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Focus Article, *Mendeleev Commun.*, 2019, **29**, 479–485

Mendeleev Communications

Periodic table of elements and nanotechnology

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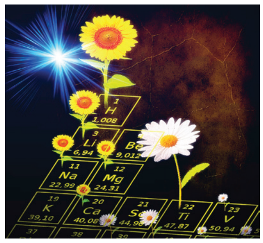
DOI: 10.1016/j.mencom.2019.09.001

The periodic table of elements published by Dmitri Mendeleev 150 years ago plays a fundamental role in chemistry, physics, biology and other natural sciences. Each of the *s*-, *p*-, *d*-, and *f*-blocks brings their own features in the design, production technologies and functional properties of modern materials as building units of our civilization. A multidisciplinary area of nanomaterials and nanotechnology sheds light on Mendeleev's periodic law from a special angle, as discussed in this article.



Introduction

The United Nations General Assembly proclaimed 2019 as the International Year of the Periodic Table of Chemical Elements underlining the highest importance of the periodic table in modern sciences as a deeply fundamental paradigm for various branches of chemistry, physics and biology. The periodic table is an important universal tool for the predictable design of new materials;[1–3] however, nanotechnologies change the view angle on this most important discovery. This happens due to the complexity and high structural and chemical specificity of new generations of construction and functional bio- and nanomaterials. Figure 1 demonstrates the 2D and 3D representations of the popularity and Informational NanoClarks (INCs) of elements (alike geological clarke values). The highest INCs are observed for only 15–30 elements most frequently used for the design of single- and multicomponent nanostructured materials, and this situation is stable for years. Most of the elements are widely spread and cheap light elements with large geological clarke values and reasonable biocompatibility, chemically inert elements, or elements with special redox and crystal chemistry. Another highly important factor counts the most demanded practical applications such as electrochemical, hydrogen and solar energetics; traditional electro- and photocatalysis; theranostics and medicine; optical, magnetic recording, and informational technologies and electronics; and novel construction materials for space, aviation and car industries. In other words, nanotechnology utilizes the best chemical properties of each element and joins them together for practical needs at a lower cost. Additionally, nanomaterial preparation processes include special approaches such as tailoring magnetic, electrical and optical properties by the design of motives, sizes and shapes of construction blocks to build up nanostructures with desired functional characteristics; this means either the nanoscale engineering of important nanomaterials[3] or simultaneous control of interfaces. An interface with abnormal atomic coordination and a large superficial energy often becomes the aim of nanotechnological practice. The last point seems to be possible nanotoxicity and its official regulations predetermining the preferable selection of biocompatible or bioinert elements for most of nanomaterials.

Elements of *s*- and *p*-blocks and their impact

The most demanded nanotechnological elements are located in the *s*- and *p*-blocks (Figure 1) including the C, N, O and Si *p* nonmetals and H and Li *s* elements. A low ionization potential of the only external *s* electron of light alkaline elements results in single-charged cations of small radii demonstrating high diffusivity in electrolytes and membranes; this property makes lithium a modern 'gold' in electrochemical energetics. At the same time,

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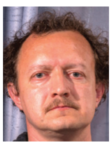

