key properties, that make them particularly attractive as suitable materials for an important use in the direction of environment. Nanomaterials can also serve as high capacity/selectivity and recyclable ligands for toxic metal ions, radionuclides, organic and inorganic solutes/anions in aqueous solutions, progressively becoming critical components in all sectors related to the environment protection. For these reasons, the improvement in the ideation and creation of new nano-bio-devices for the environment is as much desirable as mandatory.

Through theoretical studies, the peculiar characteristics of nanomaterial-based devices can be determined. In this direction a new recently appeared theoretical model is offering new possibilities in the determination of the most important functions related to the charge transport at nanolevel. As parameters for varying the performance of nanobiodevices, the analysis indicates the temperature of the system, the variation of the effective mass of carriers inside the nanodevice, the variation of center frequency and relaxation times, the possibility to consider the weights of each mode and to vary the carrier density *N*, if a quantum treatment is considered, the possibility to relativistic velocities of the carriers, also for ultrashort times. The considered nanomaterials can meet, through appropriate combinations of the indicated parameters, a very large spectrum of practical and technological needs, moving towards a safer and cleaner world.

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