NANOSYSTEMS

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Summary

Inorganic nanosystems are defined as nanosized chemical objects whose composition is merely inorganic and which exhibit peculiar features due to quantum-size and
geometrical effects. Two are the general synthetic pathways by which nano-objects are obtained: the so-called ‘top-down’ and ‘bottom-up’ approaches. Mainly in the latter method, chemistry plays a unique role in assembling and building up nanometric units from smaller ones. The nanosystems can be defined and classified according to the hierarchical order of dimensionality. Zero-dimensional systems include pseudospherical objects such as nanoclusters and nanoparticles, supported onto inorganic bulk supports as well as in colloidal solutions, or ceramic nanopowders. One-dimensional systems take into account carbon-based, metal-based or even oxide-based systems in which the extension over one dimension is predominant over the other two, such as solid nanofibers, nanowires or nanorods, as well as hollow nanotubes. As two-dimensional nanosystems, the crystalline flat nanometric materials, such as nanodiscs or nanoprisms, and the amorphous nanofilms and nanomembranes are considered. Then, three-dimensional nanosystems consist of both crystalline and amorphous nanostructures, such as nanocrystals and a very large variety of ordered nanoarranged porous materials. Three-dimensional arrangements can be also created from simpler components, as nanoparticles or nanorods, and superstructures or superlattices with improved features are thus obtained.

The description, the synthesis, the properties and the main applications in technology and industry of the chemical systems at nanoscale most commonly found in inorganic chemistry are here summarized and reviewed. Finally, few highlights are given on inorganic-organic hybrid nanosystems and on systems with applications in biochemistry, as these subjects are on the borderline with organic chemistry and biology.

1. Introduction

The prefix “nano” has found in last decade an ever-increasing application to different fields of the knowledge. Nanoscience, nanotechnology, nanomaterials or nanochemistry are only a few of the new nano-containing terms that occur frequently in scientific reports, in popular books as well as in newspapers and that have become familiar to a wide public, even of non-experts.

The prefix comes from the ancient Greek να̃νος through the Latin nanus meaning literally dwarf and, by extension, very small. Within the convention of International System of Units (SI) it is used to indicate a reduction factor of $10^9$ times. So, the nanosized world is typically measured in nanometers (1 nm corresponding to $10^{-9}$ m) and it encompasses systems whose size is above molecular dimensions and below macroscopic ones (generally $> 1$ nm and $< 100$ nm).

1.1. Distinctive Features of Nanosystems

Inorganic nanosystems are defined as the chemical objects whose composition is merely inorganic and which exhibit new phenomena due to quantum-size effects and to the occurrence of large amounts of surfaces and interfaces because of their reduced size in the nanometer scale (1 - 100 nm). In fact, isolated molecules exhibit properties that follow quantum mechanical rules, while the chemical and physical properties of bulk materials obey the laws of classical mechanics. In the middle, nanosystems display
electronic, photochemical, electrochemical, optical, magnetic, mechanical or catalytic properties that differ significantly not only from those of molecular units, but also from those of macroscopic systems.

Quantum-size effects arise in nanosized objects because their global dimensions are comparable to the characteristic wavelength for fundamental excitations in materials. These excitations (including the wavelength of electrons, photons and so on) carry the quanta of energy through materials and therefore govern the dynamics of their propagation and conversion from one form to another. However, if the size of the structures falls in the same order of magnitude of these characteristic wave functions, the propagation and the behavior of quanta are noticeably perturbed and thus quantum mechanical selection rules, which are not usually evident at larger scale, appear. For example, in the case of metals, typical "metallic" properties, like conductivity, decrease when the size is reduced and when the number of constituent atoms in the sample is significantly diminished. Indeed, the electronic conduction band of a metal gradually evolves from continuous levels of a bulk infinite material into discrete states as a function of size reduction, resulting in an increase in the band-gap energy (Scheme 1).

Nanoscale materials also exhibit size-dependent magnetic behavior. For instance, at very small sizes, magnetic nanoclusters have a single magnetic domain and the strongly coupled magnetic spins of each atom combine cooperatively to give rise to a system with a single “giant” spin.

In addition, nanosized materials possess very high surface to volume ratios because of the fine grain size and they are characterized by a very large amount of low-coordination number atoms at edge and corner sites. Such preponderance of surfaces is a major reason for the change in chemical behavior of materials at the nanoscale. The atoms in nanostructures have a higher average energy than atoms in larger structures,

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because most of them are surface atoms. Consequently, the activity of a catalytic material can be exponentially improved as the catalyst is reduced in size at the nanoscale. In summary, in the nanometric world, the properties of nanosystems are remarkably affected by sometimes minor changes in size, shape or surface state of the structures. Indeed, three factors, namely (1) synthesis, (2) composition and structure and (3) functional properties, represent the essential relations in nanoscience.