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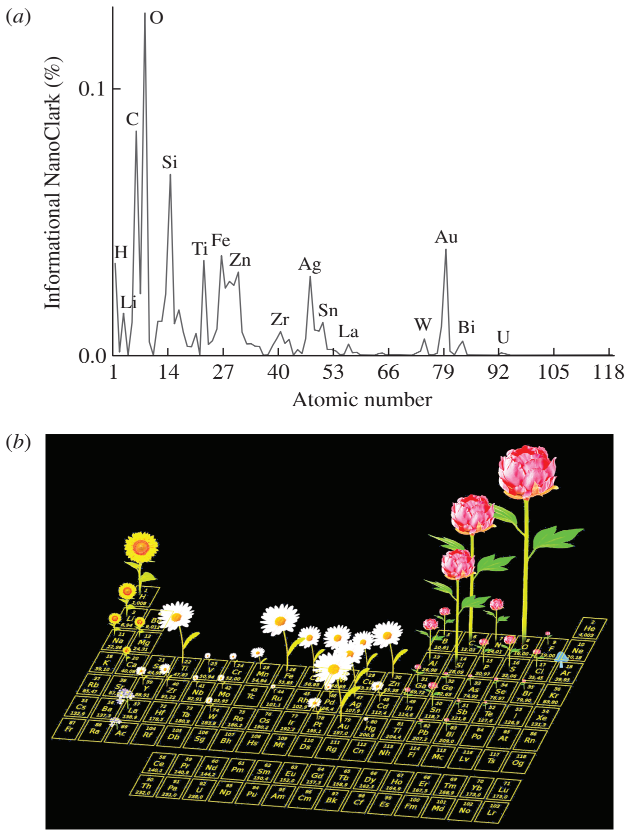

Figure 1 Nanotechnological element popularity (data counted from the Web of Science records): (*a*) Informational NanoClarks of chemical elements expressed as the numbers of published articles related to a particular element in connection with nanomaterials or nanotechnology, 150000 papers are equal to 0.1%. (*b*) Art representation of a ‘nanotechnological garden’ of the popular elements in the whole periodic table of elements; the first letters of the flower names correspond to the filling of electronic shells for different *s*-, *p*-, *d*-, and *f*-blocks (sunflower, peony, daisy, and forget-me-not, respectively).

complex electrochemical charge and discharge processes result in new features of chemistry and phase stability of lithium compounds formed in lithium-based batteries[4–9] (Figure 2). Low-temperature fuel cells utilize natural ecologically safe hydrogen for operation; thus, this element is a vital part of hydrogen energetics and, on the other hand, it should be produced by advanced water splitting systems or from by-products of oil industry.[4,10] Hydrogen is a constituent of biology-related compounds and sensor systems; hydrogen bonding enables the self-assembling of supramolecular compounds.[11–13] Hydrogen, deuterium and tritium isotopes are traditionally used in NMR-spectroscopic investigations of nanomaterials; radioactive tritium is used in labeling, studying isotope effects, and developing thermonuclear energetics.[14] The ionic radius and weight still make sodium available for construction of sodium ion batteries, supercapacitors and NASICON superionics;[15,16] however, larger and heavier potassium becomes much less attractive for the same purposes. Oppositely, large potassium, rubidium, and cesium are useful for templating in the case of octahedral molecular sieves of manganese dioxides and for superconductive fullerides.[17,18] Calcium is a usual component of biomineralization and mesocrystal growth;[19] magnesium forms piesoelectrics and aluminosilicate minerals with nanocell structures, and it is used in the form of light alloys, in particular, for hydrogen storage.[20] Toxic beryllium forms nanocrystalline glass alloys, and it is used for X-ray windows.[21] Strontium and barium are the well-known components of piesoelectrics and multiferroic materials.[22]

The growth of atomic numbers in the second period results in the compaction of atomic radii, an increase in ionization potentials, and the appearance of *p* electrons forming strong oriented covalent bonds in the compounds of B, C, N, O and F or the anions of electronegative O and F. The *p* electrons lead to conjugated π bonds in addition to σ bonding, and this new ability is responsible for a tremendous number of so-called inorganic polymers. As a result, various 1D, 2D and 3D nanomaterials are formed from B, C, and N, including fullerenes, graphene, nanotubes and their BN analogues, Mxens, C_3N_4, and onion nanodiamonds. Detonation diamonds were initially found in 1963 in the USSR; carbon nanotubes were observed in the USSR in 1952 and 1977 but officially reinvestigated in Japan in 1992 only. This discovery predetermined the development of a new nanotechnology area, although other nanocarbon materials initiated even faster growth of worldwide interest in nanomaterials. First, fullerenes were predicted in Japan in 1971 and modeled in 1973 in the USSR followed by a Nobel Prize in 1996; graphene was awarded by another key Nobel Prize for nanomaterials in 2010. At the moment, the potential use of fullerenes is drastically narrowed, and the industrial production of carbon nanotubes gave no expected impact; however, graphene-based materials and other 2D systems like Mxens and C_3N_4 derivatives demonstrate a gradual expansion of their fundamental and practical impact. In general, this important family of nanomaterials initiated the first step forward of a nanotechnology revolution and brought to light various architectures suitable for supercapacitors, batteries, molecular electronics, fuel cells, sensors, and advanced construction materials.[5,7,23–33]

