Nanoscience: Whence it entered our World

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The popularity of nanoscience as a special field of inquiry within materials science and engineering has on been on the rise among the researchers. The US federal funding for nanoscience and nanotechnology, for example, has been steadily increasing from $270 million in 2000 to $1.08 billion in 2006 to the projected $1.7 billion in 2014. This communication begins with the proposition that the interest in physical chemistry of nanoscale phenomena is a natural consequence of the spatial refinement of the human ability to controllably manipulate the material substratum of physical reality. Examples are given to illustrate an immense sensitivity of material properties to grain size on the nanoscale, a phenomenon that directly contributed to the rise and development of nanoscience as a special field of scientific inquiry. Systematic observation of these and other peculiarities occurring at the nanoscale and a belief that they could be explained within a single framework of thought led to the rise of a special new scientific discipline: nanoscience, or the science of the small, as it has been informally baptized. At the same time, elucidation of the exact particle size dependencies of properties of interest opened up a possibility of their tailoring by controlling the particle size on the nanoscale instead of altering the composition, the strategy that has been utilized by the materials scientists for many generations.

Key words: Nanoscience, Materials Science, Size dependent properties, Strategy, Nanotechnology

From 1857 when Michael Faraday reported the first synthesis of gold sols, which are still stable and on exhibit in the British Museum [1] (Figure 1), to 1900s when Richard Adolf Zsigmondy characterized the first nanoparticles, as small as 10 nm, to one of the last days of the 1950s when Richard Feynman argued in a lecture at Caltech that “there’s a plenty of room at the bottom” [2] to 1974 when Norio Taniguchi coined the word “nanotechnology” at a summit of the Japanese Society of Precision Engineering to 1989 when 35 Xenon atoms were used to spell IBM on a nickel substrate by means of a scanning tunneling microscope to this very day when tens of thousands of papers on nanoscience are annually published, nanosciences’ popularity has on been on the steady rise among the researchers. The US federal funding for nanoscience and nanotechnology, for example, has been increasing from $270 million in 2000 to $1.08 billion in 2006 to the projected $1.7 billion in 2014. According to the statistical data provided by the US National Science Foundation, in 2015 there will be 800,000 professionals working in the field of nanoscience and nanotechnology in the US alone and approximately 1.2 million more worldwide [3]. Also, what at conferences only a decade ago used to be specialized symposia dedicated specifically to nanoscience is all gone now, as practically every subject of research in materials science and engineering is more about nano than it is not. The dream of every creator of a new idea, that its idea virtually disappears by becoming dissolved in all things, has certainly become true for the forefathers of the field of nanoscience.

Although nanoparticles have existed on Earth since the earliest days of our planet, in the form of volcanic and wildfire smoke, weathering products and microbial artifacts, and have been used in pigments across the world for millennia [4] nanoscience still stands as one of the newest and most prosperous subfields of materials science. Beliefs are shared among practically all members of the materials science community that there has not been a field of science opened with as much potential to revolutionize life on Earth as nanoscience has it. In this communication, we will be walked through alleys and galleries whe-
rein we would be able to glance exactly where nanoscience originated from.

Figure 1 - These liquids may seem ordinary, but, in fact, they are some of the most famous sols ever made by the human hand. Shown here are the original bottles containing colloidal gold prepared by Michael Faraday in 1850s, stable for more than 150 years now and displayed as such in the British Museum in London.

Figure 2 - Critical length scales for some of the key inventions from the history of humanity. A shift across this scale towards ever smaller dimensions paralleled the advancement of humanity from the Stone Age to the Modern Age. Hence, as the products of the most sophisticated technologies of the day progressed from prehistoric huts, cutting tools and garments to modern musical instruments, automobiles and mechanical clocks to computers, nanocopters and nanomotors, the critical lengths shifted from millimeter to micrometer to nanometer scale, respectively.

The progress of humanity over millennia has been paralleled with an increase in the fineness with which we, humans, have been able to controllably reshape the material substrate of our environment [5]. As shown in Figure 2, critical boundaries incorporated within the products of human creativity have thus been created at an ever finer scale. As the result, we have witnessed miniaturization of devices in our everyday surroundings. The natural consequence of this is that, as of a few decades ago, materials science has entered the era of controlling physical processes at the nanometer (10^{-9} m) scale.

