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Key trends in basic and application-oriented research on nanomaterials

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Abstract. Key trends in basic and application-oriented research on nanomaterials are considered. It is noted that some studies are now carried out abroad and in domestic laboratories, while some other are to be initiated in the near future. It is emphasized that effective research in the field in question is possible only provided that laboratories are equipped with advanced instrumentation. The bibliography includes 276 references.

I. Introduction

The terms 'nanomaterials' and 'nanotechnologies', in their modern sense, appeared in scientific literature only a little more than three decades ago.[1] Meanwhile, the technology of fabrication of metal nanoparticle coloured glasses was known in Ancient Egypt while the age of biological nanoscale objects is comparable with the lifetime of life on Earth. A number of researchers[2,3] relate the fabrication of nanomaterials to colloid systems. An outstanding role in studies of such systems was played by R Zsigmondy and T Swedberg awarded with the Nobel prize in chemistry in 1925 and 1926, respectively. However, it was the Nobel Prize laureate R Feynman[4] whose understanding of 'nanotechnologies' and 'nanomaterials' was like a twin of modern concepts. Feynman proposed two basically different (so-called 'bottom – up' and 'up – down') approaches to the design of nanoscale products. The former approach involves self-assembly on the atomic or molecular level while the latter is associated with mechanical dispersion, intense plastic deformation, decomposition of solid solutions, *etc*. Noteworthy, both approaches were proposed long before the creation of scanning tunnelling microscopes, atomic force microscopes and electron microscopes, which allow one not only to investigate, but also prepare the desired nanostructures under controllable conditions.

Experimental investigations carried out in the last decade showed that progress in nanotechnologies aimed to produce and utilize solid nanodisperse substances is hampered by the lack of information on the regularities of their behaviour in technogenic and natural systems. At present, there is a need for systematic basic research aimed at establishing the possibility of fabrication and use of nanodisperse substances in technology, medicine and agriculture. Here, we deal with interdisciplinary research involving various branches of physics, chemistry, biology and medicine that form a wide front of interdisciplinary search.

The lack of consensus in the understanding of what are nanomaterials and nanotechnologies is due to different scientific approaches. Therefore, corresponding definitions should be revised. Nanotechnologies include a variety of processes for fabrication of materials and production of devices and technical systems whose operation is first of all determined by their nanostructures, *i.e*., structural fragments 1 to 100 nm in size. Nanomaterials are products of nanotechnologies and should be treated as materials whose functional properties are governed by the nano level of their structures.

It should be noted that most materials, irrespective of their functional or structural purposes, have multilevel structures (Fig. 1).† The nano level is intrinsic in all materials, but it does not always play a decisive role in the

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† Most images of nanoscale objects appeared in the review are courtesy of researchers working at the Department of Materials Science, M V Lomonosov Moscow State University.

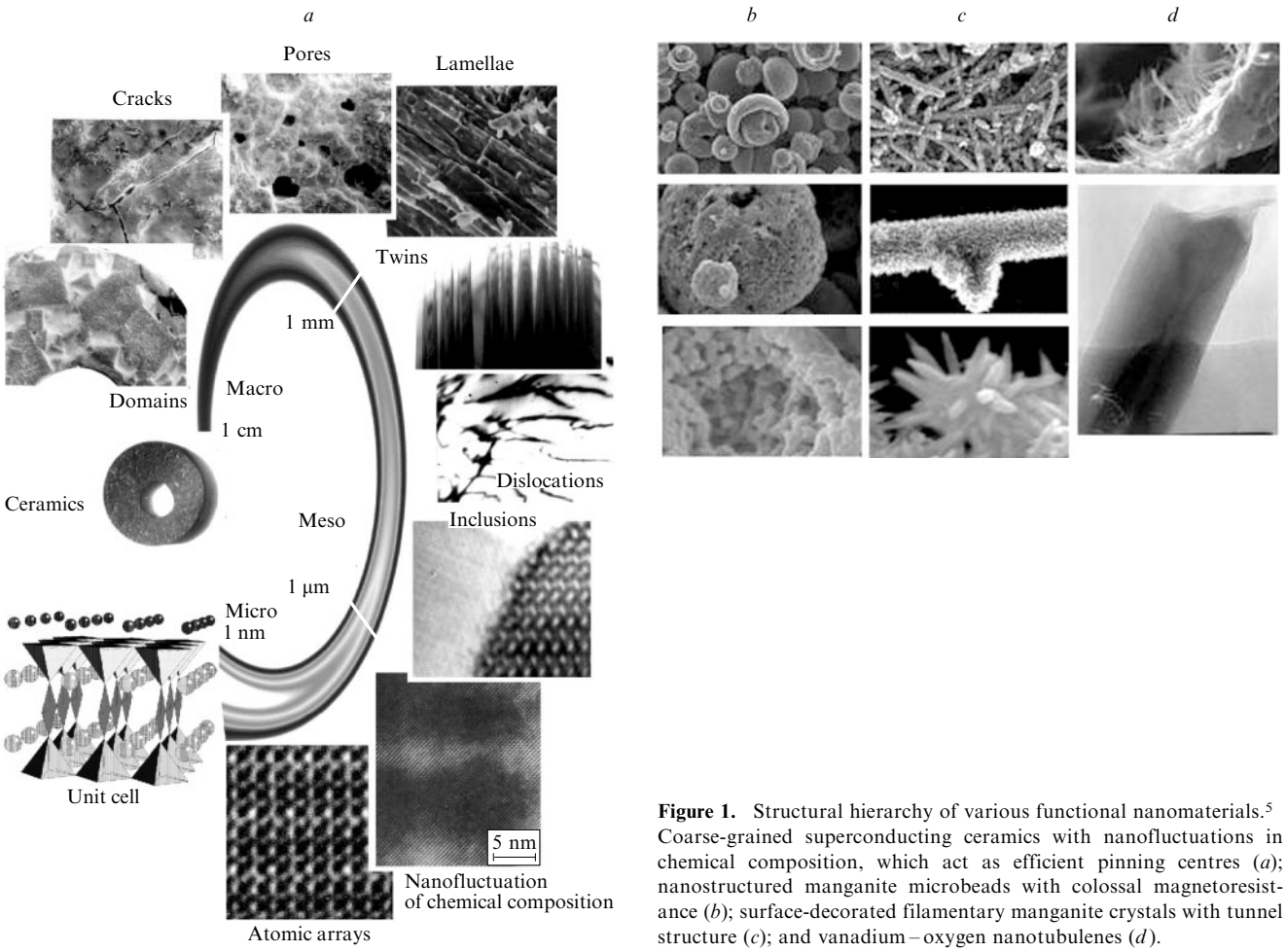


Figure 1. Structural hierarchy of various functional nanomaterials.[5] Coarse-grained superconducting ceramics with nanofluctuations in chemical composition, which act as efficient pinning centres (*a*); nanostructured manganite microbeads with colossal magnetoresistance (*b*); surface-decorated filamentary manganite crystals with tunnel structure (*c*); and vanadium – oxygen nanotubulenes (*d*).

formation of functional properties.[6] Moreover, the nano level of a structure whose evolution depends on the synthesis conditions or on the operating conditions of a material, varies with time; these changes became controllable quite recently as a result of the so-called instrumental revolution.[7]

The existence of hierarchically structured systems is a manifestation of the complexity and variety of interactions on different organization levels (scales) of matter. At present, research on and simulation of the behaviour of various hierarchically structured systems become particularly important in connection with progress in information technologies, energy-saving technologies, biochemistry and, of course, nanotechnologies.

Here, a key problem is the design of to some extent nanostructured materials whose unique functional properties or polyfunctionality are due to the contributions of different (both nano and micro) structural levels. This concept was mentioned in Ref. 8 and more recently in considering the concepts of real structures of ceramic materials and topochemical memory effects.[9, 10]

Melikhov[11] was among those who pioneered in posing the problem of rational balance between basic and applied knowledge in the design of novel nanomaterials and nanotechnologies. He proposed to consider scientific information on phenomena and processes in nanosystems as basic knowledge and information on practical implementation of these phenomena and processes in actual devices as applied knowledge.

Unlike conventional technologies, nanotechnologies are characterized by high research intensity and investment, the need for intellectual activity and expert activity. Therefore, in this case successful solution to various problems by the method of 'trials and errors', which is traditionally used in many applied studies,[12] is much less probable. For nanoproducts, the way from laboratory experiments to the nano industry is undoubtedly more complicated than the route to large-scale production of conventional products.

An intimate interrelation between basic and applied research on nanomaterials and nanotechnologies is apparent. Undoubtedly, the pathways of basic research are governed by the need for the design of new-generation functional and structural materials for almost all fields of activity including power engineering, mechanical engineering, chemical industry, electronics and information technologies, aviation and outer space exploration, automotive industry and railway transport, shipbuilding, building industry, medicine and public health service, design of novel pharmaceuticals and biomaterials, production and storage of food, desalination technology, production of textiles with improved functional properties, biotechnology and agriculture including soil reclamation, creation of novel home appliances and, finally, for production of various dual-use products.

At the same time, basic research is fundamentally different from applied/application-oriented research in that the efficiency of the former, especially in such high-tech avenues, as nanomaterials design and nanotechnologies, is not

a priori evident, often being unclear to the researchers. Therefore, the way from an original scientific idea to its practical implementation may appear to be very crooked and not always foreseeable. That is why in many countries basic research is funded by government grants. Examples are provided by the US 'National Nanotechnological Initiative'[13] and similar prorgrammes in Japan[14] and EU.[15] Unfortunately, for some reasons this is not the case for Russian Federation. Owing to disintegration of the USSR and struggle for survival the scientific community in Russia lose a decade of intensive research activity. Of course, this concerned not only progress in nanotechnologies, but this field of research was touched first of all, because visualization and controllable fabrication of nanoproducts required too costly equipment unavailable at that time; unfortunately, the situation still to a great extent persists.[16,17]

Similarly to other materials, the properties of nanomaterials depend on their chemical composition, structure, morphology, size, dimension and degree of ordering of constituent nanofragments. Natural methods of fabrication of nanomaterials include self-assembly and self-organization. Self-assembly is the formation of an ordered supramolecular structure or a medium in which only components (elements) of the original structure, which are used as building blocks for additive 'assembly' of a resultant complex structure, retain their original form. Nanostructural ordering in the course of self-assembly is mainly controlled by the competition between various forces of (most often) molecular nature, such as hydrophilic–hydrophobic interactions, gravitational force, van der Waals forces or Coulomb interactions.[18] Self-organization can be used as a formation mechanism of complex templates, processes and structures on a higher hierarchical organization level compared to the original system, due to numerous and multivariant interactions between components at lower levels characterized by some local regularities that differ from the regularities of co-operative behaviour of the system being ordered. Peculiar to self-organization are different-scale interaction energies and limitations on the degrees of freedom of the system at certain structural levels.