Oxygen, as a widespread oxidizing agent of the environment, forms various nanostructured oxides possessing unique physical and chemical properties. For instance, porous anodic alumina, a compound of a *p* metal and a *p* nonmetal, gives 1D photonic crystals, porous ceramic membranes, catalytic supports, templates, and nanoreactors for the preparation of nanomaterials and nanocomposites.[34,35] The heavier analogues Ga (eca-aluminum according to Mendeleev) and In demonstrate different applications in nanotechnology such as transparent ITO conductors, semiconducting LEDs, and quantum dots (GaN, InP), and they are used for the preparation of nanostructures by focused ion beams.[36–38]

Silicon is far from its light analogue, carbon, in properties and applications, but it remains a leading *p* nonmetal in terms of

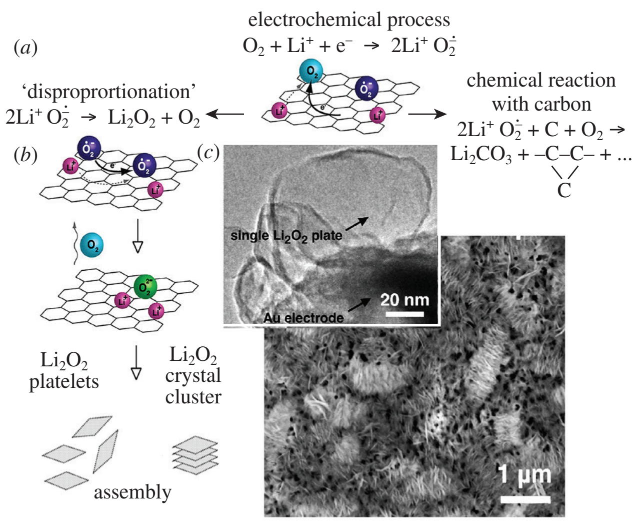

Figure 2 Unusual Li_2O_2 mesocrystals formed electrochemically on a graphene porous electrode in the course of discharge of a new-generation rechargeable lithium–air battery: (*a*) electrochemical reaction scheme, (*b*) self-assemblage process, and (*c*) TEM (upper panel) and SEM images of the self-assembled ‘worms’ of lithium peroxide (data from refs. 6, 8).

semiconducting nanostructures like porous and black silicon, SiC, nontoxic quantum dots for solar cells, photodynamic therapy and fluorescent biological labels, as anode nanowire materials with record properties, for traditional and soft lithography, graphene production, AFM cantilevers; silica forms traditional insulator layers in nanoelectronics, nanoparticle shells and layers or mesoporous nanomaterials, drug delivery capsules, photonic crystals, nanocell zeolites.[39–44] On the contrary, germanium is very limited in semiconducting and thermoelectric applications.[45] Tin dioxide is used in transparent conductors and semiconducting sensors.[46,47] Lead demonstrates applications in thermoelectrics, multiferroics, and new generations of quantum dots and solar cells based on hybrid perovskites.[48–53] Such cells demonstrate a joint work of lead itself in the light absorbing perovskite layers, titanium in mesoporous titania blocking layers, tin in ITO transparent conducting layers, silicon in covering protective (sealing) glasses, and carbon in organic cations like methylammonium and formamidinium; this domain grows quickly at the moment.