However, as is the case with every new field of scientific inquiry, there is a Sphinx, holding an unanswerable question in her hands, standing at the point of its origins and the entrance to it, with nanoscience no being an exception to this rule by any means. The question of the Sphinx here relates to the peculiar and oftentimes highly attractive properties of materials that occasionally appear when their grain sizes drop down to the nanometer scale.

One of the underlying premises of materials science is that properties of materials can be deduced from the elucidated microstructure, the term that describes ways in which the perfect symmetry of an ideal crystal of a given composition is disrupted by imperfections. In addition to intracrystalline defects, these intrinsic imperfections are also directly proportional to the concentration of grain boundaries, which is, in turn, inversely proportional to the grain size. Consequently, many are physical properties that could be described as a function of the size of the grains, alongside their shape, orientation, spatial distribution, etc. Nanoscience as a special field of inquiry spontaneously emerged a couple of decades ago as a branch of solid state physical chemistry from the need to explain peculiarities observed upon extrapolation of specific physical qualities that are a function of the grain size and entrance into the size region lower than 100 nm (Fig.3). Namely, the competition between high interfacial energy and the quantum nature of many physical properties at such a small scale produces drastic changes in the properties of materials following negligible modifications of the particle size, polydispersity, inter-particle interaction or morphology.

Figure 3 - A hypothetic curve illustrating deviation (--) from a theoretically predicted dependence of a physical quantity on the particle size of a material (- - -) once the latter enters the domain of nanosizes (< 100 nm).
Figure 4 - (a) Hardness or strength of a material as a function of normalized grain size, demonstrating the deviations of experimentally obtained values from those predicted by the Hall-Petch law at sufficiently low, sub-100-nm grain sizes; (b) the particle size dependence of the transition pressure for the polymorphic transformation of PbTe alloy. Reprinted with permission from Refs. [6] and [7]

The first observation of such deviations from a law that describes a physical property of a material as a function of its grain size came from the failure of the Hall-Petch law [8]. The Hall-Petch equation can be represented in the following form:

\[ \forall T < 0.4T_m \text{ and } D < 10 - 100 \text{ nm} \neq \sigma_y = \sigma_0 + k_v D^{1/2} \]

Here \( \sigma_y \) is the yield strength, \( \sigma_0 \) is a material-specific constant describing the resistance of the lattice to dislocation movement, \( k_v \) is the Petch parameter and yet another material-specific constant, and \( D \) is the average grain diameter. This equation indicates that the lower the grain size, the larger the yield strength, which is the stress under which the material begins to deform plastically, irreversibly, as a result of the grain boundaries acting as obstacles for the propagation of dislocations under stress. The strength of the metal correspondingly varies reciprocally with the size of the grains, but only down to \( D = 10 - 100 \text{ nm} \), depending on the material in question, which is the size limit below which any further reduction in the grain size would no longer decrease, but rather increase its microhardness. Finally, \( T_m \) is the melting point of the material, which indicates that this increase in the yield strength that entails reduction in the grain size is no longer valid at higher temperatures.

However, although the Hall-Petch law suggests inverse proportionality between the grain size and the yield strength due to the ability of grain boundaries to impede the movement of dislocations, Fig.4a demonstrates a typical drastic drop in microhardness at sufficiently low, sub-100-nm particle sizes and the concomitant deviation from the function predicted by the Hall-Petch relationship. Another example pertaining to the same effect is presented in Figure 4b.

Shown here is the particle size dependence of the transition pressure for the polymorphic transformation of PbTe alloy. Normally, for a microparticulate material of the given composition and the one wherein the particle size exceeds 13 nm, its face-centered cubic (fcc), rocksalt formation, crystallizing at ambient pressure, transforms above 8 GPa into a mixture of orthorhombic and CsCl-type structures. However, as we see from Figure 4b, a decrease in the particle size below 13 nm triggers the reverse Hall-Petch effect and causes the corresponding deviation from the transition pressure vs. particle size curve applicable for particle sizes larger than 13 nm.