All nanomaterials (Fig. 2) can be classified into the following groups:[19]

— bulk (3D) nanostructured materials formed upon heat treatment and mechanical treatment (metals and alloys with ultrafine-grained structure), spinodal decomposition of glassy materials, solid solutions or by sintering of preliminarily compacted arrays of nanoparticles (nanoceramics) (Fig. 2 *a*);

— 2D nanostructured materials including thin and thick films and coatings, nanolithography products and self-assembling monolayers (Fig. 2 *b*);

— 1D nanostructured materials including nanotubes, nanofibres, nanoaggregates and nanowires formed from supersaturated vapours, solutions or by electrochemical and plasmachemical syntheses (Fig. 2 *c*);

— 0D nanodisperse materials (nanopowders, nanocrystals, quantum dots) prepared by mechanical grinding of bulky aggregates, by crystallization of supersaturated systems (from vapour phase, from liquid phases including

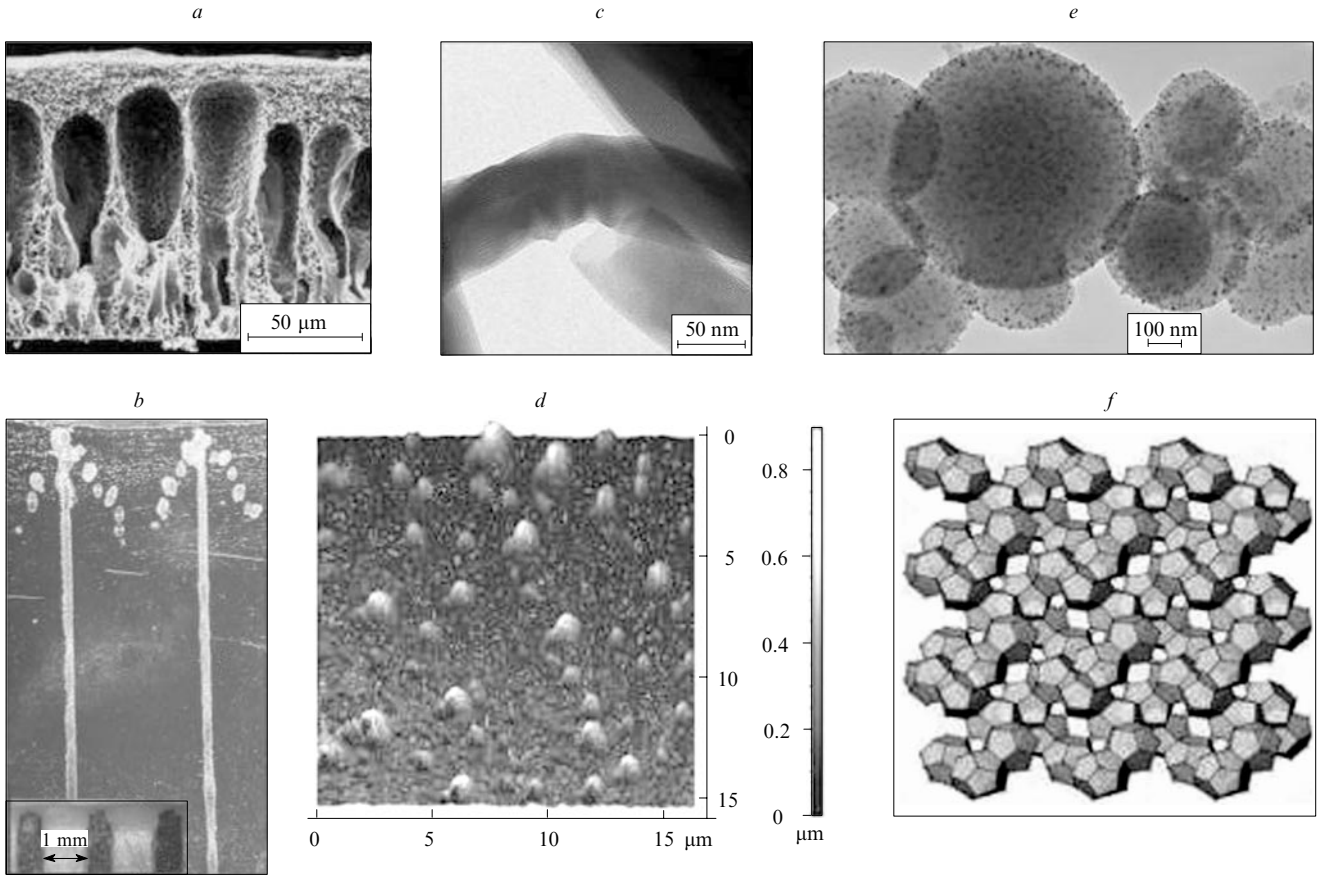


Figure 2. Classification of nanomaterials with respect to their dimension.[19] For notations (*a*–*f*), see text.

aqueous and nonaqueous solutions or melts), and self-assembled nanoclusters or template-stabilized nanoclusters (Fig. 2*d*);

— nanocomposites representing mesoporous matrices with 1D channels or 2D layers filled with the nano phase or nanowhiskers, nanotubes and nanoparticles in polymeric, metallic or ceramic matrix (Fig. 2*e*);

— supramolecular materials formed from simpler molecules to create molecular devices or machines simulating biological processes in living organisms, nanoporous structures (Fig. 2*f*).

We believe that the choice of the key avenues of pure basic and applied research on nanomaterials is a problem of paramount importance. In the text below we will consider a number of research avenues selected by an expert group headed by academician E N Kablov. Some studies are now carried out abroad and in Russia, while some other are to be initiated in the near future.

Each Section of this review includes general remarks, which are followed by a list of basic research avenues and high-priority investigation lines related to the general subject of the Section, a number of relevant examples (mainly results of investigations carried out at the Department of Materials Science and at the Chair of Inorganic Chemistry, Department of Chemistry, M V Lomonosov Moscow State University) and is completed by relevant discussion. All references were chosen to serve as a basis for investigations in the fields mentioned in the text.

II. Key chemical, physical and mechanical features of the nano state

A key issue in studies of nanomaterials is the onset of particular chemical, physical and other features upon transition of matter to the nano state. Changes in the chemical properties are due to a rather high proportion of 'surface atoms' and, correspondingly, a large contribution from the interface energy to the thermodynamic characteristics of the entire system. In some cases one deals with changes in the relative stability of modifications of ultradisperse phases with different crystal structures (some of them do not exist in the bulk state), agglomeration or aggregation of nanoparticles, changes in the mechanism or kinetics of topochemical reactions, diffusion transport of matter as well as ion and electron transfer through developed interfaces. These features are responsible for significant changes in the mechanisms of formation of nanoparticles and their aggregates, which leads to morphological diversity of nanoscale objects. Large surface area and the existence of metastable phases with rather large number of potentially active centres of heterophase interaction favour a significant enhancement of catalytic activity of such objects. These features correlate with changes in thermal stability of nanosystems, changes in thermal conductivity, heat capacity, *etc*.

The physical properties are strongly affected by the so-called 'proximity effects' related to the overlap of the Fermi bands when components of a nanomaterial or nanocomposite contact one another and by the vapour-phase or liquid environment. A significant role is also played by tunnelling effects and by the quantum size effect, which leads to the onset of unusual optical, electronic and magnetic properties, especially if the nanoparticle size is comparable with the size of 'quasi-particles' (the case for, *e.g*., specific behaviour of excitons in quantum dots, plasmon resonance, *etc*.). It should also be noted that such nanosystems may be characterized by specific manifestation of magnetic and other types of long-range exchange interactions, which rule out the block (domain) structure of single nanoparticles; however, this can also be accompanied by some interaction between nanoparticles in the ensemble, which may compete with thermal fluctuations of their properties and positions. Thus, ensembles of nanoparticles can exhibit new co-operative properties that 'sense' external conditions. In this case, cross-correlation between various physical properties is possible, which may favour the synthesis of polyfunctional (in all senses) materials with unique properties. Approximate correspondence between the size of nanoscale objects, supramolecular ensembles and biological (protein) objects deserves particular attention; in addition, all these 'ensembles' are usually characterized by rather weak bonds including hydrogen bonds, van der Waals bonds, dispersion interactions, *etc*., whose energies are significantly different from those of the interactions responsible for the formation of nanosized objects. Similar values of energy characteristics and unusual coordination of 'coordinatively unsaturated' surface atoms in nanoparticles predetermine the possibility of binding them to biological objects for implementation of nanobiotechnological approaches in medicine. These 'chimeras' can readily 'bypass' the immune system of an organism, penetrate through cell membranes as well as the blood–brain and placental barriers, *i.e*., this offers prospects for the design of novel means for drug delivery for therapeutic effect.