Contrary to the lightest pnictogen nitrogen, phosphorus composes 3D printed biomaterials and implants, biomimetic and bioinsiped materials,[54] and semiconducting nanomaterials (like InP).[36] Unique olivine-based electrochemical nanomaterials of the $LiFePO_4$ family are of special interest.[16,55] Other elements of this group demonstrate, as usual, distinctly different applications. Arsenic is used in LEDs, semiconducting nanostructures, quantum dots, wires, and heterostructures and as a promising component of solar cells.[56] Antimony is a part of transparent oxide conductors, semiconductors, and thermoelectric nanocell materials.[57–59] Bismuth, the heaviest nonradioactive element, forms IR quantum dots, thermoelectrics, layered compounds, multiferroics, photoanodes, photocatalysts, and topological insulators.[60–63]

Post oxygen chalcogens (S, Se, and Te) are known due to quantum dots and self-organized superlattices, semiconducting heterostructures, solar cells, nanocell thermoelectric materials, energy conversion and storage materials, nanowires, nanolasers, single layer dispersions, and LED.[36,39,64–70] Sulfur also forms quantum dots; however, it also participates in Li–S batteries and disulfide memristors, in the technology of self-assembling thiol monolayers, and in soft lithography.[71–74]

Heavy halogens like iodine are the well-known components of traditional Graetzel-type and modern perovskite solar cells or perovskite quantum dots (lead halide perovskites); periodate salts are used in protonic conductors.[48–63,75–77] At the same time, a recent discovery of reactive polyiodide room-temperature melts (Figure 3) opened up a highway to a new family of perovskite photovoltaics technologies. Bromine and chlorine compose popular ionogenic surfactants; chlorides are biocompatible, and they form various saline and buffer systems for biomaterials; these anions can control the growth of noble metal nanoparticles like silver; the synthesis of nanomaterials using ionic liquids among halides and polyhalides is a modern trend.[49,51,53,78,79] Fluorine and fluorides are different in applications connected with luminescence and bioimaging, up converting materials, conducting doped oxides, and dielectric elastomers; ^{19}F is useful for NMR studies of condensed phases, nanostructured solids, and interfaces in medicine, while ^{18}F is vital for positron emission tomography; the latter exemplifies also an important streamline of future progress in practical implementation of the periodic table – the physics and chemistry of isotopes.[80,81]

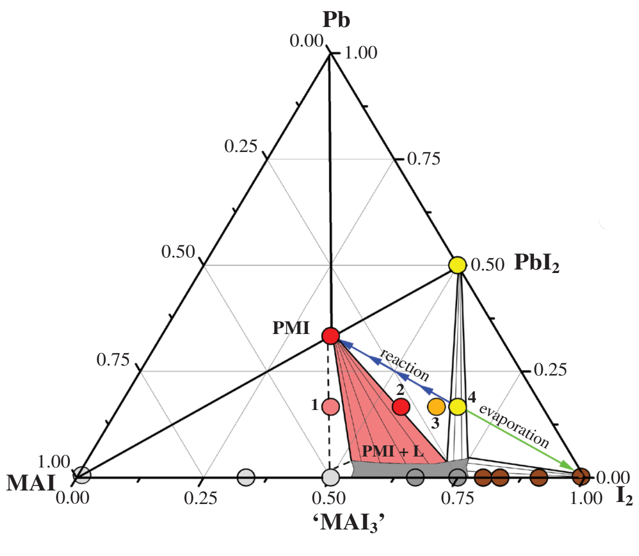

Figure 3 Phase diagram of the methylammonium iodide (MAI)–Pb–I_2 system demonstrating a new unique feature of the formation of room-temperature reactive polyiodide melts (RPM, connected with a perovskite phase PMI with connodes) rising a new common branch of hybrid solar cell production technologies using melt techniques (data from refs. 49, 51).

