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Conceptual study on a new generation of the high-innovative advanced porous and composite nanostructural functional materials with nanofibers

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Education and research trends

ABSTRACT

Purpose: The purpose of the paper is to analyse theoretically the possibilities of the development of a new generation of the high-innovative advanced porous and composite nanostructural functional materials with nanofibers and to study into the material science grounds of synthesis and/or production and formulation of such materials' structure and properties and to characterise and model their structure and properties depending on the compositional, phase and chemical composition and the applied synthesis and/or production and/or processing processes, without the attitude towards any direct practical application or use, but with confirming the highly probable future application areas, using the unexpected effects of formulating such materials' functional properties.

Design/methodology/approach: In general, the study is of priority cognitive importance as theoretical considerations and the author's initial analyses related to technology foresight concerning this group of issues as well as sporadical results of research provided in the literature, usually in its incipient phase, indicating a great need to intensify scientific research, to develop the new groups of materials with quite unexpected predictable effects, resulting from the use of nanofibers for fabricating super advanced composite and porous materials.

Findings: The description of the state of the art for the subject of the study has been limited to the issues initially selected with an analysis with the method of weighted scores.

Practical implications: The outcoming materials may have direct influence on the development of electronics and photonics, medicine and pharmacy, environmental protection, automotive industry, space industry, machine industry, textile and clothing industry, cosmetic industry, agriculture and food sector.

Originality/value: The value of this paper lies in the fact that it proposes a new generation of the high-innovative advanced porous and composite nanostructural functional materials with nanofibers.

Keywords: Materials science and engineering; Nanotechnology; Nanofiber; Composite materials; Porous materials; Nanostructural materials; Functional materials

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1. Introduction

The subject matter of the paper is pursued in the field of nanotechnology as designing and producing structures with new properties resulting from a nanosize [1]. Nanotechnology is regarded as one of the key fields of science in the 21st century and the main driving force of economic and technological advancements in the nearest future [2-7]. The development of nanotechnology will concern all the aspects of our reality and will surely contribute to industrial revolution. For this reason, nanotechnology holds great promise of developing products with unmet advantageous physiochemical properties. The BCC estimates the global market for nanotechnology products at about $15.7 billion in 2010, growing to 2015 with an approximately average compound annual growth rate of 11.1%, including well-established commercial nanomaterials applications [8], such as nanoparticle-based sunscreen products and nanocatalyst thin films for catalytic converters, as well as new technologies, such as nano-thin film solar cells, nanolithographic tools, and nanoscale electronic memory. Sales of nanodevices will experience moderate growth. This market segment will increase at a 45.9% compound annual growth rate to 2015. The largest nanotechnology segments in 2009 were nanomaterials. All nanomaterials will increase with nearly a compound annual growth rate of 14.7% to 2015 [9]. Nanostructural materials, being the main item of interest in nanotechnology, represent a class of materials where the size of atomic aggregates (crystalline grains, phases with specific composition, amorphous aggregates) is between 1 to 100 nm. Basically, they can be grouped into zero-size nanostructures (e.g. nanoparticles, nanocrystals, quantum points), one-dimensional (e.g. nanofibers, nanotubes, nanowires), two-dimensional (nanolayers) and special nanomaterials – considered to be a separate group or a special kind of zero-, one- or two-dimensional nanostructures (fullerenes, carbon nanotubes, nanoporous materials). One-dimensional nanostructures are defined as objects whose dimensions exceed the value of 100 nm in one direction only. There are many expressions used in the literature to describe one-dimensional nanostructures, notably: nanowhiskers, nanofibers, nanorods, nanowires, nanotubes. Some of them are used alternately, the usage of others is limited to structures having specific characteristics (e.g. nanotubes are hollow inside). It is generally accepted in this group that "nanowhiskers" and "nanorods" are characterised by much smaller length than the other structures. The term nanofiber is used further in this paper for all one-dimensional nanostructures, except when such term would cause ambiguity.

Nanofibers generate a great interest in certain industry segments, where alternative materials are characterised by limited performance or a much higher unit price (a good example is the utilisation of carbon nanofibers as complementary to carbon nanotubes for electron emitters in flat panel displays) [10]. Sales of nanofiber-based products are projected to continue growing at a very healthy rate during the next 5 years, driven by further penetration of nanofibers in the above sectors and by various newer, high-tech applications that are entering mainstream commercialisation in other fields such as the consumer and medical/biological/ pharmaceutical sectors. The global market for nanofiber products is forecast to grow at a compound annual growth rate of 34.3% through 2015, and at a 37.2% from 2015 through 2020, reaching nearly $2.2 billion in total revenues by 2020 [9]. The mechanical/chemical sector is estimated to account for 73.2% of all revenues in 2010. This sector is forecast to grow at a compound annual growth rate of 33.4% from 2010 through 2015, and a compound annual growth rate of 35.3% from 2015 through 2020. Electronics is the fastest growing segment, increasing at a compound annual growth rate of 45.3% from 2010 through 2015, and a compound annual growth rate of 50.7% from 2015 through 2020 [11].

The purpose of the paper is to analyse theoretically the possibilities of the development of a new generation of the high-innovative advanced porous and composite nanostructural functional materials with nanofibers and to study into the material science grounds of synthesis and/or production and formulation of such materials' structure and properties and to characterise and model their structure and properties depending on the compositional, phase and chemical composition and the applied synthesis and/or production and/or processing processes, with confirming the highly probable future application areas, using the unexpected effects of formulating such materials' functional properties. An unexpected effect is a meaning as a concept introduced from patent practice, meaning a case where seemingly known actions, materials or technologies are applied in a new, unknown manner, e.g. by changing the sequence of manufacturing operations or changing the composition or sequence of structural or phase components or elements forming composite materials or, as is the case here, by reducing the same scale many times – they offer a completely new group of properties, unachievable with the known, conventional or repetitive actions.