1.2. General Aspects of Synthesis

Atoms and molecules are the essential building blocks of every object. The manner in which things are constructed with these basic units is vitally important to understand their properties and their reciprocal interactions. An efficient control of the synthetic pathways is essential during the preparation of nanobuilding blocks with different sizes and shapes that can lead to the creation of new devices and technologies with improved performances. To do this, two opposite, but complementary approaches are pursued. One is a top-down strategy of miniaturizing current components and materials, while the other is a bottom-up strategy of building ever-more-complex molecular structures atom by atom or molecule by molecule. These two different methods highlight the organization level of nanosystems as the crossing point hanging between the worlds of molecular objects and bulk materials.

The top-down approach has been advanced by Richard Feynman in his often-cited 1959 lecture stating that “there is plenty of room at the bottom” and it is ideal for obtaining structures with long-range order and for making connections with macroscopic world. Conversely, the bottom-up approach was pioneered by Jean-Marie Lehn (revealing that “there is plenty of room at the top”) and it is best suited for assembly and establishing short-range order at the nanoscale. The integration of the two techniques is expected to provide, at least in principle, the widest combination of tools for nanofabrication.

1.2.1. Top-down Approach

The top-down approach is based on miniaturizing techniques, such as machining, templating or lithographic techniques. Top-down methods usually start from patterns generated at larger scale (generally at microscale) and then they are reduced to nanoscale. A key advantage of the top-down approach is that the parts are both patterned and built in place, so that no further assembly steps are needed.

By means of electronic, ionic or X-ray lithography, a monolith can be cut step by step in order to generate a quantum well (a bidimensional structure, with two finite dimensions) at first, then a quantum wire (a monodimensional structure, one finite dimension), and finally a quantum dot (a zero-dimensional structure, all the dimensions being in nanoscale). Current short-wavelength optical lithography methods can reach dimensions not less than 100 nanometers (the traditional threshold definition of the nanoscale). Extreme ultraviolet and X-ray sources are being developed to allow lithographic printing techniques to reach dimensions from 10 to 100 nanometers, but the principal limits are still due to the difficulty of beam focalization. Likewise, scanning beam techniques such as electron-beam lithography provide patterns down to about 20
nanometers and still-smaller features are obtained by using scanning probes to deposit or remove thin layers.

The general procedure of mechanical printing techniques consist on making a master “stamp” by a high-resolution lithographic technique, as described above, and then applying this stamp, or subsequent copies of it, to a surface to mould the pattern. The last step is to remove the thin layer of the masking material under the stamped regions. These nanoscale printing techniques offer several advantages due to the possibility to use a wide variety of materials with curved surfaces.

As a general drawback, these techniques are not cheap and require a complex manufacturing. In addition, top-down methodologies: (1), even if they work well at the microscale, they collide with some difficulties at nanoscale dimensions and (2) they usually lead to the formation of bidimensional structures and hence, as they are carried out by the addition or subtraction of patterned layers, they cannot easily give rise to the production of arbitrary three-dimensional objects.

It is worth underlining that the development in the top-down methodology was mainly driven from the traditional disciplines of materials engineering and physics, whereas the role of inorganic chemists has been minor in the exploitation of these techniques.

1.2.2. Bottom-up Approach

Bottom-up, or self-assembly, approaches to nanofabrication involve gradual additions of atoms or groups of atoms. This technique uses chemical or physical forces operating at the nanoscale to assemble basic units into larger structures. The chemical growth of nanometer-sized materials often implies colloidal or supramolecular systems and it frequently passes through phase transformations, such as vapor deposition on surfaces or precipitation of a solid phase from solution. Inspiration for bottom-up approaches comes from biological systems, where nature has employed chemical forces to create essentially all the structures needed by life. Researchers try to mimic nature's ability to produce small clusters of specific atoms, which can then self-assemble into more-elaborated structures (Figure 1).
Figure 1. Bottom-up approach. The precursors (left) can react and assemble to form nanosystems with a large variety of shapes and sizes (right), depending on the reaction conditions.

In order to reach the desired shape and dimension of the new nanosystem, the nucleation and growth of the material have to be directed and controlled. This synthesis approach is of sure the most stimulating for the chemist. Indeed, bottom-up approaches, starting from single atoms and molecules have more affinity with chemistry and molecular biology, as much of chemistry already implicates the control of nanodimensional objects or the self-assembly of molecules into larger structures.