Unique properties and applications of the *d*-block elements

The *d*-block metals demonstrate new possibilities compared to those of the *s*- and *p*-blocks since *d* electrons and *d*–*d* transitions generate variable redox, magnetic and polyfunctional properties, some elements of this block such as vanadium, zirconium, manganese, and tin easily form oxide nanostructures with a highly developed surface area and unique active centers to be used for adsorption and as supports in heterogeneous catalysis with transition metal compounds. Scandium, titanium, and vanadium have no *d* electrons in their easily achievable highest oxidation states; therefore, they do not demonstrate magnetic applications typical of many other *d* elements. The first *d* element scandium with a small ionic size favors the creation of superalloys, metal fullerenes, and ferroelectrics; however, a high cost of such materials limits their nanoscale applications.[82,83] Titanium is a famous component of nanomaterials like nanotubes, nanorods, and nanoparticles with potential applications in photocatalysis and water splitting, photoprotection, solar cells, anode materials with zero expansion, and multiferroics; titatnium gives famous layered carbides (Mxens) and biocompatible alloys and coatings.[5,30,84–89] The next *d* element, vanadium, has a wide range of oxidation states with the most interesting +4 and +5 species since a high oxidation state promotes covalent bonding with oxygen instead of the formation of free metallic ions. Vanadium(IV) retains one *d* electron; therefore, VO_2 is a special case of famous magnetic conductors, polyfunctional materials, and metamaterials.[90] Vanadia precursors demonstrate a unique polymerization ability by olation and oxolation (Figure 4) thus forming aero-and xerogels, inorganic liquid crystals, nanotubes, nanobelts, hybrid organo-inorganic materials, catalysts, solar water splitting nanomaterials, thermochromic materials, phosphors, $BiMeVO_x$ ionic conductors, insertion and redox-flow battery materials, and supercapacitors.[5,91–98]

The d^6 configuration makes chromium the first *d* element focused on magnetic applications in high-entropy and ferromagnetic glass alloys and magnetic recording materials.[99,100] Manganese, iron, cobalt, and nickel are the most nanotechnology relevant domain among magnetic *d* elements with the typical chemistry of transition metal ions. Manganese is known due to materials and heterostructures with giant magnetoresistivity for spintronics, octahedral molecular sieves, electrochemical batteries and supercapacitors, oxygen reduction systems, and catalysts for fuel cells and as a ferromagnetic dopant.[100–107] The low cost, easy production, and biocompatibility of superparamagnetic iron oxide nanoparticles (SPIONs) make iron the most demanded for hyperthermia, drug delivery, magnetic fluids, MRT bioimaging, and theranostics.[108–111] In addition, iron compounds are the components of multiferroic composites, metal organic frame-

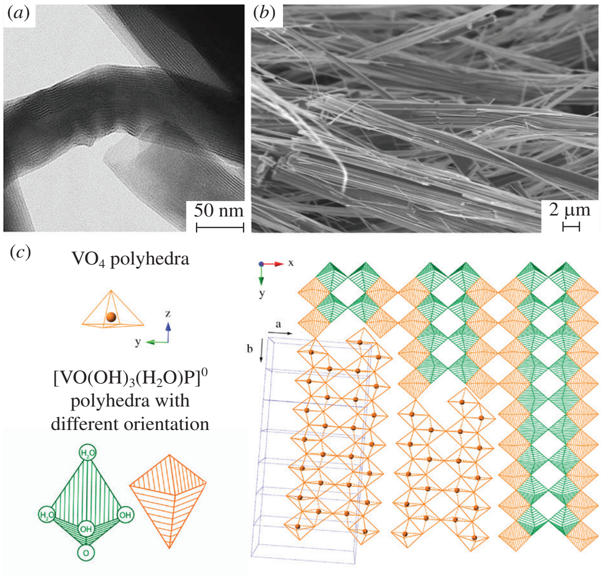

Figure 4 Unique features of vanadia derivatives to form (*a*) 1D nanotubular, ribbon, sheet-like, (*b*) 2D, and (*c*) 3D xerogel materials due to polymerization of building units in the course of olation and oxolation followed by self-assembly into a higher dimension structures (data from refs. 95–97).