2. General characterisation of porous and composite functional nanostructural materials with nanofibers

Special characteristics of nanofibers justify a search for new uses for such materials. The characteristic that is decisive for their unique properties, i.e. a diameter of not more than 100 nm, is now also very often a barrier for application at a scale greater than laboratory research. Efforts are being made for this reason to produce hierarchical, three-dimensional structures and to combine them with other materials, i.e. to produce nanocomposite materials. By 2014, the market of global consumption of nanocomposites should exceed a compound annual growth rate of 27.1%. Global consumption of clay-based nanocomposites will exceed a compound annual growth rate of 32.2%. The total world market for ceramic-containing nanocomposites is expected to grow to 2014 [12] with a compound annual growth rate 12.5%. Nanoporous materials made up of polymeric nanofibres can be considered here (as is the case in this paper) to be a special kind of nanocomposite material where the function of matrix is played by empty space (air, vacuum). The properties of nanocomposites are determined by the properties of their matrix, the properties of the reinforcing phase, the geometry of the reinforcing phase

Table 1.
Potential, new properties of porous and composite functional nanostructural materials with nanofibers and the potential areas of application

Type of nanofibers	Matrix material	Potential, new properties resulting from combining nanocomposite components	Potential area of interest
Carbon nanofibers	metal	improvement of mechanical properties, improvement of thermal and electric conductivity	automotive industry, aviation industry, space industry
	ceramics	improvement of thermal and electric conductivity	electronics and photonics, medicine, automotive industry, space industry, machine industry
	polymer	improvement of electric properties, possible development of hierarchical structure	electronics and photonics, medicine, automotive industry, textile and clothes industry
	air	possible development of hierarchical structure, higher porosity	electronics and photonics, medicine and pharmacy, environment protection
Polymer nanofibers	metal	higher porosity (after removing nanofibers)	electronics, medicine, environment protection, automotive industry, space industry
	ceramics	higher porosity (after removing nanofibers)	electronics , medicine, environment protection, automotive industry, space industry
	polymer	improvement of mechanical properties, bacteriocidity, absorptivity, porosity, resistance to chemical factors, possible development of hierarchical structure	electronics and photonics, medicine and pharmacy, environment protection, automotive industry, textile and clothes industry
	air	improvement of mechanical properties, bacteriocidity, absorptivity, porosity, resistance to chemical factors, possible development of hierarchical structure	electronics and photonics, medicine and pharmacy, environment protection, automotive industry, textile and clothes industry
Inorganic nanofibers	metal	improvement of mechanical properties	automotive industry, space industry, machine industry
	ceramics	improvement of mechanical properties, improvement of thermal and electric conductivity	medicine, automotive industry, space industry, machine industry
	polymer	improvement of mechanical properties, improvement of thermal and electric conductivity, possible development of hierarchical structure	electronics and photonics, medicine and pharmacy, automotive industry
	air	possible development of hierarchical structure	environment protection

Table 2.
The types of nanofibers used for producing porous and composite functional nanostructural materials

Type of nanofibers	Morphology	Structure
Polymer nanofibers	• full nanofibers, • hollow nanofibers, • coaxial nanofibers, • nanofibers containing liquid capsules, • porous nanofibers	• amorphous • semicrystalline

Carbon nanofibers	• full nanofibers,
	• hollow nanofibers,
	• porous nanofibers
		• amorphous
		• crystalline
		  • single walled
		  • multi walled

Inorganic nanofibers	• full nanofibers, • hollow nanofibers, • porous nanofibers • coaxial nanofibers,	• amorphous • polycrystalline • crystalline

(quantity/number, length, diameter, structure and orientation of fibres) and the quality of linkage between the matrix and the reinforcing phase. Potentially, the new properties resulting from combining nanocomposite components are presented in (Table 1), where the areas of potential applications for such conceived materials are shown. An opportunity of producing new materials featuring innovative properties is offered by appropriate selection and correct application of different matrix materials (metallic, ceramic, polymer or air), the use of nanofibers with a diverse chemical composition, structure and morphology (Table 2), the use of the available technologies or developing new ones for producing composites (Table 3) and using the available or developing new technologies for the modification of nanofiber structure and surface and other processes leading to the improved

Table 3.
Key technologies of producing porous and composite functional nanostructural materials

Powder metallurgy	Mechanical alloying and sintering Mixing/mechanical alloying and hot pressing Spark plasma sintering Deformation processing of powder compacts
Melting and solidification	Casting Metal infiltration Melt-blending Melt-mixing Melt-compounding Melt spinning Laser deposition
Thermal spray	Plasma spraying and HVOF Cold spraying
Electrochemical deposition	Electrodeposition Electroless deposition
Electrospinning	Melting electrospinning Solution electrospinning Coaxial electrospinning
Chemical	Solution processing In-situ polymerisation Heterocoagulation
Others	Molecular level mixing Sputtering techniques Sandwich processing Torsion welding Vapour deposition Mixing as paste Nano-scale dispersion

Table 4.
Nanofibers structure and surface modification technologies and other processes leading to better combination / improved wettability / adhesion of components of the produced nanostructural composite materials

Type of nanofibers	**Modification technology/process**
Polymer nanofibers	Functionalisation – joining the function groups Polymeric layer deposition Metallic layer deposition Reductive post-reaction Gas-phase post-reaction Decoration or exocomposite nanofibers (dry methods, wet methods)
Carbon nanofibers	Metallic layer deposition Polymeric layer deposition Functionalisation – joining the function groups Graphitisation
Inorganic nanofibers	Metallic layer deposition Functionalisation – joining the function groups Improvement of crystalline structure

connection / improved wettability / adhesion of composite nanostructural materials components (Table 4), as well as using the available and modifying the known methods of nanofibers production. At present, many methods are used to produce nanofibers and the most important ones include (Table 6): Spontaneous Growth, Template-based Synthesis, Electrospinning and Lithography. The first three methods are classified as bottom-up techniques, whereas lithography is classified as top-down technique. The structure of produced nanofibers depends on the selected method – Spontaneous Growth allows to formulate crystalline nanostructures, whereas Template-based Synthesis usually leads to the formulation of polycrystalline and amorphous structures.