Figure 5 - (a) The melting point of Al₂O₃-Cr₂O₃ alloy as a function of Cr₂O₃ content and the particle size; (b) the melting point of indium as a function of the particle size for two different preparation procedures; (c) the phase diagram for a germanium-based alloy and two different particle sizes - 54 and 32 nm; (d) local density of states, a measure of the band gap, decreasing in direct proportion to the particle volume and indicating a metal-insulator transition at \( V \approx 0.01 - 1 \text{ nm}^2 \) in case of three different metals: Au, Cd and Ag, but not Pd. Reprinted with permissions from Refs. [9], [10], [11]
Other examples of such dramatic changes in material properties upon seemingly minor variations in the particle size are given in the figures that follow. In Fig. 5a, shown is the melting point of Al2O3-Cr2O3 alloy, approximately constant with respect to the chromate content, but greatly depending on the particle size when the latter reaches the nanosized range (<100 nm by convention [12] although this limit is often taken to be 300 nm in the biomedical milieu [13]). This so-called melting point depression effect is due to the larger number of surface atoms, directly exposed to heat, in samples composed of smaller particles. However, note that a greater difference in the melting point is produced by a drop in the particle size from 20 to 8 nm than by a reduction in the particle diameter from 100 to 20 nm, demonstrating that not only does a micro-to-nano transition in the grain size of a material entail drastic changes in the material properties, but also that a minor change in the grain size at the nanoscale can have far more drastic effects on the materials properties than the very transition from bulk to nano. Note, however, that exceptions to the melting point depression effect have been found, as in the cases when 1-nm sized particles would exhibit a lower melting point than 3-4 nm sized particles, which would, on the other hand, have a higher melting point than 10 nm sized particles [14]. These and similar anomalies, consequential to the complex changes in the grain boundary structure depending on the nanoparticle size, further illustrate the intricacy of the nanoscale systems. Figure 5b shows the melting temperature of indium as dependent not only on the particle size, but on the method of preparation too; thus, a sample prepared by ball-milling exhibits the melting point that exponentially decreases with a decrease in the particle size, while an opposite trend is displayed by the sample synthesized by melt-spinning (Fig. 5b). This highlights another truism of particularly critical relevance for the field of nanoscience: by producing a unique structure on the nano scale, the method of synthesis frequently has a crucial effect on the materials properties. For, as demonstrated in Figure 5b, material properties other than the grain size, including morphology, crystallinity, crystallographic orientation, concentration and type of defects, grain boundary structure, etc. can either alone or in synergy oftentimes outweigh the sheer size effect.

![Graph A](image1)

**Figure 6** - The particle size effect on: (a) the resistivity of nanostructured Nb films at different temperatures (the scale on the left corresponds to the films with d ≥ 8 nm and the scale on the right to the films with d < 8 nm); (b) the resistivity of the same material at 10 and 300 K; (c) specific conductivity of CaO as a function of the grain size; (d) specific conductivity of Gd-doped CeO2 as a function of the grain boundary surface area per unit mass. Reprinted with permissions from Refs. [15], [16], [17].

It has been known for a long time that phase diagrams of multicomponent systems need to be redrawn when the grain size is reduced down to the nano scale. However, as in the case of melting point depression (Fig. 5a), when the ratio between the melting temperature of 20-nm sized particles and that of 10-nm sized ones could be higher than the ratio between the melting temperature of 10-μm sized particles and that of 20-nm sized ones, the same effect applies here as well. For example, the phase diagram for a germanium-based alloy is shown to drastically differ depending on whether the particle size is 32 or 54 nm (Fig. 5c).

Local density of states, a measure of the band gap of a conductive material, is then shown to depend on the particle size and reaches values around 1, indicating the virtual nonexistence of the band gap and thus the loss of conductivity of metallic particles (Fig. 5d). A similar conductor-to-insulator transition induced by a decrease in the particle size is displayed in Figure 6a-b for the case of nanostructured Nb films. The logarithmic dependence of resistivity on the particle size shown in Figure 6b dictates that the transition from micrograins to 10-nm-sized particles produces the same magnitude of increase in resistivity as the transition from 10-nm-sized particles to 5-nm-sized ones does.

As we see, most metals become insulators when their particle size reaches nano scale, which is the result of the reduced free path of electrons traversing disordered grain boundary. On the other hand, some ceramics undergo the opposite transition and become conductive in the nanoparticulate form, the effect that is either associated with increased concentration of vacancies along the grain boundary with decreasing
grain size, contributing to higher lattice entropy and higher ionic conductivity, as in the case of CaO (Figure 6c) and ZrO$_2$-Y$_2$O$_3$ [18], or is due to electronic conductivity resulting from the accumulation of free electrons in the space charge layer at the grain boundary, as in the case of CeO$_2$ (Figure 6d). Figure 6d shows how electrical conductivity of Gd-doped cerium oxide increases in direct proportion to the grain boundary surface area per unit mass. How dramatic this change in the overall conductivity of the material can be is demonstrated by the case of rutile [19], TiO$_2$, where a fivefold reduction in the particle size, from 260 to 50 nm, led to a few thousands of times higher conductivity, from $1.4 \times 10^6$ to $4 \times 10^3$ $\Omega^{-1}$cm$^{-1}$.