Considerable progress in the understanding of fundamental features of the nano state of materials can be made provided successful investigations aimed at establishing

— the physicochemical nature of morphological variety of organic and inorganic nanoscale objects including nanoparticles, nanotubes, nanoclusters, nanostrips, nanowhiskers and tetrapods;[20, 21]

— the nature of functional diversity of the properties of hybrid materials based on fullerenes and their derivatives, single- and multiwalled carbon nanotubes, graphene, *etc*.;[22–25]

— mechanisms of defect formation in the 3D, 2D and 1D nanomaterials;[26]

— influence of defects in nanocrystalline semiconductors on the efficiency of charge transfer and emission of radiation;[27]

— peculiar features of ion and electron-ion transport in nanostructured materials;[28]

— cross-correlations between the magnetic, electrical and optical properties of nanomaterials based on oxides, chalcogenides, pnictogenides, metal halides, *etc*.;[29]

— regularities of the evolution of electrical, magnetic, optical and thermal physical properties of nanodisperse compounds and materials during their formation from the vapour phase and liquid media including supercritical ones;[30]

— evolution of structural and phase transformations on going from bulk to nanodisperse samples of materials of the same chemical composition;[26, 31]

— effect of the template nature on the formation of nanostructures;[20, 32–34]

— failure strain mechanisms in metallic, ceramic and polymeric 3D nanomaterials, which are due to specific features of nanostructuring;[35, 36]

— the nature and ways of improving the wear resistance and impact strength in nanostructured solid alloys;[37]

— prospects for the design of novel nanostructures and nanomaterials possessing quantum effects at room temperature;[18]

— the nature of luminescence from nanoscale objects;[36]

— peculiarities of the morphology of nanosized inclusions in composites, which could be used for controllable changes in their properties;[38]

— the physicochemical nature of processes permitting the attainment of high strength and plasticity of nanocomposites;[39]

— the role of nanostructuring of metals and alloys in corrosion protection, mechanisms of anticorrosion action of coatings;[40–42]

— mechanisms of the onset of unique catalytic activity of nanodisperse systems;[43–46]

— specific features of the behaviour of nanostructured dielectrics.[47]

A typical example of a functional material is provided by zinc oxide, a wide-gap semiconductor of the $A^{II}B^{VI}$ family. Morphological diversity of ZnO particles (Fig. 3) offers prospects for a wide range of practical applications.[48–51] Using vapour-phase, hydrothermal and melt methods, 'soft lithography', controllable hydrolysis of aqueous solutions, micellar and template syntheses,[52–56] one can prepare nanowhiskers, nanostrips, tetrapods, 1D ordered arrays on flat substrates and zinc oxide beads, which are used in opto-electronics, for laser emission, optical information storage and in micro- and nanoelectronics.[57–60] Zinc oxide is not a unique example. From the standpoint of morphological diversity, a related compound is titania,[61–64] which is obtained as nanopowders, nanotubes, whiskers, monolayer dispersions, aerogels for photocatalysis, heterogeneous catalysis and chemical power cells. Unique nanostructured materials based on vanadium oxides,[65–71] which exist in different forms (xerogels with ordered structure, various nanotubes, filamentary crystals, vanadium bronzes, hybrid organo-inorganic materials) depending on their prehistory, have found application in chemical power cells, sensorics and in catalysis.[72–76]

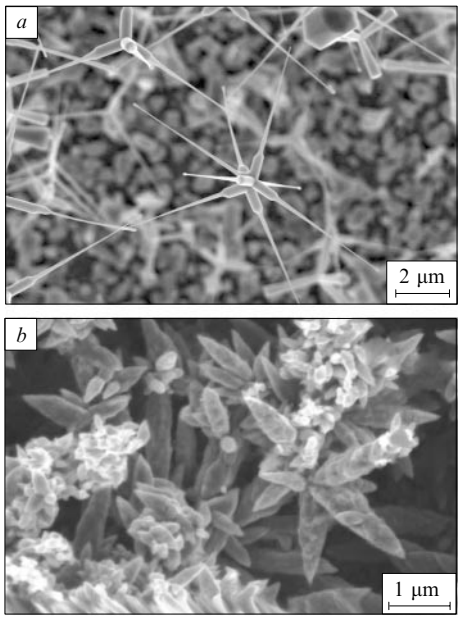


Figure 3. Zinc oxide tetrapods and nanostructures prepared from the vapour phase (*a*) and electrochemically (*b*).[48–51]

Provided a constant chemical (in some cases, phase) composition, in all these and other typical cases the morphological characteristics determining the specific features of heterogeneous interaction, defectiveness of the structure and manifestation of the anisotropy of crystallographic and physical characteristics can serve as key factors responsible for the possibility of practical use of a particular form as a functional material.

III. Investigations of interactions in ensembles of nanoscale objects

The formation of deaggregated nanoparticles, stable suspensions, emulsions and other colloid systems without significant contribution of interparticle interaction and aggregation is often difficult and even undesired in some cases. Therefore, studies on the nature of various phenomena in nanosystems and processes occurring in the course of fabrication and operation of nanomaterials should be accompanied by careful analysis of interactions within ensembles of nanoscale objects. These interactions can be due to formation of new chemical bonds in ensembles of nanoparticles, their physical aggregation, as well as mass or energy transfer. Investigations of specific interactions differing in nature, energy and action range at the existing levels of structural hierarchy becomes particularly important. Only this approach is suitable for prediction of the behaviour of real systems.

Yet another important feature determining a number of key functional characteristics is the dynamics and directionality of various transport phenomena including mass and energy transfer, charge transfer, *etc*., through developed heterogeneous interfaces. Clearly, not only the size effects, which to a great extent modify the properties of an ensemble of nanoscale objects with respect to the properties of a bulk sample, but also the effects of dimensionality (in morphological context, as well as the anisotropy of physical characteristics) and ordering of elements of a system will manifest themselves in nanosystems; this should lead to significant changes in the integrated characteristics of an ensemble of ordered nanoscale objects interacting with one another.

The most efficient approaches to the design of ordered (nanostructured) systems include those based on self-assembly and self-organization. Studies of the interactions of ensembles of nanoscale objects with one another and with bulk items (substrates, matrices, *etc*.) undoubtedly represent a key theoretical and practical problem. To solve it, one should establish the following:

— peculiarities of the thermodynamics of nanodisperse systems including colloid solutions and supramolecular structures;[2,77–79]

— mechanisms of noncovalent interactions and self-organization of molecules in supramolecular systems;[80]

— evolution of nanosystems exposed to gradients of temperature, pressure and other external factors;[77,81,82]

— hierarchy and interrelations between different (nano, meso, micro and macro) structural levels in nanomaterials;[83,84]

— regularities of formation and properties of 'nanoliquids';[85]

— nature of synergism in the properties of constituents of nanocomposites based on metallic, polymeric and ceramic matrices and fillers and on carbon nanotubes;[86, 87]

— principles of functionalization of textiles to impart protective properties against the action of thermal, chemical, optical and biological factors to them;[88]

— mechanisms of chemical and structural transformations of matter in nanoreactors;[89, 90]

— mechanism of interactions on the surface of solids covered with nanoparticles;[91]

— physical chemistry of interactions of metallic, magnetic and semiconductor nanoparticles with components of bioactive fluids and cell membranes;[92]

— nanofragmentation of crystals on intense plastic deformation of metals;[93]

— mechanisms of organization of matter in the course of compaction and sintering to form nanoceramics;[94–96]

— migration of nanodisperse compounds in natural and technogenic media;[97]

— formation of supramolecular materials for the design of chemical and biological sensors and active elements for micro- and opto-electronics;[29, 98, 99]

— mechanisms of aggregation and agglomeration of nanoparticles in the formation of nanodisperse products;[100, 101]

— tixotropic structure recovery in nanodisperse systems;[102]

— structural transformations in metal and nonmetal nanoclusters;[26]

— operation of elements of molecular electronics and nanoelectronics, molecular devices and machines.[103]

Typical examples of nano- and microstructured materials prepared by self-assembly are shown in Figs 4 and 5. In the former case these are colloidal crystals comprised of quantum dots that form a closest sphere packing and

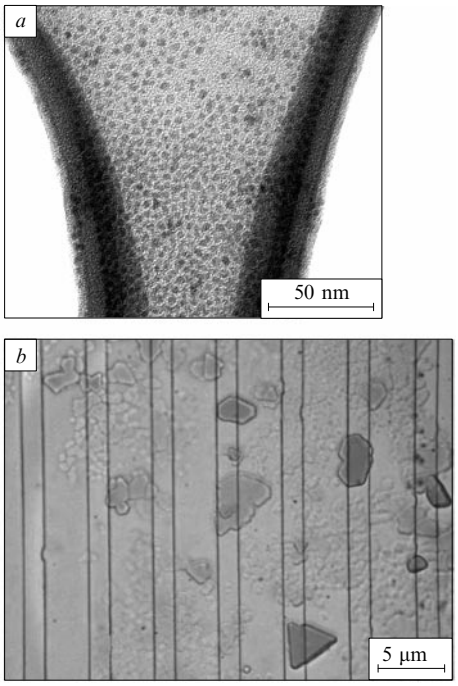


Figure 4. Zinc oxide quantum dots (*a*) and colloidal crystals comprising ordered selenium chalcogenide quantum dots on graphoepitaxial silicon substrate (*b*).

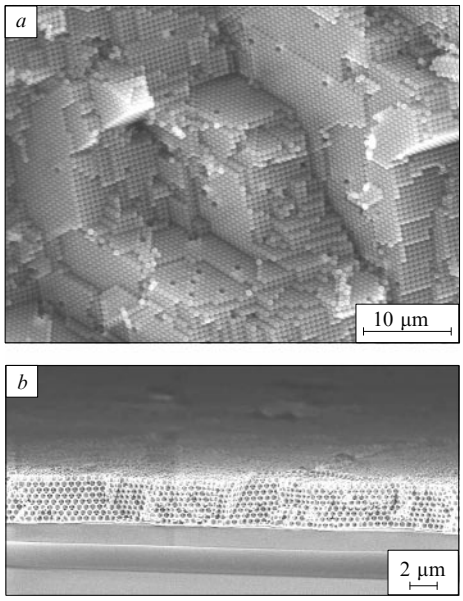


Figure 5. The structure of a photonic crystal built of ordered monodisperse polystyrene beads (*a*) and a metallic photonic crystal (*b*) with a structure of inverted opal on a conducting glass substrate.[105, 106]

aggregate to give particles 10–30 μm in size. The morphology of these aggregates was confirmed by transmission electron microscopy (TEM) and by diffraction of synchrotron radiation.[104] In the latter case one deals with a 3D diffraction grid, a photonic crystal built of monodisperse microbeads.[105–107] To date, organized arrays of nanocrystals Pt, Pd, Ag, Au, Fe, Co, FePt, Fe_3O_4, Co_3O_4, CoO, CdS, CdSe, CdTe, PbSe, alloys Fe–Pt, Au–Ag, 'core–shell' nanostructures CdS/CdSe, CdSe/CdTe, Pt/Fe, Pd/Ni, *etc*., are known.[108–110]

The size of modern microelectronic devices approaches the lithographic limit. Therefore, it seems promising to develop those fields of nanotechnology that concern the assembly of functional networks from single nanocrystals.