Table 5.
Key nanofibers fabrication methods

Manufacturing process type	
Spontaneous Growth	Evaporation (Dissolution)-Condensation Growth
	Vapour (or Solution)-Liquid-Solid (VLS or SLS) Growth
	Stress-induced Recrystallization
Template-based Synthesis	Electrochemical Deposition
	Electrophoretic Deposition
	Template Filling
	Converting through Chemical Reactions
Electrospinning	Melting Electrospinning Solution Electrospinning
Drawing Phase Separation Template Synthesis Self – Assembly	
Lithography	

Table 6.
Detailed criteria for evaluating the attractiveness and potential of the individual nanostructural composites

No.	Criterion	Weight
	Potential	
1	Possibility of achieving unusual properties resulting from nanosize that cannot be achieved traditionally	0.3
2	Possibility of eliminating important defects / limitations in matrix material	0.1
3	Possibility of significant miniaturisation (construction of devices sized approx. a micrometer)	0.25
4	Possibility of producing materials with unusual resistance to external factors unachievable with traditional methods (chemical factors, extreme temperatures, loads ….)	0.25
5	Availability of manufacturing equipment for production and research apparatuses for characterisation	0.1
	Total criteria 1-5	1.00
	Attractiveness	
1	Positive impact on health and natural environment (bacteriocidity, smaller allergenicity, smaller toxicity, biodegradability, ….)	0.25
2	Considerable reduction in manufacturing costs	0.1
3	Large improvement of aesthetic values and usage convenience of the products produced	0.25
4	Significant improvement in durability of produced materials and recyclability	0.25
5	High improvement of mechanical properties of materials produced	0.15
	Total criteria 1-5	1.00

3. Selection of the most interesting area of the study

The presented information indicates a very broad scope of scientific focus included in the presented research concept (Table 1) that requires launching a very extensive, costly and long-term research programme to study into all the aspects of developing so many new groups of nanocomposite materials with nanofibers. In such a case it is reasonable to limit the scope of the study to selected areas only that can be solved under the study in a question with the adequately high success indicator. Although the full potential of forecasting resulting from the foresight methodology cannot be applied at present, however, by using the Authors' experience, it has been possible to use some of the methods to narrow down the area of the study to 3 groups of the most prospective materials considering their potential applications and the expected physiochemical properties. The method of weighted scores [13] has been used to evaluate the new generation of the high-innovative advanced porous and composite nanostructural functional materials with nanofibers. The method analyses preferences with the procedural benchmarking technique consisting of using the existing, proven procedures in relation to another thematic area or field of knowledge. The preference analysis consists of classifying objects in a specific scale as expressed by the hierarchy of importance relevance presenting preferences in an orderly way. The method of weighted scores has been used in this paper to determine prospects related to producing, characterising and modelling a structure, properties and technology of producing a new generation of nanostructural composites for comparative evaluation aimed at classifying the relevance of specific composites in the context of relations between them. Note that the described method is connected with using the principle of evaluation criteria relativisation, i.e. differences are assumed in the relevance of the criteria used and the principle of acceptability assuming a special group of acceptability conditions being a selection filter, classifying a given object positively or negatively. The method of weighted scores allows for a multi-criteria aggregate evaluation using a scale with intervals. A single-pole positive scale without zero called a universal scale of relative states is used in the paper, according to which 1 is a minimum score and 10 is maximum [13].

Detailed criteria have been assumed in the initial foresight research for evaluating the attractiveness and potential of individual nanostructural composites (Table 7) and their gradation has been introduced by ascribing relevant weights to specific criteria based on the analysis of references and experts opinions. Next, weighted values were calculated for the individual criteria that have been summed up and values were obtained being a basis for a comparative analysis as presented in Table 7. Afterwards, using the dendrological matrix of technology attractiveness [13], the results obtained are presented in graphical form (Fig. 1).

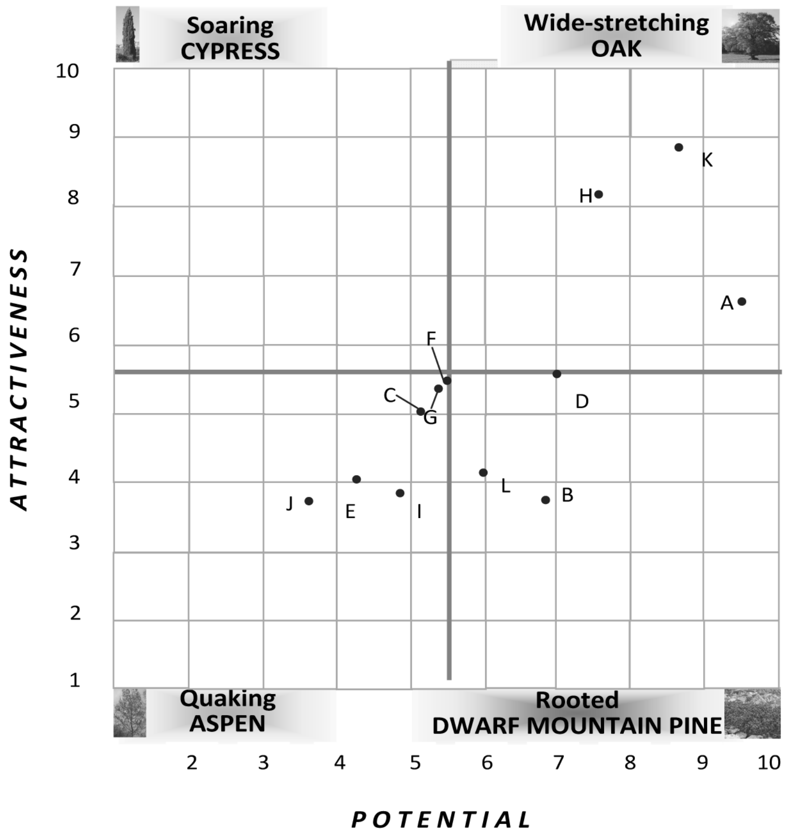

Fig. 1. Positioning of the individual nanostructural composites

Table 7.
Results of the analysis of nanostructural composites with the method of weighted scores

Symbol	Type of composite	POTENTIAL						ATTRACTIVENESS					
		Criterion 1	Criterion 2	Criterion 3	Criterion 4	Criterion 5	Sum	Criterion 1	Criterion 2	Criterion 3	Criterion 4	Criterion 5	Sum
A	Carbon nanofibers / metal	3	1	2.5	2	1	**9.5**	2	0.5	1.25	1.25	1.5	**6.5**
B	Carbon nanofibers / ceramics	1.5	0.8	2	2	0.6	6.9	0.5	0.5	1.25	1	0.45	3.7
C	Carbon nanofibers / polymer	0.6	0.5	2	1.25	0.7	5.05	1	0.6	2	1.25	1.05	5.9
D	Carbon nanofibers / air	0.6	0.9	2.5	2	1	7	1.25	0.5	1.25	1.25	1.35	5.6
E	Polymer nanofibers / metal	0.3	0.7	2	1.25	0.1	4.35	1.5	0.2	0.5	1.5	0.3	4
F	Polymer nanofibers / ceramics	1.5	0.4	1.25	1.75	0.7	5.6	2.1	1.5	0.1	0.9	0.75	5.35
G	Polymer nanofibers / polymer	1.2	0.4	2	1	0.8	5.4	1.75	1.75	1	0.6	0.45	5.55
H	Polymer nanofibers / air	2.4	0.4	2.5	1.5	1	**7.8**	2.8	2.5	1	1.2	0.6	**8.1**
I	Inorganic nanofibers / metal	1.8	0.4	2	0.5	0.1	4.8	1.05	0.25	0.3	1.05	1.05	3.7
J	Inorganic nanofibers / ceramics	0.9	0.3	1.25	1	0.1	3.55	1.05	0.25	0.3	1.05	1.05	3.7
K	Inorganic nanofibers / polymer	3	0.5	2.25	2.25	0.7	**8.7**	3.5	2	0.8	1.05	1.5	**8.85**
L	Inorganic nanofibers / air	1.8	0.5	2	1	0.7	6	1.05	1	0.3	1.05	0.75	4.15