The elastic modulus, the intensive measure of the stiffness of a material, can also experience drastic changes in magnitude following the micro-to-nano transition, as exemplified by Ag and Pb, whose Young's modulus doubled with respect to the corresponding bulk compositions when they were prepared in the form of nanowires with 30 nm in diameter [20]. At the same time, bond stiffness can also be subject to an abrupt decrease at particle sizes smaller than a few nanometers. Graphs displayed in Fig. 7a, for example, evidence a sudden and significant bond softening and an increase in the bond entropy in platinum nanoparticles when their sizes dropped below 2 nm in diameter. In this case, the lesser number of neighbors of surface atoms, whose proportion increases inversely with the particle size, directly implies softening of the average atomic bond in the material.

A direct consequence of this effect is the fact that below a certain particle size, the equilibrium particle shape becomes non-crystalline, assuming the form of dodecahedra or icosahedra instead of parallelepipeds or hexagons (Figure 7b).

As for magnetic properties of materials, ferromagnetic compounds in their bulk form typically transform to one of two forms of paramagnetism as their magnetic domain size begins to exceed the particle size: (a) regular paramagnetism in cases when the combination of surface relaxation, lattice expansion and incorporation of impurities interferes with the magnetic ordering to a drastic enough extent, or (b) superparamagnetism in cases when magnetic ordering in the particle core is still sufficient to enable significant collective dipole orientation in the external field (Figure 8a). On much rarer occasions, however, observable is the opposite effect: transformation of a paramagnetic material to a ferromagnetic one paralleling the bulk-to-nano transition, as exemplified by the case of ZnFe$_2$O$_4$ (Fig. 8b). Fig. 8c-d furthermore shows the effect of increased sensitivity of sensory surfaces of SnO$_2$ and In$_2$O$_3$ to different gases as a result of the smaller particle size and increased surface area. The increased reactivity of nanoscale surfaces is an effect utilized in various biomedical microelectromechanical systems (Bio-MEMS) for detection of physicochemical agents, including disease biomarkers, at ultralow concentrations [23], [24]. Also, owing to large specific surface areas typifying nanoparticulate samples, the smaller the particle size, the larger the drug loading capacity, provided adsorption or surface chemistry are used as the loading mechanism (Figure 9). As a result, there is a far greater demand for nanoparticulate drug carriers in pharmacy and medicine than for their microparticulate or single-crystalline counterparts.
Figure 8 - The parallel increase in nickel-zinc ferrite particle size, saturation magnetization (a, bottom, left Y-axis) and remanence (a, bottom, right Y-axis) with an increase in the annealing temperature, indicative of ferromagnetic-to-superparamagnetic transition that entails a drop in the particle size below circa 5 nm; magnetization and particle size of zinc ferrite thin films as a function of the substrate temperature, indicative of the paramagnetic-to-ferromagnetic transition following the transformation of the material from bulk to nanosized form (b); the effect of particle size on sensitivity of SnO2 (c) and In2O3 sensors (d) in detecting CO/H2 (a) and NO2 gases. Reprinted with permissions from Refs. [25], [26], [27], [28]

Surface effects are, however, only one reason behind the appearance of novel properties of materials when their grain sizes become reduced to nanoscale. Namely, as the particle size decreases, more and more atoms find themselves positioned on the comparatively disordered particle surface and exposed to greater interfacial energies than those experienced by the atoms in the interior of the particle (Figure 10a). For example, a half of approximately 1500 atoms in a Cds particle with 4 nm in diameter reside on the particle surface and it has been shown that every atom comprising a 1.2-nm sized gold particle becomes oxidized in the presence of oxygen, achieving full catalytic reactivity for its content [29]. Another effect coupled to the surface one comes from the quantum confinement apparent when the critical dimensions for a physical quality, often defined by the particle size limits, become comparable to the wavelength of the wave function used to describe the given quality in quantum terms. Quantum confinement effect is demonstrated in Fig.10b on standing waves that fit within a resonance box only in specific wavelengths, without permitting any intermediate wavelengths to occur. In other words, as the space in which the physical quality describable by the wavelength of electromagnetic radiation becomes limited, the given quality tends to adopt highly specific and well-defined states. Quantization, that is, formation of discrete, precisely
determined and oftentimes tunable energy levels takes place under such conditions of confinement. Fig.11 thus demonstrates how minor changes in the size of Au particles modify their quantum states and thereby their optical response. The color of the particle sols correspondingly becomes tunable by controlling the particle size. More specifically, it is collective oscillation of conduction electrons, the effect known as surface plasmon resonance, that is responsible for (a) scattering the incident visible light at wavelengths that are different from those of the bulk material and (b) allowing for these dominant wavelengths to be tuned via controlling the size of dispersed particles or particle aggregates [30].