Indeed, colloid systems can be treated as nanosized structural elements or mutually replaceable blocks for various nanomechanisms and nanodevices. Unfortunately, the possibility of manipulating single nanoparticles is principally limited and, therefore, the range of objects to be designed is also limited. That is why self-organization or self-assembly can serve as alternative approaches to the organization of complex systems from individual building blocks. On the one hand, control of self-organization processes is a complicated task, which requires the understanding of not only interparticle interactions, but also knowledge of such physicochemical characteristics, as the electron density distribution over the crystallite surface, the elasticity and deformability parameters of a particle, kinetic factors, *etc*. On the other hand, control of self-assembly will be a powerful tool for fabrication of nanostructured systems.

In addition to self-organization effects, self-similarity effects in nanostructures may also manifest themselves. For instance, when a nanoparticle is considered as an elementary building block, one can expect the formation of 'superclusters' comprised of a few nanoparticles.[111] Considering such an aggregate as the 'next' building block, one can go to the next level of structural organization of the system, *etc*.

The model thus constructed is self-similar and can be described in the framework of fractal geometry. The possibility of formation of self-like ensembles on the nano level is related to the effect of ligand shell surrounding clusters or nanoparticles on their stabilization in colloid solutions.

Other typical nanosystems leading to ordered structures are provided by self-assembling monolayers, Langmuir–Blodgett films,[112–115] liquid-crystalline materials, polymers and composites based on them.[116, 117]

IV. New approaches to nanomaterials technology

Target design of nanomaterials with reproducible, specified properties is a very complicated task. To solve it, researchers should take into account both the fundamental peculiarities of nanomaterials and specific features of interactions in ensembles of nanoscale objects and their structural hierarchy. Fabrication of nanomaterials means creation of metastable systems with specified hierarchical structural organization suitable for realization of the desired unique physical, physicochemical and biological properties. Clearly, not all traditionally used methods of fabrication of nanomaterials can lead to desired results provided such initial conditions. Therefore, the development of unique methods for particular classes of nanomaterials is required.

For most researchers it is undoubtful that 'atom-by-atom' assembly of nanomaterials is a scientific Utopia and that the main methods of fabrication of nanomaterials should be based on the self-assembly, self-organization and template principles. The most pronounced effect is expected for a combination of such methods with chemical methods of homogenization of the starting precursors, 'soft chemistry' methods, *etc*. The evolution of a nanosystem in different stages of fabrication of a target nanomaterial can be described using the temperature–time transformation (TTT) diagrams and includes the key parameter, namely, time. By and large, improvement of the reproducibility of fabrication of nanomaterials requires analysis of the influence of the synthesis conditions on the hierarchical structural organization of the final ensemble of nanoscale objects. This influence manifests itself as the known effects of 'prehistory' and 'topochemical memory'. Once the conditions for self-assembly or self-organization are known for a system, they can be used for elaboration of efficient methods for fabrication of nanomaterials with specified characteristics.

Structure-forming templates including surfactants, polydentate ligands, liquid-crystalline matrices, dendrimers, as well as 1D and 2D nanoreactors can also be introduced into the system. Templates are elements of a complex system, which belong to a certain level of spatial organization. The introduction of templates ensures predominance of particular rather than all possible types of interactions or favours creation of steric hindrances during the formation of nanostructures. Owing to its specific features template synthesis belongs to the most efficient and predictable methods and enables fabrication of nanostructured materials with high reproducibility and high yields of target products.

Development of novel methods in nanomaterials technology, including self-assembly and self-organization, requires conducting research in the following avenues:

— mechanisms of formation of nanomaterials involving conservative and dissipative self-organization;[5, 118, 119]

— peculiar features of template synthesis of 1D, 2D and 3D functional and polyfunctional nanomaterials;[20, 33, 120, 121]

— synergism in physicochemical actions as a route to new-generation nanomaterials;[122]

— formation of 3D and 2D nanostructured materials as a result of intense plastic deformation of metals and alloys, spinodal decomposition of solid solutions and crystallization of amorphous phases;[101, 123]

— regularities of formation of spatially ordered nanoparticle arrays using nanoreactors of different nature and dimension;[124, 125]

— physicochemical methods of fabrication of artificial nanostructures in confined colloid systems using the principles of operation of living systems;[119, 126]

— mechanisms of surface functionalization of 0D (quantum dots) and 1D (nanotubes) materials and monolayer dispersions;[83, 127–129]

— possibility of formation of nanosystems, nanocomposites and nanodevices based on crown ethers, cryptands, porphyrins and phthalocyanines;[130, 131]

— design of magnetically, optically, thermally, chemically and mechanically sensitive nanomaterials;[29, 132, 133]

— prospects for utilization of coordination compounds as precursors of nanostructured materials of different dimension;[83, 134, 135]

— clustering mechanisms in liquid, solid and vapour-phase systems;[136–138]

— possibilities of utilization of supercritical media for fabrication of unique nanostructures and nanomaterials;[135]

— mechanisms of self-assembly of single nanoparticles to 2D and 3D nanomaterials including colloid and photonic crystals;[83]

— exposure to laser emission as a route to novel nanostructures and nanomaterials;[139, 140]

— combined synthesis and assembly of nanoparticles to 2D or 3D macroscopic structures;[27, 141]

— utilization of scanning probe microscopy (SPM) for assembly of complex nanostructures based on graphene, fullerenes, metal clusters and semiconductor nanocrystals;[27, 142]

— prospects for the use of protein engineering in fabrication of 3D nanomaterials combining biological and non-biological functional fragments;[27, 143]

— surface adsorption as efficient tool for modifying the optical properties of nanocrystalline materials;[26]

— possibilities of diversification of the structure and properties of nanodisperse functional materials using plasmachemical and hydrothermal syntheses;[144, 145]

— prospects for progress in 'soft' nanotechnology based on 'smart' polymers as nanoscale actuators utilizing the energy of chemical transformations for mechanical deformations;[146–149]

— 2D or 3D microprinting of integrated devices (solar cells, flexible displays, RF labels, sensors, *etc*.);[150–152]

— preparation of thermally stable aerogels and aerogels with specific functional properties;[153]

— peculiar features of fabrication of nanomaterials for chemical power cells, fuel cells and molecular recognition gas and biological sensors;[154, 155]

— methods of preparation of efficient catalysts of water photosplitting for hydrogen power engineering and photodegradation of industrial waste;[156, 157]

— methods of deposition of functionalized layers on the surface of ceramic and metallic microfilters and foams for

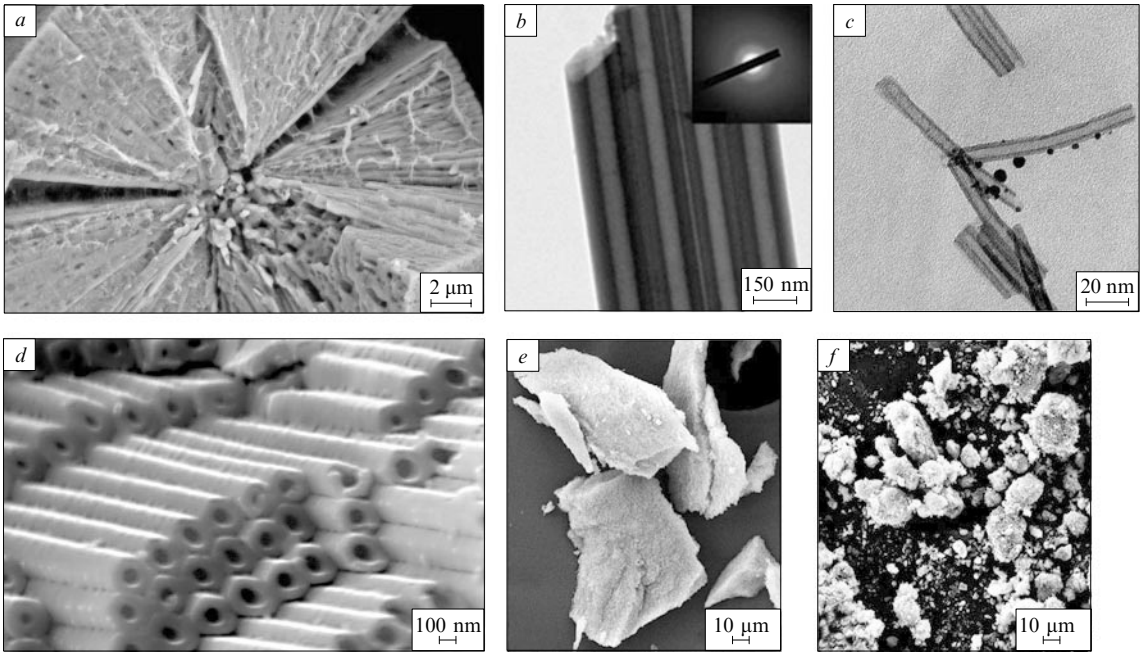


Figure 6. Nanostructured titania samples prepared by hydrothermal treatment (*a*) and anodic oxidation of titanium (*b*); nanocomposite comprised of titania nanotubes and metallic Pt nanoclusters for catalytic applications (*c*); titania nanotubes prepared by anodization (*d*) and titania aerogels (*e*, *f*).

fabrication of mesoporous membranes for chemical technology, ecology and medicine;[158]

— efficient methods of fabrication of nonvolative, ultrahigh capacity memory devices;[159]

— design of novel high-permittivity materials for nanoelectronics, based on ultrathin ($\sim 3-5$ nm) metal oxide layers.[160]

Figure 6 presents various titania-based morphological derivatives (nanomaterials). Titania obtained using hydrothermally treated spherical microbeads (Fig. 6 *a*) provides an example of a micro/nanocomposite in which titania nanotubes formed within internal radial pores of the initial microparticle. TiO_2 nanotubes shown in Fig. 6 *b*,*c* are similar, although prepared by different methods. The former are a product of titanium anodization with the formation of a porous surface film comprised of cylindrical fragments (Fig. 6 *d*) whose size depends on the synthesis conditions; here, the similarity of geometric parameters is a result of self-organization occurring at the background of competition between various processes and phenomena accompanying anodization. Nanotubes in Fig. 6 *c* were prepared by 'rolling' a layered precursor under hydrothermal synthesis conditions. Such a rolling is a manifestation of a general principle of reduced stability of planar (layered) (nano)systems that tend to decrease the energy of edge 'unsaturated' atoms by closing the plane. Figure 6 *e*,*f* presents aerogels, *i.e.*, products of supercritical drying of titanic acid gels. In fact, by choosing specific synthesis conditions above the critical point of the solvent (or by replacing the solvent under these conditions) one can with a high probability retain the 3D structure of inorganic framework of the original gel after removal of solvent molecules. Unique ultralight materials thus prepared are characterized by high porosity and. therefore, a large surface area. In fact, they are prepared by a topotactic reaction occurring within a very narrow range of conditions.