An analysis with the method of weighted scores has shown (Table 7) that the highest values were obtained for the following combinations forming a composite:

- Carbon nanofibers/ metal (A),
- Polymer nanofibers/ air (H) and
- Inorganic nanofibers/ polymer (K),

that ranked in the most promising quarter of the matrix (wide-stretching oak) signifying their high potential and attractiveness and predestines them to detailed material science research and thus only such materials are covered by the study.

The detailed objectives of the study concern the scope of research referred to the following newly developed composite and porous materials selected for research based on the results of the analysis with the method of weighted scores:

- light composites with improved electric, thermal and mechanical properties (Mg, Al + carbon nanofibers) for the predicted applications in the automotive, aviation, space and electronic industry,
- light composites with high aesthetic values (transparent) with improved electric and thermal properties (polymer + nanowires Cu/Ag, Au, Pd, Pt) for the predicted applications in the automotive, electronics, for electronic equipment enclosures, for the parts of solar cells,
- porous materials with high absorptivity, air and liquid permeability, barrierity and low density (polymer + air) with the possibility of filling pores with active substances, e.g. liquid light substances or lubricants or other fire- and heat-insulating substances imparting special properties, for the predicted applications in medicine, cosmetic industry, textile and clothing industry, in the defence and civil industry (fire service, uniforms and protective clothes, e.g. non-flammable clothes).

4. The current state of the art for the subject of the study

The description of the state of the art for the subject of the study has been limited to the issues initially selected with an analysis with the method of weighted scores.

Metallic composites reinforced with carbon nanofibers are the first mentioned group of the newly developed high-innovative advanced porous and composite nanostructural functional materials with nanofibers. There are two methods of producing carbon nanofiber composites according to the state of concentration of the matrix during production thereof [14]. The methods where the matrix material remains in a solid state (**solid state fabrication methods**) includes solutions used in powder metallurgy. Metal in form of powder is mixed uniformly with carbon nanofibers, and then pressed at a higher temperature, usually under pressure, to obtain material not containing pores or with low porosity. Pressing is used for composites with a small concentration of carbon nanofibers and then sintering. This permits to formulate products with the set, final shape, without further, usually costly processing being necessary. If the concentration of nanofibers exceeds 5-10%, it is necessary to apply additional processes (mainly hot pressing) to densify the material produced. This can be supported with plasma in the most advanced solutions. Carbon nanofibers can be pre-coated with a thin layer of matrix metal enabling to achieve a higher density, more uniform distribution of nanofibers, better bonding between the matrix and a reinforcing phase and lower porosity. **The liquid phase fabrication methods**, referred to as infiltration processes, are used to produce strongly densed composites with a high share of carbon nanofibers. A layer of metal or alloy is applied onto a pre-mould containing nanofibers, usually as a mat, and then it is all heated to the temperature above the melting point with spontaneous wetting occurring as a result and the infiltration of a material containing nanofibers. Usually pressure needs to be applied (gas pressure infiltration, squeeze casting) due to the poor wettability of carbon nanofibers by metal or their surface needs to be modified. An addition of alloy elements that can largely enhance the degree of infiltration is also very important.

Composites of aluminium and alloys thereof with an addition of carbon nanofibers pose additional difficulties relating to fabrication with an addition of carbon nanofibers (CNF) stemming from the reactions occurring in the boundary layer between nanofibers and the matrix material the result of which is the formation of carbides (Al_4C_3) in form of elongated needles on the surface of carbon fibers leading to the dramatic reduction of the composite's mechanical properties. The phenomenon usually does not relate to composites containing carbon nanotubes (CNT). The existing research has corroborated the influence of an addition of carbon nanofibers on the mechanical properties of composites [15]. Tensile strength and the Young's modulus are rising for the contents of up to 1% wt of nanofibers while falling afterwards. An addition of carbon nanofibers allows to improve tensile strength by over 100% [16, 17] and elastic strength by over 300% [18]. Decisive for fabricating aluminium composites and for enhancing their mechanical properties will be to enable the formation of carbides and increase interaction between nanofibers and the matrix material, hence it becomes possible to produce ultra light and very strong composites [19].

Composites of magnesium and alloys thereof with an addition of carbon nanofibers, just like magnesium and its alloys can be used in the car industry and aviation industry due to their low density and a possibility of achieving good mechanical properties after introducing the particles of graphite, aluminium, silicone carbides and carbon nanofibers. The simple and efficient methods of producing magnesium composites with an addition of carbon nanofibers have been developed so far [20], however, the improvement of mechanical properties achieved due to the agglomeration of nanofibers is insignificant. Further research is needed to fully utilise the potential of using carbon nanofibers, in particular the aspects must be investigated of dispersing nanofibers uniformly (agglomerates become the source of cracks, whereas the bundles of single fibers laid parallel prevent their propagation) [21, 22], controlling the carbides formed [23] and covering the surface of nanofibers with a thin layer of other elements, e.g. Si [24].

Copper composites and alloys thereof with an addition of carbon nanofibers represent an area of research connected with their fabrication to improve their mechanical and electric properties. Hardness increase between 20% to over 200% has been achieved depending on the technology employed [25-27], yield point by 200% and elasticity modulus by 70% [28].Carbon nanotubes may be used for improving the hardness of copper (increase by 47% after adding 0.1% wt of multi-walled nanotubes) and to improve the conductivity of copper alloys (increase by 20% after adding 0.1% wt of single-walled nanotubes) [29]. The article [30] indicates a possibility of producing a composite with the share of up to 3% of carbon nanotubes dispersed uniformly in the copper matrix with the Spark Plasma Sintering technique with thermal conductivity growth accomplished by over 10 $Wm^{-1}K^{-1}$. A declining heat expansion coefficient has been found using the molecular-level mixing process with the simultaneous reduction in the thermal conductivity of the composite with an addition of carbon nanotubes between 5-10% [31]. Investigations must be continued to produce composites with high thermal conductivity and a low heat expansion coefficient.