As main advantages, bottom-up techniques display a wide variety of preparation methods, they allow a good control onto scale dimension, even from atomic or molecular level, and they are not as expensive as top-down approaches. Nevertheless, the advent of pre-programmed self-assembling of arbitrarily large systems, with complexity comparable to that found in natural systems, is still a challenge.

In the following chapters, the attention will be focused only onto inorganic nanosized structures and the nanosystems will be defined and classified according to the hierarchical order of dimensionality: zero-dimensional systems, including spherical, pseudo-spherical or point-like objects; one-dimensional systems, in which the extension over one dimension is predominant over the other two, such as nanorods, nanowires, nanofibers, nanotubes; two-dimensional systems, such as flat or membrane-like materials, nanosheets and nanoscale discs; three-dimensional systems, both crystalline and amorphous nanostructures as well as porous and non-porous materials, which exhibit nanometric features, even if they extend over the three dimensions.
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**Biographical Sketches**

**Rinaldo Psaro** was born in Milan (Italy) in 1953. He studied chemistry at the University of Milan (Italy), where he became doctor in chemistry in 1978. He spent two postdoctoral periods in the group of Prof. J. M. Basset at the IRC in Lyon (France) and in the group of Prof. F. S. Stone at the University of Bath (UK), in 1979 and 1983, respectively.

In 1983 he became Research Scientist at the Italian National Research Council (CNR) in Milan and in 1993 he became Research Director in the same institution. Since 1989 until 2005 he has been Contract Professor in Industrial Chemistry (Surface Organometallic Chemistry and Heterogeneous Catalysis) at the University of Milan. He is author or co-author of 2 patents and ca. 150 papers on international journals on the field of surface organometallic chemistry, catalyst characterization and heterogeneous catalysis. His general scientific interests deal with the development of new methods for the preparation of more efficient and eco-compatible catalytic systems for fine chemicals and commodities, to achieve higher performances, simpler preparation methods, conditions allowing for extended recycling. In particular, his studies focus on three kinds of materials: metallic nanoparticles supported on inorganic oxides surfaces; metallic nanostructures entrapped and stabilized in zeolite cages and in mesoporous structures; hybrid molecular-nanoparticle systems supported on inorganic oxides surfaces. Recently in cooperation with a SME he has developed an innovative electrocatalyst for low-temperature fuel cells based on first-row transition metals. He is also responsible for several industrial contracts in catalytic applications.
technologies and consultant of the Italian Ministry of University and Research and of Production Activities.

Matteo Guidotti was born in Milan (Italy) in 1972. He studied chemistry at the University of Milan, where he received his degree in chemistry in 1997 and his Ph.D. in industrial chemistry in 2000. In 2001, he became Research Scientist with permanent position at the Institute of Molecular Sciences and Technologies (ISTM) of the Italian National Research Council (CNR) in Milan. He spent a 10-month period in the group of Prof. M. Guisnet at the LACCO of the University of Poitiers (France) as a visiting researcher. His current research fields deal with the design and use of heterogeneous catalysts for the environmentally sustainable transformation of fine chemicals and renewable raw materials. In particular he is involved in the preparation of nanosized bimetallic heterogeneous catalysts and the design of single-site mesoporous systems to be used in the liquid-phase selective oxidations of terpenes and fatty acid derivatives from vegetable oils. He is author of 18 articles on these topics in international journals and of 3 book chapters.

Dr. Guidotti is the treasurer of the Lombardy Section of the Italian Society of Chemistry and he was member of the organizing committee of the VIII Italian Seminar on Catalysis (Verbano, Italy) and of the XII International Symposium on Relations between Homogeneous and Heterogeneous Catalysis (Florence, Italy) in 2005. He is also Second Lieutenant of the reserve of the Italian Army and in this role he is involved in teaching and training for defense against chemical warfare agents.

Maila Sgobba was born in Milan (Italy) in 1981. She started studying chemistry at the University of Milan in 2000, where she received her first-level degree in Chemistry in 2004 and her magistral (second-level) degree in chemistry in 2005. During her studies, she spent a 6-month period at the university of Leiden (The Netherlands), where she worked on mimetic studies of Cu(II) oxidases as Erasmus student in the CBAC group of Prof. Jan Reedijk. She finished her thesis in Milan with Professor Michele Gullotti’s group, studying the catalytic activity of new chiral models of copper enzymes. After her degree, she started a fellowship with the Center of Excellence CIMAINA. Her current research field deals with the synthesis, characterization and use of mesoporous materials as heterogeneous catalysts for the oxidation of terpenes and fatty acids.