Tin dioxide for sensorics and electrochemical applications (Fig. 7) can be obtained by specific methods [161–163] that can be regarded as typical for other systems and nanomaterials. For instance, filamentary crystals and per-

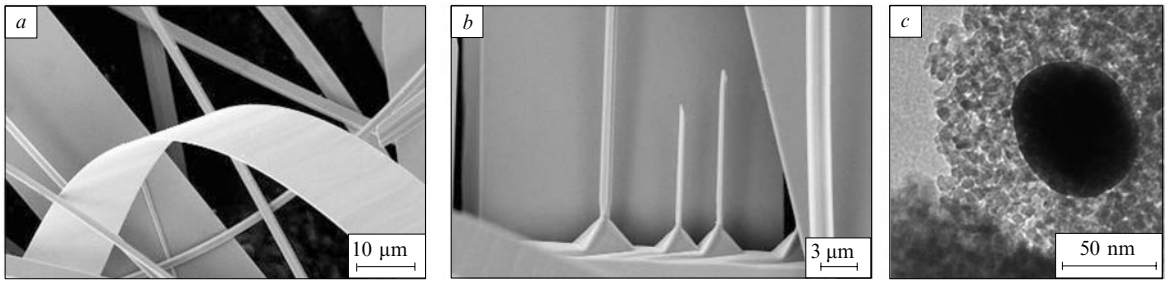


Figure 7. Tin dioxide, a material for sensorics and electrochemical applications.
Filamentary crystals (*a*), whiskers (*b*) and Sb-doped tin dioxide nanoparticles for preparation of stable suspensions ('ink' for microprinting of conducting structures) (*c*).

forated strip tin dioxide nanostructures are formed by the vapour–liquid–crystal mechanism on disproportionation of volatile tin monoxide in the vapour phase at high temperatures. At the same time, conducting Sb_2O_3 (or In_2O_3) doped tin dioxide particles are formed upon hydrothermal treatment of co-deposited hydroxides.

Not only vanadium pentoxide nanostructures, but also hybrid materials based on them can be formed with ease including the hydrothermal synthesis conditions. In particular, filamentary nanocrystals of vanadium bronzes (Fig. 8) are to some extent derivatives of the precursor, *viz*., a xerogel formed by ordered strips based on polyvanadium acids. Nanotubes (see Fig. 6*b*) provide an example of a hybrid organo-inorganic nanomaterial in which 'nanoscrolls' are formed by binding a template (long-chain amine) to the acid protons of the vanadium-oxide layer and rolling this 'sandwich'; the average interplanar spacings in this structure are to a great extent determined by the length of the aliphatic chain in the surfactant molecule.

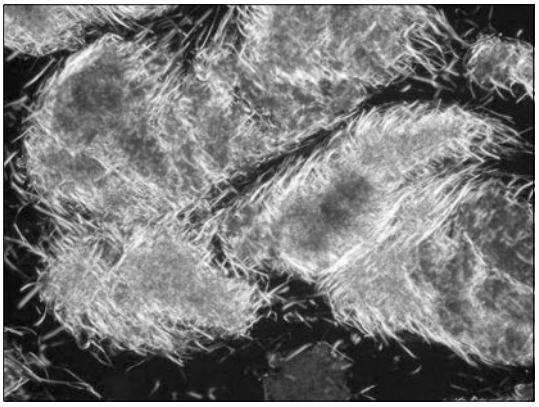


Figure 8. Nanowhiskers based on vanadium pentoxide for catalytic and electrochemical applications prepared by hydrothermal method.

Surface-decorated filamentary crystals of a complex manganese/barium oxide with a tunnel structure (Fig. 9) were prepared by two-step synthesis.[164–166] In the first stage, such crystals can be formed on isothermal evaporation of chloride fluxes. Quire recently, it was established that this type of manganites can be chemically and morphologically modified by treatment with strong mineral acid (*e.g*., nitric acid) solutions to split into a bundle of nanowhiskers. Partial removal of barium and disproportionation of Mn(III) imparts the properties of a 1D proton conductor to these filamentary crystals. As nitric acid interacts with the filamentary crystals in the presence of Mn(II) in solution, the surface of these modified whiskers is covered with a layer of hydrated manganese dioxide nanocrystals, which can also have a tunnel structure. Taking into account the template effect of different cations during the formation of the crystal structure of manganese dioxide, the tunnel structure can be specified by choosing the chemical composition of the electrolyte solution.[167]

Figure 10 shows surface-modified nontoxic γ-Fe_2O_3 magnetic nanoparticles synthesized by a new method [168–170] in water-soluble salt granules using pyrolysis of aerosols under optimized conditions. The technique was used to prepare ferromagnetic and superparamagnetic particles 5–100 nm in size as aqueous suspensions and to study the physicochemical characteristics of novel γ-Fe_2O_3 magnetic nanoparticles stabilized by humic acids that form suspensions stable for 10–100 h. It should be noted that the use of

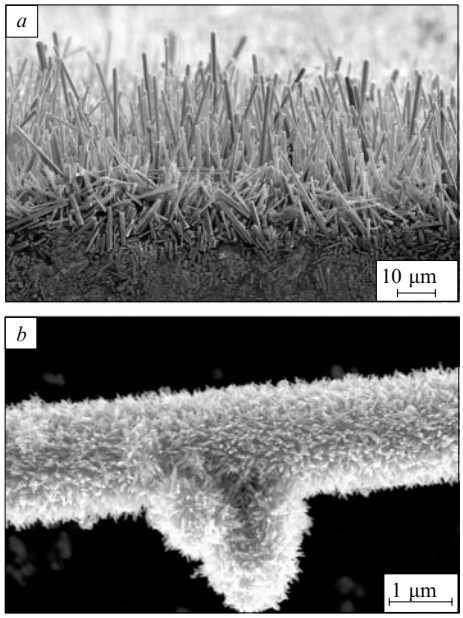


Figure 9. Manganite $Ba_6Mn_{24}O_{48}$: filamentary crystals (*a*) and their nanostructured analogues (*b*) with tunnel crystal structure for catalytic applications.[164–166]

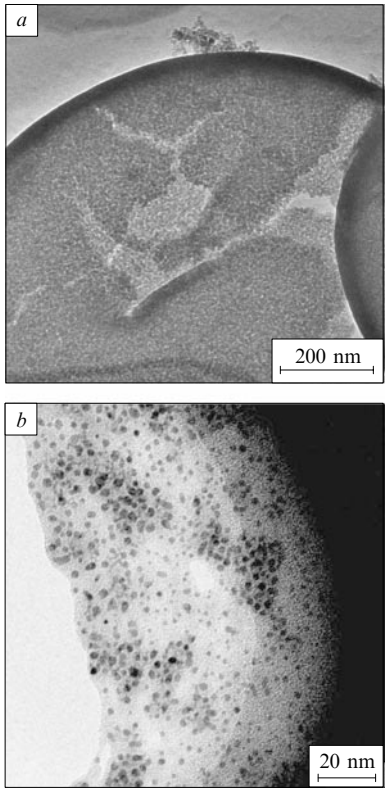


Figure 10. γ-Fe_2O_3 magnetic nanoparticles as constituents of hollow water-soluble salt microbeads (*a*) and a nanocomposite prepared from these particles after binding by humic acids (*b*).[168–170]

humic acids as the new type of organic 'modifiers' for nanoparticles allows a number of problems to be solved. Humic acids are natural polyelectrolytes with branched molecular structure and a large number of functional groups that coordinate the Fe^{3+} ions. Iron oxide nanoparticles can incorporate into their structure and form a distributed associate of nanoparticles whose size is approximately equal to that of the original humic acid 'coil'. Additional advantages of humic acids are as follows: low cytotoxicity both in the initial state and after formation of a nanocomposite with magnetic nanoparticles; the possibility of varying the size of the humic acid 'coils' containing associates of nanoparticles by varying the molecular mass of humic acids; ready chemical modification and, correspondingly, the modification of magnetic nanocomposites by various functional groups present in the humic acid molecules. It should also be noted that humic acids are cheap natural compounds and therefore manufacturing of novel magnitoactive agents based on humic acids and iron oxide magnetic nanoparticles is pragmatically substantiated.

Materials with pores of specified size and shape can be obtained by, *e.g.*, template synthesis. The template serves as a centre for organization of main structural blocks of the matrix and formation of a framework. Micelles formed by surfactant molecules in solutions can also play the role of a template.[171, 172] Removal of the template should be followed by the appearance of a cavity which exactly matches the size and shape of the micelle. The accuracy of the pore shape match depends on three factors including the nature of the interaction forces acting between the template and matrix; the ability of the matrix to match the template shape; and the template-to-building block size ratio. For instance, mesoporous oxide materials are obtained by hydrolysis of precursors (organic, complex or inorganic compounds containing target metal and nonmetal atoms) in solutions containing template molecules. Mesoporous structures with uniform pore size distribution are formed using supramolecular structures (organic micelles) as templates. They are formed in solutions when single molecules interact with the 'building blocks' of the matrix, *i.e.*, oligomeric polyhydroxy complexes. To date, the synthesis of mesoporous SiO_2 has been best studied (this compound was first obtained in 1992).

Templates can conditionally be divided into two large groups including covalently bonded and noncovalently bonded ones. The first group includes organosilicon compounds with bulky organic groups, *e.g.*, octadecyltrimethoxysilane. Such templates are used for the synthesis of mesoporous silica with functionalized pore walls. The second group includes organic molecules, which interact with polyhydroxy complexes and with the matrix through electrostatic and van der Waals forces and hydrogen bonds. Depending on the nature of molecules, they are divided into the following groups: anionic, *e.g.*, sulfo acids (n-$C_nH_{2n+1}OSO_3H$), phosphoric acids (n-$C_nH_{2n+1}OPO_3H_2$) and carboxylic acids (n-C_nH_{2n+1}. .COOH); cationic, *e.g.*, various alkylammonium or alkylpyridinium salts; nonionic, *e.g.*, primary amines in basic or neutral medium, block copolymers and ethers.