The basic geometric characteristic of **carbon nanofibers** is a high length-to-diameter ratio making the issue of their placement in a metallic matrix significant. A privileged orientation of nanofibers is a consequence of composite production processes (e.g. oriented pressure applied), and also influences its anisotropic properties, e.g. thermal properties. Depending on the future applications, the phenomenon represents an advantage or disadvantage for the material produced. Due to the nanometric size of nanofibers and a significantly higher ratio between nanofibers surface and composite volume, the effects taking place in the boundary layer have decisive influence on the properties of the composite produced, mainly on its mechanical and thermal properties. The surface of nanofibers is modified to improve the mechanical and thermal properties of the composites produced, for example by increasing its roughness, by coating with a thin interlayer or an addition of alloy elements is introduced leading to separation processes or chemical reactions, e.g. carbides being formed in the boundary layer. Carbon nanofibers, representing a composite reinforcing phase, may assume the form of carbon nanotubes built of graphene layers (single-wall SWCNTs or multi-wall MWCNTs) or nanofibers (amorphous CF, of Herringbone, Platelet, Screw type). Their properties depend most of all on the fibre type – single-wall carbon nanotubes (SWCNT), multi-wall carbon nanotubes (SWCNT), carbon nanofibers CF and many other factors, with the most important being the method and parameters of the formation process, homogeneity and purity of a carbon material containing carbon nanofibers and the processes to which it has been subjected after completing the formation process. The use of carbon nanotubes built of graphene layers creates the greatest opportunity to considerably improve mechanical, thermal and electrical properties of metallic composites reinforced with carbon nanofibers (Table 8). The three techniques are used predominantly to fabricate them:

- arc discharge,
- laser ablation,
- Chemical Vapour Deposition (CVD).

Table 8.
Typical properties of SWNT, MWNT and CF (properties of Akzo Nobel Fortafil 243 PAN-based fibres) [32]

Property	**SWNT**	**MWNT**	**CF**
Diameter, nm	0.6-1.8	5-50	7300
Aspect ratio	100-10000	100–10000	440
Density, gcm^{-3}	1.3	1.75	1.74
Thermal conductivity, $Wm^{-1} K^{-1}$	3000–6000	3000-6000	20
Tensile strength, GPa	50-500	10-60	3.8
Tensile modulus, GPa	1500	1000	227

Catalysts are used in the majority of nanotube production techniques. The role of catalysts can be played by metals (e.g. Co, Fe, Ni or Pt, Cu, Al), metal oxides (e.g. Al_2O_3), semi-conductor compounds (e.g. SiC) or a synthesis can be carried out catalyst-free. The structure of achieved carbon nanotubes depends on the process parameters, most of all temperature, pressure and type of gas being the source of carbon atoms [33]. The CVD method allows to synthesise carbon nanotubes at a mass scale. There are multiple variations of this method, and its significant advantage compared to arc discharge techniques or laser ablation techniques is that carbon nanotubes can grow directly on the prepared substrate. It is thus possible to synthesise a "forest" of nanotubes with a specific orientation. Hydrocarbons such as, e.g. benzene, cyclohexane, acetylene, methane and carbon oxide and dioxide are used in the Chemical Vapour Deposition as a source of carbon atoms. Metallic particles deposited on special carriers (e.g. MgO, Al_2O_3, ZrO_2, CaO, SiO_2) have the function of catalysts. A synthesis temperature of carbon nanotubes is usually within the range of 500 to 1200°C. The reaction occurs in vacuum or an inert environment produced by introducing inert gas into the system (e.g. Ar, N_2, He). In most of the applications, it is essential to produce homogenous material in terms of its morphology, meaning a specific length and diameter of nanofibers most of all. It is especially significant for single-walled nanotubes whose properties largely differ from the other types of nanofibers. The presence of impurities in the carbon material next used as a reinforcing phase of composite is a major issue. The impurities include metallic particles, mainly the particles of the catalyst used in the production process (Ni, Fe, Co) and carbon impurities – amorphous carbon, graphite particles, carbon black and other forms of carbon.

Purifying is an important stage of forming carbon nanofibers. In order to remove the particles of the catalyst from nanotubes, the material is subjected to inorganic (diluted or concentrated) acids. The process is supported with an increased temperature, microwaves or ultrasound waves. The metallic catalyst nanoparticles are usually surrounded with graphene layers. For this reason, carbon impurities must be removed in the first place by oxidising in the gaseous phase, exploiting the effect of different rate of the thermal oxidisation of nanotubes and other carbon particles to enable access to metallic impurities [34]. The carbon material containing carbon nanotubes is added to a composite as powdered or pressed, as mats or pellets. The carbon material containing carbon nanofibers can be used to produce an as-received composite or may be subjected to purification, functionalisation, metal layer deposition and heat treatment processes. Carbon pollutants are removed by heating in the air at the temperature of 500°C (single-walled nanotubes) and 760°C (multi-walled nanotubes), and metallic pollutants by means of acids. A process of functionalisation refers mainly to joining function groups (COOH, OH) to the surface of carbon nanotubes, and the purpose of heating at the temperature of 2000°C/3000°C in a protective atmosphere is to remove defects and improve the structure of carbon nanotubes.