![Image](image.png)

**Figure 9** - Quantified adsorption of Cytochrome c, a protein component of the electron transport chain, on diamond particles with 5 and 100 nm in size at different concentrations of the protein. Reprinted with permission from Figure [31].

![Image](image.png)

**Figure 10** - (a) Dispersion as a measure of the percentage of atoms located on the particle surface as a function of the number of atoms comprising the particle; (b) quantum confinement effect illustrated on standing waves that fit within a resonance box only in specific wavelengths.

All in all, a systematic observation of these and other peculiarities occurring at the nanoscale and a belief that they could be explained within a single framework of thought led to the rise of a special new scientific discipline: nanoscience, or the science of the small, as it has been informally baptized. At the same time, elucidation of the exact particle size dependencies of properties of interest opened up a possibility of their precise tailoring by controlling the particle size on the nano scale instead of altering the composition, the strategy that has been utilized by the materials scientists for many generations.

However, we should remember that as time passes by, this early fascination with size and size only is gradually winding down and starting to cede place to the particle surface properties, thus restoring the classical approach that saw grain boundary as the key factor in defining and modifying the material properties. Other elements of the particle structure are also becoming increasingly seen as crucial in defining their physical properties, including shape, crystallinity, concentration and type of defects, polydispersity, surface charge, etc., contributing to the ever growing complexity of this exciting new field that we may now be a bit more familiar as to whence it entered our worlds carrying the enlightening slogan Small is Beautiful: nanoscience.

![Image](image.png)

**Figure 11** - Color of the gold sols displayed here, essentially identical in composition to the Faraday's sols shown in Fig.1, is tunable within a relatively wide window of wavelengths by controlling their size, thus demonstrating that size-dependent properties are the clue to the tremendous potential of nanoscale objects. A blue shift in the extinction spectra of aqueous dispersions of gold nanoparticles of various sizes, ranging from 10 to 100 nm, corresponding to the lowering of the particle size.
from 100 to 10 nm is shown too. Reprinted with permission from Refs. [32], [33]

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**SUMMARY**

**NANONAUKE: ODAKLE SU DOŠLE U NAS SVET**

Popularnost nanonauka kao posebnog i jedinstvenog polja istraživanja u okviru nauke o materijalima nalazi se u stalnom porastu. Državna ulaganja u ovo polje istraživanja se u Sjedinjenim Američkim Državama, na primer, povećavaju iz godine u godinu, krećući se od 270 miliona dolara u 2000. godini do 1,08 milijardi dolara u 2006. pa sve do predviđenih 1,7 milijardi za 2014. Ovaj članak započinje tvrdnjom da je zanimanje za fizičku hemiju nanodimenzionalnih fenomena prirodna posledica kolektivnog usavršavanja u domenu sposobnosti usmerene manipulacije materijalnim supstratom fizičke stvarnosti u kojoj naša bića obitavaju. Dati su primjeri koji ilustruju izrazitu oteljivost osobine materijala od veličine crna nanometarskih razmera, što čini fenomen koji je direktno uzrokovao nastanak i razvoj nanonauke kao posebnog polja naučnog istraživanja. Sistemična analiza ovih i drugih neobičnosti opaženih u nanostrukturnim sistemima, kao i verovanje da bi se sve ove neobičnosti mogle objasniti u okviru jedinstvenog analitičkog i epistemološkog sistema doveli su do radanja posebne naučne discipline: nanonauke, ili nauke malih stvari, kako je ona često nezvanično nazivana. Istovremeno, definisanje preciznih zavisnosti osobina materijala od veličine sadržanih kristalnih crna nanometarskih razmera je otvorilo mogućnosti njihovog preciznog podešavanja putem kontrole veličine nanočestica i postavilo se kao alternativa tradicionalnom pristupu podešavanju osobina materijala putem variranja njihovog sastava.

**Ključne reči:** nanonauka, nauka o materijalima, osobine koje zavise od velicine kristala, strategija, nanotehnologija