A mesoporous matrix obtained as mentioned above was used to form ferromagnetic nanofilaments based on different phases including hexaferrites, iron oxides and metallic iron (Fig. 11) in an ordered system of pores.[171, 172] Such a nanocomposite is a promising medium for ultrahigh density magnetic information storage devices. Obtaining porous alumina by anodization is accompanied by the formation of a system of vertical ordered pores of variable diameter; by choosing the conditions for electrochemical deposition after the formation of porous oxide film one can prepare arrays of not only ferromagnetic filaments (Fig. 12 *a*), but also nanostructured metallic nanorods with a ferromagnetic–antiferromagnetic junction (Fig. 12 *b*). This is not only a clear demonstration of the potential of the method, but also an example of target design of a unique novel material. The use of classical ceramic technology for fabrication of a microporous (macroporous) bone implant is shown in Fig. 13. Improved biocompatibility of the implant is due to the use of hydroxyapatite nanoparticles whose shape and size are similar to the corresponding characteristics of natural hydroxyapatite (component of human bone tissue). In fact, here the principle of target design of a multilevel hierarchical structure of an artificial biomaterial mimicking a natural material is implemented beginning with the design of the initial building blocks of the ceramic structure, namely, hydroxyapatite nanoplatelets with desired micromorphology and chemical composition, and is followed by the formation of porous structure for proliferation of osteoblasts using a polymeric template and by control of the ceramic structure and mechanical properties of the resultant material by sintering.

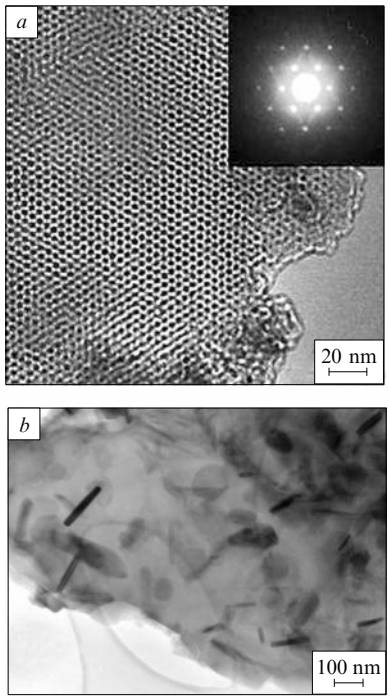


Figure 11. Magnetic nanocomposites.[171, 172]
Iron nanofilaments in mesoporous silica structure prepared using liquid-crystalline templates (*a*) and strontium hexaferrite monodomain nanocrystals in a glassy matrix (*b*).

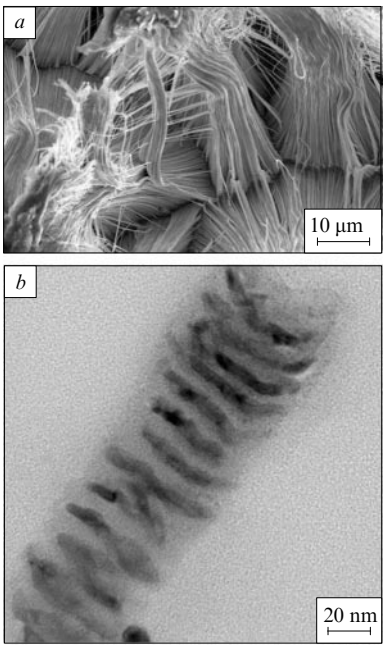


Figure 12. Nickel magnetic nanowire prepared by electrochemical deposition of the metal on a porous anodized aluminium substrate and dissolution of the substrate in alkali (*a*) and a 1D sandwich structure with a ferromagnetic–antiferromagnetic junction prepared analogously (*b*).[171, 172]

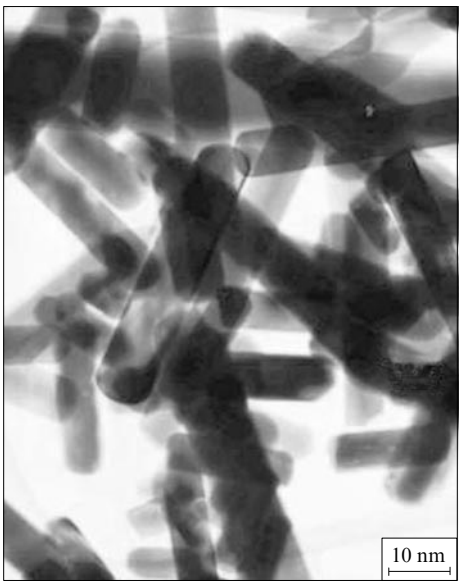


Figure 13. Hydroxyapatite nanoparticles used for preparation of bioceramics.

V. Design of novel types of nanomaterials

Design of novel types of nanomaterials is an immediate indicator of the efficiency of basic research on the foundations of novel nanotechnologies. The development is carried out in application oriented manner. This implies that the choice of methods of synthesis and corresponding technological rules is governed by the desired parameters of the final product. Clearly, the understanding of the processes underlying modern and future methods for the synthesis of nanomaterials is a key condition for fabrication of novel types of nanomaterials. There are two main reasons determining the appropriateness of carrying out the synthesis of novel nanomaterials. One of them is related to the expectations of significant improvement of the existing or the onset of novel unique properties due to the use of more costly and labour-consuming methods for the synthesis and storage of nanomaterials instead of the use of 'conventional' materials; this will make additional expenditures for implementation of the 'nanotechnological approach' reasonable. The second reason is related to the need for multiparametric miniaturization of home appliances and instruments, reduction of energy capacity and power consumption, improvement of the efficiency of utilization. Miniaturization, especially in such areas, as medicine, nanoelectronics, ecology, *etc.*, may appear to be a key condition; meeting it will offer prospects for the design of new-generation materials and devices. The design of novel types of nanomaterials requires investigations in the following areas:

— structural design of nanomaterials;[173]

— synthesis of novel polyfunctional nanomaterials with cross-correlated magnetic, electrical and optical properties;[29]

— search for novel materials with controllable photonic band gap;[27, 174]

— development of foundations of the design of new-generation thermo-electric and magnetocaloric materials based on 'nanoblock' and 'nanocellular' structures and supramolecular compounds;[175–177]

— studies on the mechanisms of formation of magnetic nanostructured materials from glassy precursors;[178]

— fabrication of thin-film piezoelectric coatings and heterostructures for mechanical-to-electrical energy conversion;[27, 29]

— fabrication of nanostructured coatings with maximum light absorbance for direct conversion of electromagnetic radiation to thermal energy[27] or exhibiting the photoelectric effect;[179]

— elaboration of fundamental grounds of design of nanostructures with large-amplitude sensor signal, sensitivity and selectivity;[29]

— studies of mechanisms of formation of nanocomposites stable under extreme operating conditions (aviation, outer space exploration, nuclear reactors);[123, 180]

— design of thermally stable and corrosion-resistant nanocoatings;[181, 182]

— synthesis of mesoporous, high-uptake hybrid materials for hydrogen, methane, *etc.* energetics;[183–185]

— design of highly selective membrane nanomaterials for filtering of water and use in extractive and petrochemical industries;[186]

— synthesis of novel bioinspired nanomaterials;[187–190]

— design of novel biosimilar dendrimer nanostructures;[27, 123]

— synthesis of fractal nanomaterials;[191, 192]

— synthesis of bulk biomaterials by assembly of nucleic acid molecules;[143]

— design of bioinspired superhydrophobic nanocoatings as a mean for improvement of the functional properties of textiles, polymeric, building materials and glasses;[101, 193]

— elaboration of principles of engineering of artificial bone tissues and skin, based on the design of novel types of hybrid nanomaterials;[194–196]

— development of the foundations of the design of nanocomposites including thermoplastic polymers;[197]

— search for novel polymeric materials for nanolithography;[198]

— elaboration of polymer crazing processes in liquid media as a route to novel types of carbon nanomaterials and nanocomposites;[199]

— elaboration of nanosized metal-complex catalysts for the synthesis of promising polymeric materials and fine organic synthesis;[200]

— design of highly efficient nanoporous sorbents of environmentally hazardous substances (heavy metals, radionuclides), search for new-generation nanomaterials for solving 'environmental safety' problems;[27, 123, 177]

— design of nanomaterials for emission, conversion and utilization of THz electromagnetic radiation;[201]

— search for novel nanomaterials for highly efficient, high-brightness, 'white' light-emitting diodes;[179, 202]

— design of materials based on nanostructures absorbing electromagnetic radiation in a wide frequency range;[203]

— design of metamaterials based on nanocomposites for opto-electronics, sensorics, magnetic resonance imaging, ultrahigh resolution microscopy;[204, 205]

— elaboration of new approaches to the design of nanomaterials for spintronics;[206, 207]

— search for novel nanomaterials for alternative energy sources including flexible solar cells; ultrasmall power cells, hydrogen accumulators, electrochemical power cells, thermoelectric power cells and supercapacitors;[184, 208–210]

— elaboration of nanomaterials for memory devices, switches, information storage, detectors, displays, filters (optical, multiplication, holographic), insulators, molecular devices and micromachines;[211, 212]

— design of chemosensory nanomaterials and micro/nanochips for devices for noninvasive investigation of human state;[213, 214]

— design of structural and refractory alloys reinforced with nanoscale objects;[207]

— investigations on possibilities of the design of novel multifunctional nanocomposites and hybrid organo-inorganic materials;[208, 215]

— design of different-size nanocomposites possessing the properties of multiferroics including magnetoelectric materials.[121, 216]

VI. Modelling of nanomaterials and their formation

Modelling is a key stage and, at the same time, independent component of the studies on nanosystems, nanomaterials and nanotechnologies. The results obtained by modelling confirm or reject the available interpretations of experimental data and in some cases serve a basis for unique prognoses that significantly simplify the design and practical implementation of novel nanomaterials. Correct simulation of nanoscale objects and nanotechnology processes[217–220] requires basic (including first-principle) knowledge, databases filled with reliable reference data, conceptual theories of the structure and behaviour of complex systems and the design of software for parallel computing. The last-mentioned stage is extremely labour-consuming because it involves processing (often, in the real-time mode) of huge data arrays using heuristic and other numerical methods, which complement mathematical modelling of key phenomena and objects. In addition, modelling of nanomaterials and nanotechnologies is a complex and multiscale process, which combines essentially different algorithms that describe the behaviour of a system under study in different hierarchical levels from the nano and meso to the macro level. Only this approach allows one to expect a nonzero predictive power of the final model with respect to the functional characteristics of the entire resultant system (nanomaterial). Clearly, the design of nanomaterials and modelling of their fabrication, as well as prediction of the properties and behaviour of nanomaterials under specified operating conditions is only possible when using powerful computational facilities including parallel supercomputers. The key avenues of modelling of nanomaterials and their formation are as follows:

— modelling of formation of various types of nanostructures and nanomaterials under quasi-equilibrium and strongly nonequilibrium conditions;[221]

— design and mathematical modelling of nanostructured structural materials with record-high mechanical parameters using supercomputers;[222]

— modelling of self-healing metallic, ceramic and polymeric materials by their nanostructuring;[223]

— *ab initio* modelling of the deformation and fracture of nanostructured structural polymeric materials, metals and alloys;[224, 225]

— computer simulation of spinodal decomposition in metallic, ceramic and polymeric systems;[226]

— modelling of formation of dislocation structures in 3D and 2D materials;[227]

— mathematical modelling of self-organization in nanosystems and nanomaterials;[228]

— mathematical modelling of transport phenomena in nanostructured materials;[229]

— elaboration of methods of physical modelling to reveal the possibility of designing novel nanomaterials;[27]

— molecular modelling of nanosystems based on empirical (10^6 atoms), semiempirical ($< 10^6$ atoms) and *ab initio* (> 100 atoms) methods and on the density functional theory ($\geqslant 100$ atoms);[27]

— simulation of nanoclustering in amorphous and glassy systems;[140]

— computer simulation of the evolution of fractal nanostructures in sol–gel processes;[191]

— modelling of formation of carbon nanoparticles and nanotubes;[230]

— elaboration of combinatorial chemistry methods as applied to the design of novel nanomaterials;[231]

— modelling of phase state diagrams of nanodisperse compounds;[232]

— modelling of social impacts of and environmental risks from nanotechnology;[233, 234]

— development of grid technology in nano-industry;[235]

— modelling of elementary operations with quantum bits (q-bits);[236]

— mathematical modelling of functional properties of nanomaterials;[237–240]

— molecular modelling of proteins, biomolecules and nanomaterials, computer simulation of the interaction of nanomaterials with cell membranes, cell compartments, biomolecules and proteins.[241]

In 2008, a Russian company 'T-Platforms' made a poll of students, post-graduate students and young researchers at the Department of Materials Science, M V Lomonosov Moscow State University concerning the need of using computer simulation and high-performance computing in

studies of nanoscale objects and nanotechnology research. The largest proportion (25%) of respondents believe that the use of high-performance computers can be useful for research on nanoscale objects to obtain basic knowledge about the structure and experimentally observed phenomena, to shorten the practical development stage (16%), to fabricate yet unavailable promising nanomaterials and devices (9%) and to construct virtual real-time models (16%). At the same time, 31% of respondents believe that supercomputers are no more useful than conventional computers in nanotechnology research and development. Nearly 49% of respondents do not use computer modelling/simulation methods. Respondents who use these methods are aimed to solve problems in nanochemistry (11%), physics of nanosystems (14%), nanoelectronics and nanoengineering (13%), design of novel materials (6%) and development of nanobiotechnologies (3%). Clearly, utilization of supercomputers in domestic research on nanosystems, nanomaterials, nanotechnologies and nanobiotechnologies is in its infancy.

Since the availability of supercomputers is still low, recent attempts to improve their efficiency include provision of remote access or, generally, development of the so-called grid systems. An example of realization of efficient Internet access to modern scientific equipment is provided by the use of scanning probe microscopes.[242] This makes it possible not only to obtain and process experimental data, but also helps in immediate practical implementation of a key step in nanotechnological education.

The quantum and coherence effects, strong electric fields leading to avalanche breakdown, the problem of heat sink from close-packed structures and the effect of point defects are severe obstacles to miniaturization. The understanding of the transport mechanism on the nano scale and the possibility of reliable prediction of the behaviour of nanodevices require fundamentally different methods of simulation, because the cost of new-generation chips permanently increases and any error, especially in the stage of circuit design, will be too costly. But the cost of the errors related to underestimation of risks from the interaction of nanoscale objects with biological structures (Fig. 14) can be at least comparable. As mentioned above, nanoparticles and many other nanoscale objects differ from microscopic objects in that the nanoscale objects can remain unrecognized by human immune system and thus penetrate with ease into organisms and spread there not only through the circulatory system. Nanoparticles can readily penetrate the blood–brain barrier and the placental barrier and accumulate in cells of various organs. Here, the key issue is to simulate the penetration of nanoscale objects through the cell membrane [243] (see Fig. 14), which is carried out in some Russian and foreign research groups. Successive attempts to predict the necessary composition, structure, and synthetic routes to pharmaceuticals containing nanoscale objects have been reported.

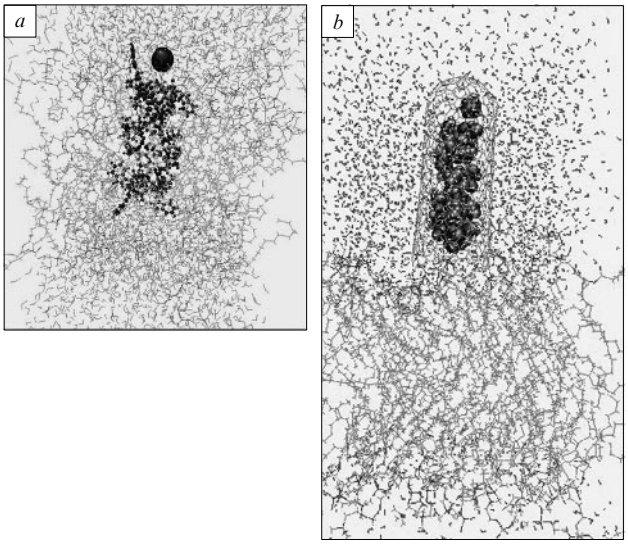


Figure 14. Simulation of interaction between nanoscale objects and biological objects on a supercomputer.[243]
Shown are different stages of the interaction (*a*, *b*).

VII. Elaboration of methods for analysis of nanosystems and nanomaterials

The role of methods for analysis of nanosystems and nanomaterials [244–251] can hardly be overestimated. Development of increasingly more powerful analytical methods, especially visualization techniques (Figs 15–18), such as scanning probe microscopy (SPM) and high-resolution TEM, has stimulated interest in nanosystems, nanomaterials and nanotechnologies. From the standpoint of practical application of nanotechnology products, reliable substantiation of results is a basis for such law procedures, as attestation and certification of 'nanoproducts', their licensing, *etc*. Clearly, elaboration of new and the use of existing methods for analysis of nanomaterials are intimately related to progress in modelling of the behaviour of nanosystems, which most pronouncedly manifests itself in the design of modern software, an essential component of analytical methods. Using analytical methods in routine research practice permits not only obtaining experimental data, but also experimental design and efficient realization of experimental strategies. A distinctive feature of studies on nanosystems is that analysis of such objects is often performed at the limit of theoretical resolution of analytical complexes. Therefore, investigations of nanomaterials require the use of a number of complementary analytical methods. Of paramount importance is also the development of method-

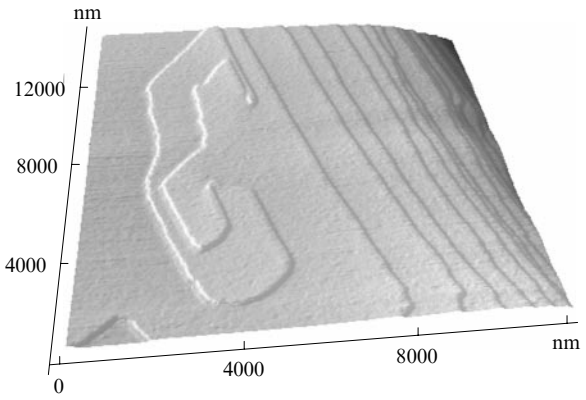


Figure 15. A scanning probe microscopy study of a lysozyme crystal.[282]
The image is courtesy of Prof I V Yaminsky, Department of Physics, M V Lomonosov Moscow State University.

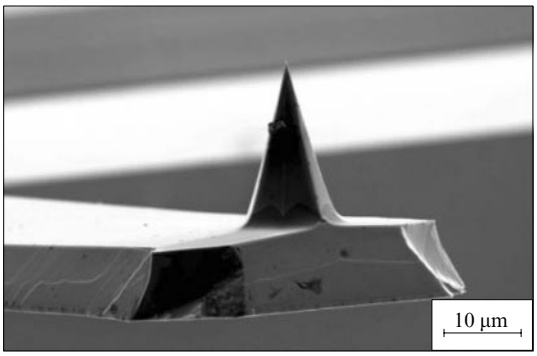


Figure 16. The tip of an atomic force microscope.