Carbon nanofibers exhibit a tendency to concentrate strongly and to produce agglomerates as a result of strong interactions (electrostatic and van der Waals interaction). To minimise the effect, carbon nanofibers are dispersed through mechanical mixing, dispersed in solvents supported with the action of surface-active substances or ultrasounds, dispersed in acids and by depositing a thin layer of metals onto the surfaces of nanotubes. The mechanical mixing technique is regarded as poorly effective – after finishing the process some of nanofibers still occur as agglomerates. High energetic mixing enables to achieve better results, but the parameters need to be chosen very carefully as damages and changes to the morphology of nanofibers are the side effect [35]. Carbon nanofibers can be dispersed effectively in certain solvents (e.g. Dimetyloformamid or N-Metylopirolidon) and in water with surface-active substances added, especially if the process is assisted with ultrasounds. Considering that for the quality of the composite produced not as much as the uniform dispersion of nanofibers prior to commencing the production process is important but rather maintaining such distribution in the final material, all the techniques mentioned above are usually combined. Carbon nanofibers treated by acids undergo chemical oxidisation, and functional groups are formed on their surface allowing to distribute evenly in water and ethyl alcohol. Nitric acid and polyacrylic acids are usually used for this purpose. The identical procedure is used as a preliminary stage before depositing thin metallic layers. The deposition of thin metallic layers on the surface of carbon nanofibers can be considered the most advanced and also most effective method of accomplishing their uniform distribution in the metallic matrix. Such approach allows to avoid the necessity of time-consuming crushing process which, most of all, destroys the structure of nanofibers. Electrochemical deposition enables to deposit a layer of Cu, Ni and Co [36, 37] onto nanofibers. Electroless deposition is used for depositing Cu, Au, Ag, Co, Ni [36, 38]. Nanofibers can be implanted into a larger piece of metal with this technique and the external surface of the fibre can be coated (decorated) with metal nanoparticles or uniformly coated. Uniform layers with nanometric thickness can be deposited with the CVD method on the surface of carbon nanofibers (metals, carbides and nitrides) and with the PVD method (metals, i.e. Ti, Ni, Pd, Au, Al, Fe) [39, 40]. Apart from such advantages as the uniform and homogenous deposition of the carbon nanofiber surface and influence on the surface properties (e.g. its purifying with plasma), the CVD and PVD methods feature important disadvantages – introduce additional pollutants into a composite and can be a source of oxygen.

Polymeric composites reinforced with metallic nanofibers have their properties largely dependent on the arrangement of nanowires in the polymeric matrix. A great emphasis is laid on their uniform dispersion for this reason. Depending on the fabrication process, the surface of nanowires is initially subjected to the functionalisation process [41] and/or the composite components are mixed intensively. The greatest hopes connected with producing polymeric composites with an addition of metallic nanowires are connected with their electrical and thermal properties. A small addition of metallic nanowires enables to increase substantially the conductivity of composite materials with their share. An electrical percolation threshold for polymeric composites for copper is 0.25-0.75% and 0.50-0.75% for silver nanowires. For comparison, the value is 1-3% for carbon nanotubes, 10-15% for carbon nanofibers and 15-20% for carbon black [42]. Good conductive properties are accompanied by very good magnetic field screening properties already with a share of nanofibers in the composite of not more than 1.3% vol. Due to the high thermal conductivity of silver and copper, an addition of metallic improves the properties of the produced polymeric composites and enables heat to be evacuated effectively. The dimensions of a composite are also stable within a broad range of temperature as nanometric dimensions and a small share of fibers prevent the negative phenomena connected with the thermal expansion of metals.

In the group of inorganic nanofibers representing a potential component of polymeric composites, attempts are made most often to use metal nanofibers and possibly their alloys: Cu, Ag, Au, Pd and Pt. The prospects of their use result from their geometric features, often matching those of carbon nanotubes. It is possible to produce crystalline or polycrystalline gold nanowires with the diameter of 2 to over 100 nm whose length exceeds 100 μm [33-46]. Crystalline silver or copper nanofibers are also produced these days with a length-to-diameter ratio exceeding 200 [42, 47, 48]. The structure, chemical composition and surface properties of metallic nanofibers may be controlled with the conditions of the fabrication process. The most popular techniques of fabricating metal nanofibers include chemical vapour deposition, electrochemical deposition, template or membrane processes and reverse micellar systems [49-61].

Progress in the field of polymers synthesis is largely dependent on recognising the mechanism of polymerisation and catalysis. Some types of polymers, e.g. natural rubber, gutta-percha, cellulose are formed as a result of biochemical reactions occurring in plants. At present, polymers are synthesised mainly from petrochemical raw materials, i.e. crude oil or natural gas. The published forecasts point out, however, that we will experience a shortage of such raw materials already in the middle of the 21st century. This will cause dramatic growth in their prices [63], hence it becomes necessary to seek alternative raw materials for polymers synthesis, including biomass as a renewable raw material. Bioplastics will grow at a significant pace over the next 5 years. The total worldwide use of bioplastics is expected to grow at a 41.4% compound annual growth rate from 2010 through 2015. By 2010, ready access to crops such as soybeans, corn, and sugarcane moved the United States strongly into bioplastics. North American usage is expected to increase at a 41.4% compound annual growth rate to 2015. Use of bioplastics got off to a faster start in Europe than in the United States. European usage is expected to increase at a 33.9% compound annual growth rate in the same time [64]. The polymers produced this way such as: polylactide, polylactate and polyalkanianes are biodegradable and exhibit mechanical properties comparable to those of typical thermoplastics [62]. Currently the most popular biodegradable polymer is probably polylactide used for producing mugs, containers, trays, foil bags and bottles for storing, in particular, edible oils, mineral water, milk and fruit juices [65]. The global biodegradable polymer market is expected to have its largest growth over the next 5 years, dominated by packaging and usage in fibers. The global biodegradable polymer market is expected to increase at a 22% compound annual growth rate by 2016. The packaging segment accounted for 70% of total volume in 2010 and is expected to slightly decrease to about 66% by 2016. This sector should increase at a 20.5% compound annual growth rate by 2016. The fibers/fabrics segment will show substantial growth over the forecast period, especially in the hygiene market segment. The use of biodegradable polymers in fibers and fabrics is expected at a 26.6% compound annual growth rate in this period [66]. Successful attempts have been made recently to synthesise supramolecular polymers [62] with their structural units of macromolecules being combined not only with chemical bonds but also as a result of formulating catenane or rotaxane systems [67] or intermolecular hydrogen bonds [68]. The polymers formed this way have unexpected properties, e.g. may act as self-healing materials or are biodegradable [62].

The following basic groups of polymers can be distinguished according to the structure of macromolecules and properties [62]:

- plastomers (also referred to as "plastics" or, less often, -plastic masses) (22 main types),
- elastomers (15 main types),
- duromers (also called thermohardening or chemohardening resins) (19 main types),
- fibre-forming polymers (often not included in the classification) (19 main types)

In case of plastomers, elastomers and fibre-forming polymers, the spatial structure of macromolecules is very important and if it is stereoregular, the relevant polymer can crystallise, which has a great influence on the properties of the polymer, including the increase of density, thermal stability and strength [62]. The total number of known polymers is many times higher as, apart from the types built of one type of mers (homopolymers), copolymers and terpolymers are synthesised containing the relevant mers of double or triple kind. Mers in the macromolecules of co- and terpolymers are usually distributed statistically, but they also can form blocks. Besides, heteroatoms or different pendant groups are built into macromolecules, and also polymers or telechelic oligozmers (compounds with molecular mass of not more than 10 000 are referred to as oligomers) are synthesised containing function groups incorporated on purpose at the ends of molecules or within their surface [62]. Duromers may differ greatly in the density of their cross-linking.