works,[112,113] low cost water splitting systems, $LiFePO_4$ cathode materials,[55,114] and catalysts for carbon nanotube growth.[115] Cobalt and nickel are also CNT catalysts, while Ni is used for epitaxial growth of high-quality graphene;[116] both of the elements are necessary components of electrochemical energy systems, batteries, oxygen reduction and fuel cells, electrocatalysts for hydrogen evolution, dopants in solar energy systems, magnetic nanowires and recording multiferroic nanocomposites, catalysts, glass metals, superalloys, and shape memory alloys.[5,117–119] The unique ^{63}Ni isotope starts the growing betavoltaic area.[118] Copper stacks formally to silver and gold, but its chemistry and applications are more similar to those of nickel.

Completed d^{10} configurations of Zn, Cd, and Hg almost exclude magnetic applications of their compounds. A common feature of these elements is a partial contribution of covalent bonding, especially for mercury. The applications of toxic mercury are limited by iron–mercury magnets, thermoelectrics, and IR luminescence.[120] Toxic cadmium forms quantum dots, nanostructured semiconductors, solar cell sensitizers, bioimaging agents, LED and nanolaser components.[39,68] Affinity of nontoxic zinc to oxygen produces a great variety of semiconducting oxide nanostructures (ZnO nanowires, nanorods, nanobelts and tetrapods) for photocatalysis, nanolasers, quantum dots, solar energy, optoelectronic devices, and sensors; zinc also composes MOF and piezoelectrics[121–123] thus becoming a distinct leader.

The lanthanide contraction effect makes zirconium and hafnium or niobium and tantalum couples to behave dissimilar compared to Ti and V analogues, respectively, and, *vice versa*, they demonstrate similar chemistry of their stable oxides. The highest oxidation states +4 and +5, respectively, exclude magnetic applications but bring to light ferroelectrics and nonlinear optic materials.[22] Zirconia is one of the most famous superionic membrane materials.[124] Metallic zirconium is used for cladding fuel elements owing to a remarkably low neutron absorption cross section.[125] Hafnium oxide forms high-*k* insulating films in nanoelectronics.[126]

Molybdenum and tungsten also prefer the highest oxidation state (+6) in stable oxides (while chromates are oxidizers). Another possible oxidation state of +4 occurs in typical disulfides forming layered, nanotubular or fullerene-like nanomaterials; as a result, Mo and W demonstrate unique applications in memristors, field transistors, catalysts and electrocatalysts, sensors, lithium storage, and polyoxometalate compounds.[71,127–130] Heavy analogues of Mn, technetium and rhenium, differ in chemistry from both manganese and their Mo and W neighbors; specific features of rhenium include catalysis and cluster compounds.[131] Technetium (eca-manganese according to Mendeleev) is known as an antirust agent in industrial alloys, but, what is more important, the nanoparticles and complexes of its β-radioactive isotopes are specifically used for diagnostics in radiomedicine.[132]

The last two useful families of nanotechnology-related elements of the *d*-block are platinum-group elements and noble metals. These elements demonstrate low chemical activity and moderate biocompatibility, and they are applied predominantly as metallic nanostructures. Undoubtedly, a prime application of platinum is catalysis focused on hydrogen and SOFC fuel cells, and less attention is paid to ferromagnets and sensors.[133–138] Palladium is related to the production of hydrogen separation membranes and processes utilizing the Sonogashira reaction; palladium catalysts also play a key role in industrial applications.[139–141] Rhodium, ruthenium, and highly expensive and rare osmium and iridium are also used as catalysts and electrocatalysts.[133] Ruthenium compounds are used in solar cells and supercapacitors, while iridium complexes are involved in LEDs and OLEDs.[142,143]

Silver and gold differ from platinum-group elements in chemistry and applications, which include conductors in electronics, single molecular junctions in nanoelectronics, hybrid nanocontainers, and catalytic systems; silver is known by its antimicrobial activity.[144–149] However, plasmonics and surface enhanced Raman spectroscopy (SERS) for ecology, biology, and medicine are prevalent demanding precisely engineered shapes and sizes in nanoparticle ensembles[150–168] and, as a trend, 'smart' hierarchic nanostructures (Figure 5) for more sensitive and more specific detection using different laser wavelengths. In addition, gold plays a great role in self-assembly, soft lithography, and photothermal therapy.[169–171]