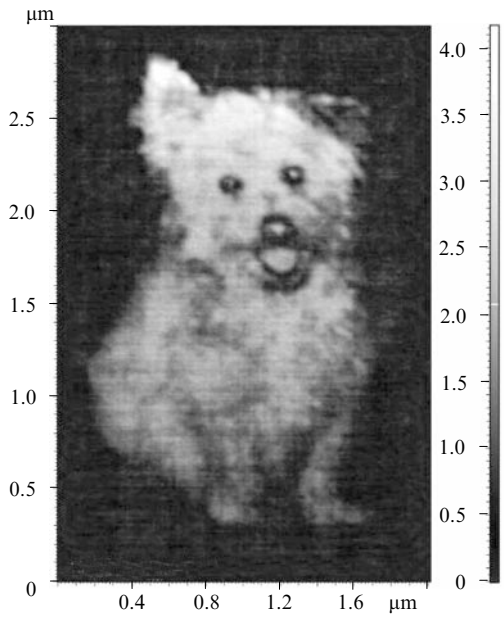


Figure 17. A nanolithography image obtained using a scanning probe microscope.
The image is courtesy of V A Smirnov, Technological Institute, The South Federal University (Taganrog, Russia).

ologies underlying the progress in metrology and standardization. By and large, key research avenues in this field include:

— elaboration of methods for visualization of nanosystems and manipulation of nanoscale objects, fabrication of micro- and nanoscale electromechamical devices;[217]

— development of methods for diagnostics of nanomaterials (electron microscopy, SPM and near-field microscopy, optical spectroscopy, Mössbauer spectroscopy, radiospectroscopy, SQUID magnetometry, analysis of surface phenomena and determination of surface area, *etc.*);[244–250]

— elaboration of methods for standardization of nanosystems and nanomaterials;[251]

— studies of geological environments and objects, nanoparticles in sediments, creation of geochemical barriers for environmental control;[252]

— development of physicochemical methods of investigation, diagnostics, metrology and quality certification of nanomaterials and nanosystems;[251]

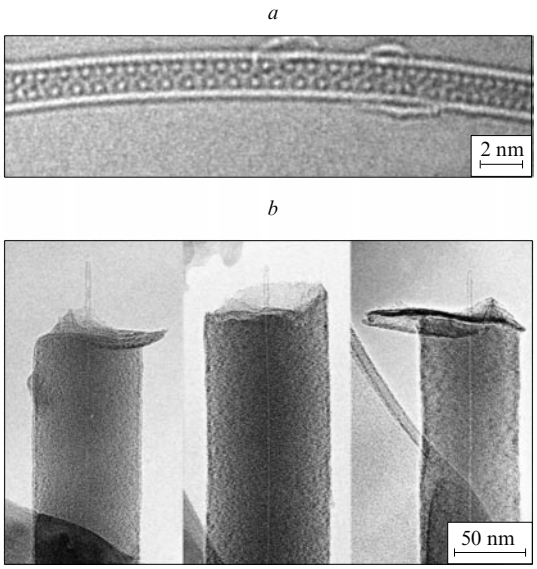


Figure 18. TEM images of carbon nanotubes filled with nanocrystals (*a*) in a protective amorphous sheath (*b*).
The images are courtesy of N A Kiselev, Institute of Crystallography, Russian Academy of Sciences, Moscow.

— elaboration of modern methods for diagnostics of nanostructures and nanomaterials using synchrotron radiation (photoelectron spectroscopy, small-angle scattering, XAFS-spectroscopy, resonant photoemission, *etc.*);[253]

— fabrication and utilization of nanoparticles for diagnostics and visualization of tumours and other pathologic paraplasms;[254]

— investigations of the interaction of nanomaterials with biomolecules and cell structures, effect on the activity of enzymes, peroxide oxidation of lipids;[255]

— studies of biodegradation of nanomaterials in different media;[256]

— elaboration of sampling techniques for identification and assaying of nanomaterials and the development of methods for isolation of nanomaterials from the environment, food, packing materials, cosmetics and biological media;[257]

— progress in photolithographic, electrolithographic and X-ray lithographic methods of formation of heterostructures;[258]

— development of methods of SPM lithography with a limiting resolution of > 10 nm.[83]

Recently, instrumental methods of investigation of *in situ* formation of nanomaterials have become increasingly significant. For instance, the formation of porous anodized alumina film and templated mesoporous silica samples with ordered system of ferromagnetic wires in pores was studied by diffraction of synchrotron radiation and by small-angle diffraction of polarized neutrons.[259–261] Significant role is played by spectral methods of analysis, in particular, Raman spectroscopy, which is widely used for analysis of carbon and non-carbon nanotubes (see Fig. 18) and quantum dot superlattices.[262–264] In some cases, dynamic light scattering and ζ-potential measurements allowed researchers to follow the evolution of colloid systems,[168–170] while Mössbauer spectroscopy appeared to be most efficient for the analysis of changes in various properties and tentative magnetic structure of nanopar-

ticles.[265–268] Visualization of the evolution of magnetic structures in nanocomposites[268,269] and charge transfer[270–272] enables construction of realistic models for cooperative behaviour of nanosystems and structural elements of nanocomposites, which can significantly extend prospects for their practical use. Improvement of scanning electron microscopy (see Figs 15 and 16) and TEM (see Fig. 18) allows one to follow the dynamic behaviour of objects in the field of an electron microscope, while a combination of electron microscopy and SPM enables manipulation of nanoscale objects, SPM lithography (see Figs 16 and 17) and nanoindentation.[273,274]

The properties of a material can be predicted only if its structure is known with certainty. Therefore, structural information is of crucial importance for the design of novel and utilization of existing materials. There is a variety of methods for determining the structure and properties of conventional materials. In the case of nanostructured materials these methods are inapplicable for precise determination of atomic ordering ('nanostructure problem')[275] and, correspondingly, structure-sensitive characteristics of materials, as well as classical 'composition–structure–properties' correlations. Probably, solutions to these issues related to both existing problems of irreproducibility of the properties of nanomaterials and difficulties in their certification will be found with progress in nanometrology. Recently, the development of nanometrology has become topical owing to dramatic enhancement of nanotechnology research and implementation of the results obtained in industrial application-oriented research.[276]

VIII. Conclusion

Eventually, basic research on nanomaterials following the investigation lines mentioned above is aimed to design new-generation nanotechnologies that will be socially demanded in a more or less distant future.[27] The latter is closely related to nanotechnological foresight activity, which dates back to the foundation of the Foresight Institute (E Drexler and C Peterson, USA) , which was then reorganized to the Foresight Nanotech Institute. Its activity is aimed to find such nanotechnology and nanomaterial roadmaps that should favour solution to the following global problems:

— creation of new environmentally safe power sources;
— gain in health and prolongation of human life;
— maximum increase in productivity of agriculture;
— meeting human demands for fresh water and clean air;
— progress in outer space exploration;
— elaboration and mass utilization of new information technologies.

Recently, the foresight activity has started in the Russian Federation. An example is provided by the Long-Term Scientific and Technological Prognosis of the Development of the Russian Federation (to the year 2030), which is currently developed at the Russian Academy of Sciences. At the same time, experience reveals a few examples of successful foresight in technological progress; often, short-term prognoses are erroneous, needless to say of long-term ones; however, sometimes dreams come true. All these considerations are to even greater extent concerned with foresight of long-term development of nanotechnologies, because they are characterized by extremely high research intensity and interdisciplinary character (see above).

Nevertheless, one can state that realization of the programme of basic research and application-oriented research on nanomaterials (see above) to the year 2030 (probably, somewhat earlier) will help to solve many problems. In particular, these are:

— development of highly efficient alternative energy sources including solar cells, hydrogen engines, and, as a consequence, significant (by 2–3 times) reduction of petroleum and gas consumption;
— design of combustion engines with an effectivenes of more than 70% due to the use of high-temperature composites based on zirconium, hafnium and tantalum borides and carbides;
— considerable (by 2–3 times) extension of the operating life of nuclear power plants by improving the quality of materials used for production of nuclear reactors and for immobilization of nuclear waste;
— fabrication of systems of energy generation, accumulation and transportation with nanostructured materials based on high-temperature superconductors as key elements;
— fabrication of sufficiently cheap biodegradable comodity polymers;
— design of efficient systems for saving of residential energy.

Taken altogether, this will to almost halve the emission of gases and thus postpone the global warming on the Earth.

Quality improvement and prolongation of human life to a nearly biological limit requires

— development and utilization of cardiostimulants with self-contained power supplies;
— creation of biocompatible and bioresorbable implants whose properties are at least comparable with those of natural bone tissue;
— development and utilization of highly efficient methods for drug delivery to malignant cells using magnetic nanoparticles and quantum dots;
— design of multifunctional nanomaterials for efficient diagnostics in medicine;
— development and utilization of biosensors based on the so-called 'smart' materials with nonlinear magnetic, optical and electrical parameters.

Significant improvement of productivity in agriculture will be possible owing to

— elaboration of large-scale production of fertilizers and prolonged-action microfertilizers based on biodegradable polymeric containers;
— development of efficient soil reclamation and soil structuring technologies using membrane technologies;
— design of new-generation pesticides including insecticides, herbicides and fungicides based on hybrid nanomaterials.

Human demands for fresh water and clean air will be met upon

— practical implementation of currently developing photocatalysts based on nanostructured metal oxides (*e.g.*, TiO_2, ZnO, CeO_2, *etc.*) for efficient decomposition of organic impurities in water and bacteria-killing, and possessing the ultrahydrophobicity effect used for self-cleaning of various surfaces (textiles, buildings, cars, *etc.*);
— wide utilization of currently developing catalysts for oxidation of products of incomplete combustion of fuel (first of all, CO) based on mesoporous oxide structures

containing nanoclusters of platinum and other catalytically active nanoscale objects;

— implementation of membrane technologies based on the use of polymeric, ceramic and metallic nanostructured membranes;

— complete rejection of conventional power plants in favour of nuclear power plants and(or) renewable energy sources (solar energy, wind, water).

Considerable progress in outer space exploration is also intimately related to progress in nanotechnologies and wide use of nanomaterials in order to

— complete the development of full, continuous-action, dual-use system GLONASS;

— run a global system of spacecrafts to obtain information on natural and technogenic phenomena at different points on the Earth to predict and prevent emergency situations (earthquakes, fire, typhoons) and to make reliable forecasts;

— develop highly efficient methods for hydrogen production;

— produce robotic spacecrafts a few kilogrammes in mass for exploration of the Solar system.

Elaboration and mass utilization of novel information technologies requires the design and fabrication of

— new-generation semiconductors based on convergence of silicon and chemically complex nanostructured semiconductors (GaAs type) and application of novel barrier materials based on heterostructures including HfO_2, TiN and $NiSi_2$;

— bright light-emitting ($\lambda \sim 200$ nm) devices based on h-BN wide-gap semiconductors;

— metal-oxide based, transparent thin-film transistors for opto-electronics;

— nonlinear optical devices based on lithium niobates and tantalates for light frequency conversion;

— optical systems based on photonic and colloidal crystals with periodically distributed quantum dots;

— magnetic recording systems (> 10 TB per sq. inch) using nanogranulted magnetic composites and multiferroics as well as dysprosium-free magnetic materials with record-high magnetic energy;

— field-emitting transistors based on single-walled carbon nanotubes;

— nanoscale electromechanical systems with extremely low power consumption and ultrahigh sensitivity for future electronics and sensorics.

There research avenues are similar to the high-priority avenues of scientific and technological research in the Russian Federation and should apparently be taken into account when carrying out basic research on nanosystems, nanomaterials and nanotechnologies.

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