Polymers are most often used as polymeric materials containing auxiliary substances such as: softeners, dispersers, anti-ageing agents, fillers and nanofillers, cross-linking agents, activators and antipyrines ensuring their desired properties, in particular as polymer matrix composite materials. As a result, polymeric materials meet various functional requirements. In particular they exhibit relatively high strength and durability and much smaller density than steel and many other metal alloys. This creates a wide range of applications for polymeric materials in the aviation sector and in transportation in general, also in the construction industry, notably in form of polymer concretes, in the arms industry (helmets, bulletproof jackets) and sports equipment (helmets, skis, poles, tennis rockets, oars, boats, yachts), and also in the following industries: shipyard industry, machine, chemical industry, electric industry, cosmonautics, mining sector and in other industries [62]. The functional properties of polymers can be often improved through their physical or chemical modification, and more often at the surface only. Many products having high practical importance are manufactured with general purpose polymeric materials, in particular packaging, tires, conveyor belts, drive belts, seals, heat insulation (forma) and electric insulation (cable sheathing), textiles, furniture, carpets, enclosures, window frames, toys and polymeric foils are used in agriculture. Prospects are looming for further advancement in the field of polymeric composites. Polymeric composites have been especially widely used recently as construction materials. The North American fiber-reinforced plastic/composite market is expected a 2.8% compound annual growth rate. Construction/infrastructure and automotive products are the key applications of this market since they comprise about 60% of total volume. This sector is expected to reach with a 2.9% compound annual growth rate. The largest growth will be experienced at the very low volume aerospace market led by the introduction of composite commercial aircraft exterior parts such as fuselages and wings. This sector should increase at a 7% compound annual growth rate to 2015 [69]. Development outlooks for this group of materials are linked, notably, to equipping them with piezoelectric sensors to indicate structure overload or damage. Systems have also been developed enabling the self-healing of a damaged composite part [62]. Successful attempts have been made to produce ultrastrong fibers to improve the strength of polymeric composites [70]. It is very important to master the technology of polymeric nanocomposites reinforced with nanomolecules or nanofibers [71]. The following nanofibers of metals and possibly their alloys have been selected for further studies in the group of inorganic nanofibers being a potential component of polymeric composites: Cu, Ag, Au, Pd and Pt. For obvious reasons, it is necessary to make limitations also concerning the polymer matrix to be chosen, especially in terms of their chemical composition and the matrix polymer materials fabrication technology. Ineffective solutions and those with poor feasibility will be eliminated in the first place. Polyethylene, polypropylene, and also polylactide as a biodegradable material will surely be classified, in particular, as those picked positively. Other polymer matrix materials will be chosen in a series of preliminary investigations. The following methods of producing composites with an addition of metallic nanowires can be distinguished: melt mixing [72, 73], solution processing [48, 74], in-situ polymerisation [75, 76] and heterocoagulation [77]. Custom achievements will also be used connected with the method of multiple reciprocating flows [78]. The manufacturing aspects of producing composites with an addition of metallic nanowires are still poorly investigated and thus have been included in the study as a priority.

Porous polymeric materials, with their reinforcing phase being nano- and sometimes microfibers with the diameter of 50-500 nm, and the matrix function played by the air, have their usage prospects resulting most of all from their geometric characteristics. Efforts have been continued to produce a polymer-air composite featuring high porosity, air permeability, absorptivity, barrierity, bacteriocidity, biocompatibility, intoxicity, a possibility of releasing medicinal agents in a controlled way, appropriate mechanical strength and its structure supporting regeneration. The efforts require multiple interdisciplinary investigations, including those connected with a study into standard polymer nanofibers with a different diameter, made both, of natural polymers and synthetic ones, in particular: PLLA, PGA, PLA, PLGA, PCL, PEO, chitosan, collagen, elastin, hyaluronic acid. The efficiency of the additions incorporated such as: silver, iodine, characterised by bacteriocidity has been ascertained with multiple studies. Chitosan, a derivative of chitin, a second, after cellulose, natural polymer most often occurring in nature, has been observed attentively for several years. It shows precious properties, notably it is: antibacterial, antifungal, biocompatible, biodegradable and nontoxic. Chitosan nanofibers can be settled on a textile carrier surface, mixed with other polymeric nanofibers such as PEO, PVA, PLA, PET, collagen or produced as hybrid nanofibers (chitosan-second polymer). The additives introduced often reduce absorptivity, elasticity, stretchability and even reduce chitosan's bacteriocidity. Designing and producing a composite material exhibiting the above properties for application to extensive wounds sustained from burning and pathogenic changes remains to be a challenge. A large surface area in relation to mass, a ratio between diameter and length of nanofibers, low density of damages on the surface of nanofibers as compared to standard fibres are just some of the advantages of the materials [79-87].

There are many methods of fabricating polymeric composites with air acting as matrix and a reinforcing phase as fibres with a different diameter (standard fibres, thin fibres, microfibres). Textile technologies are most popular, i.e.: Melt-blown [88], needlepunching [89] and spunlacing (hydroentanglement) [90], Spunbond Technology [91], Thermal Bonding Of Nonwoven Fabrics [92] and others. There are a few technologies [93, 94] for producing polymeric nanofibers. The one developed most intensively is electrospinning producing polymer nanofibers with an electric field from molten polymers (melting electrospinning), and from solutions (solution electrospinning) [95-98]. The device incorporates a container for molten or dissolved polymer ended with a nozzle, a DC HV source, two electrodes and a grounded collector (metal plate, revolving cylinder, revolving disk and others). The molten or dissolved polymer exits through a nozzle as a stream of liquid and, travelling towards the collector along the line of an electrostatic field, is strongly elongated to be settled onto the collector surface as nanofibers. Nanofibers with a different morphology can be fabricated according to the manufacturing conditions of electrospinning, including hollow, porous, flat, directed, branched, co-axial nanofibers and ones with different composition [99-102]. The other methods have rather laboratory than technical meaning [103] and include: drawing materials with high viscosity, e.g. sodium citrate that can be subjected to a large plastic deformation without losing cohesion; phase separation where a polymer and solvent solution undergo gelling, when the solvent is removed the next time; template synthesis, i.e. a nanoporous membrane made of corundum as a template for producing nanofibers under pressure pressed by the template pores to a chamber with a solidifying solution and molecular self-assembly where single molecules are linked into chains whose shape determines the shape of the nanofibers being formed.