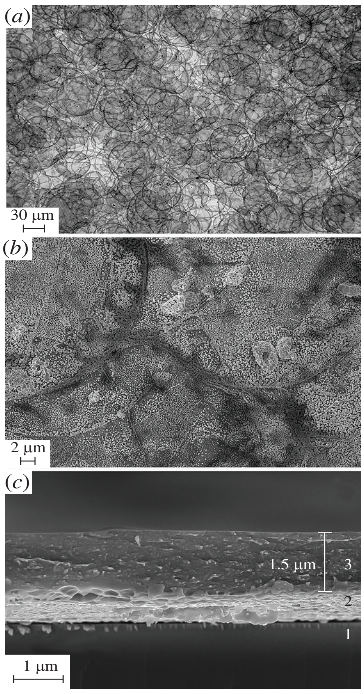

Figure 5 Structure of smart materials for SERS sensors: (*a*) nanostructured plasmonic coating as an active sensor element, (*b*) hierarchic structure of the SERS layer providing hot spots and a wider working optical range, (*c*) polymer coating (3) on the SERS layer (2) and the dielectric substrate (1) providing overall concentration and/or separation of target analytes (data from refs. 155–158).

The last but not the least *f*-elements and inert gases

The internal *f* shell is not as spread in space as *d* orbitals; therefore, filling *f* electrons retains chemical features almost unchanged but reduces atomic and ionic radii by about 15% (lanthanide contraction). At the same time, *f* elements exhibit complex spin–orbital interactions and this correlates with their leading applications in optics, LED and OLED, bioimaging, and upconversion materials (La, Eu); other lanthanide-containing materials include manganites with giant magnetoresistivity, intermetallides for hydrogen storage, SOFC membrane dopants, high-temperature superconductors, MRT contrasts (Gd), oxide quantum dots, and medical antioxidant agents (CeO_2).[80,172–177] All the actinides are radioactive, and they could be used for thermonuclear energy production (U, Pu); the role of radioactive elements is still underestimated especially in radiomedicine, nuclear batteries, and labeling.[178]

Obviously, inert gases themselves do not form nanostructured materials. At the same time, helium is related to the analysis of material mesomechanics and irradiation resistance; a helium plasma treatment and ion beams are useful for the production of nanostructures; the investigation of nanomaterial properties at helium temperatures is important, and helium atom scattering/diffraction is used to study surface properties.[179] Neon is used to study surface properties and as a working body in lasers. Argon often creates a protective inert atmosphere, and it is a working gas for plasma generation and magnetron sputtering. Krypton and xenon are gases to explore sorption and creation of model atomic superficial structures; radon therapy resorts were probably first meeting point for radiomedicine.

Concluding remarks

This brief overview shows a complex picture of the deep involvement of different elements into the design of nanomaterials on demand. Despite of a common belief that periodicity would provide a smooth and universal coordinate of the desired tuning of material properties, nanotechnology is much more focused on extraction and brewing of chemical peculiarities of each particular element of the Mendeleev's Periodic Table. These features predetermine the application areas of target nanomaterials. In these terms, the 150 old periodic table opens up inevitably new prospects in advancing nanotechnologies by exploiting the chemical diversity of elements, a search for effective combinations of the most popular nanotechnological elements for the creation of new nanomaterials, and the application of computational methods[180] to shorten a long way to new nanomaterials. However, it is evident that the periodic table promises the future innovative development and great frontiers for nanotechnology.

This work was supported by the Russian Science Foundation (grant no. 19-73-30022).

This focus article is written to celebrate the 150th Anniversary of the Periodic Table of Chemical Elements, and the authors are honored to publish it in the Mendeleev Communications journal named after Dmitri Mendeleev.

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Received: 29th May 2019; Com. 19/5938