The information presented indicates that surely the area of interest selected for the study is the technology of electrospinning polymer nanofibers having a different morphology to produce porous materials where the function of matrix is played by the air for ensuring high absorptivity, air and liquid permeability, barrierity and low density and a possibility of filling pores and/or infiltration with active substances, e.g. liquid medicines or lubricants or other fire resistant or heat insulating materials impacting special properties for the expected broad applications.

The aspects selected for the study represent a new concept which by principle, is definitely going beyond the existing state of the art. The development of this group of innovative materials will make a significant contribution towards the development of materials science and nanotechnologies.

5. The applicational opportunities and prospects for a new generation of high-innovative advanced porous and composite nanostructural functional materials

Activity in the field of materials science aimed at producing a material must take into account all the aspects – including technological, environmental and economic ones of its further use. Construction nanomaterials fabrication technologies (nanometals and nanocomposites with the desired properties) represent one of the priority direction of nanotechnology development [104]. The progress of research into the production of composites containing one-dimensional structural materials, except for studies into the production of polymeric composite materials reinforced with nanotubes, is in its initial or incipient phase. The areas of future applications have not and cannot be yet clearly defined for this reason.

Metallic composites reinforced with carbon nanofibers provide an opportunity to produce light composites with good mechanical properties and to produce composites with high heat conductivity and also a low heat expansion coefficient, and also ones with improved electrical and mechanical properties. The production of Cu, Al and Mg matrix composites draws the greatest attention. The potential fields of application include the automotive industry (composites with high strength, resistance to wear, with good heat conductivity and low density – transmission gears, braking systems, pistons and cylinders), aviation sector (composites with high wear resistance, good heat conductivity, low density and high strength – braking systems, undercarriages), space industry (composites with low density, high strength, low heat expansion coefficient and good electric conductivity – radiators, aerial supports), sports (high strength, high modulus of elasticity – light bike frames, tennis rockets) and electronics (composites with high heat conductivity, low heat expansion coefficient, high strength – enclosures of electronic systems) [105].

Polymeric composites containing metallic nanofibers (nanowires) allow to produce a light material characterised by high electrical conductivity (>10^2 S/m) already at a low concentration of nanofibers. A small, required addition of metallic nanowires (<5% wt) will allow to maintain high aesthetic values of the material, transparency in particular. The use of Ag, Au, Pd, Pt and Cu nanowires in particular attracts the greatest attention due to the expected improvement in electrical and heat conductivity. Polymeric composites may be applied in the electronic sector for manufacturing the enclosures of electronic devices, parts of solar cells and in the automobile industry [106-108].

Porous polymeric materials are characterised by high air and liquid permeability, barrierity, absorptivity and low density. Considering such properties, they can be used in medicine, environmental protection, construction, textile and clothing industry. In medicine, polymeric nanofibers, due to their similarity to a natural extracellular matrix, are used as scaffolding supporting the restoration of natural tissue. For example the global market for nanoparticles used in biomedical, pharmaceutical and cosmetic applications increased from 2006 to 2011 with an estimated compound annual growth rate of 27.3%. Biomedical applications have the largest share of the market and are expected to account for 75.9% of the market in 2012. Cosmetic applications are expected to lose market share over the next year and account for just 22.8% of the market in 2012 [109]. A mat made of biocompatible and bioresorbable nanofibers is also used as a membrane enabling to control the development of certain tissues, e.g. after implantation. A new generation of dressings has been sought for recesses formed at the surface of a body having the characteristics supporting the healing of wounds such as: ensuring physical wound continuity, maintaining a humid wound environment, correct thermal regulation, active absorption of exudation, interaction with the wound by releasing medicinal agents and easy attaching and removing from the wound surface [110-115]. Polymeric nanofiber mats can be used in personal hygiene as cosmetic pellets. For dressings, membranes and scaffolds, nanofibers can act as a carrier of bactericidal agents, notably silver, iodine [116-120]. Due to the presence of air, porous composite materials are characterised by low heat conductivity and can be used as heat insulating materials in the construction and the manufacture of household products (insulating layers in refrigerating and freezing machines) and as sound absorbing materials. Moreover, high air permeability and ability to retain a wide spectrum of differently sized particles provides a potential use for air and liquid filters.

6. Summary

In general, the study is of priority cognitive importance as theoretical considerations and the author's initial analyses related to technology foresight concerning this group of issues as well as sporadical results of research provided in the literature, usually in its incipient phase, indicate a great need to intensify scientific research, to develop the new groups of materials with quite unexpected predictable effects, resulting from the use of nanofibers for fabricating super advanced composite and porous materials. It is hard to overestimate the effects, and this requires undertaking the investigations creating a basis to develop a synthesis and/or to produce and/or to process completely new groups of new-generation nanostructural engineering materials.

Specifically, the expected outcome of the needed research connected with the production of the following composites: Carbon nanofibers + metal, Polymer nanofibers + air and Inorganic nanofibers + polymer, should include producing materials with new, also yet unpredictable, properties fulfilling numerous functions, especially resulting from or greatly intensified by using nanomaterials (catalytic, electric, optical, magnetic, textile nanomaterials) employing nanomaterials surface engineering technologies, connected with producing nanolayers and nanocoatings (nanocomposite, with heat barrier, anti-wear, hydrophobic and biocompatible ones). The out coming materials may have direct influence on the development of electronics and photonics, medicine and pharmacy, environmental protection, automotive industry, space industry, machine industry, textile and clothing industry, cosmetic industry, agriculture and food sector. Phenomena and processes at a nanoscale can be better recognised by producing a new generation of functional nanostructural materials (physicochemical basis of nanomaterials and nanostructures synthesis, with controlled architecture and properties, engineering of atomic and molecular bonds, models and theories explaining the properties of nanomaterials, surface phenomena, self-assembly phenomena in nanomaterials and nanostructures synthesis, magnetic phenomena in semiconducting and metallic nanostructures).

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