Preface

The production of materials with selected physico-chemical properties is pivotal for the development of new technologies. Apart from those directly taken from the environment and used after minor changes (stones, wood, minerals, etc.), this objective has been traditionally achieved by chemists and material engineers synthesizing new molecules or blending already known materials. Following these routes, many important classes of materials have been produced such as plastics, explosives, drugs, surfactants, metals, and metallic alloys. However, in the past decades, a novel strategy based on the reduction of well-known substances to the state of nanoparticles and the controlled manipulation of matter in space, time, and chemical composition at a very high degree of subdivision showed itself to be an alternative way to the two older and well-established techniques. Incidentally, it must be stressed that until now, no new material has been achieved by another very old route based on magic practices and esoteric rites finalised to obtain matter with miraculous properties such as the elixir of life and the philosopher's stone.

The reduction of well-known substances to the state of nanoparticles has captured the attention and the imagination of many researchers because, within a substance-specific size range, finely divided matter can exhibit properties and functionalities different from those of the same material in the bulk state as well as from those of isolated atoms and molecules. For many substances, this domain is very often located in the range of a few nanometers ($1\,\mathrm{nm} = 10^{-9}\,\mathrm{m} = 10\,\text{Å}$). Quantum size effects, confinement of charge carriers, size-dependence of nanoparticle electronic structure, effects due to the unique properties of surface atoms, and huge value of the surface-to-volume ratio are only some of the most frequently cited causes of the exotic behaviour of nanoparticles. As a consequence of their peculiar properties, the synthesis of nanoparticles has opened the door to the production of many technological and pharmacological products such as catalysts with high activity and specificity, materials for specialized optical applications, electrorheologic and electrochromic systems, superconductors, antiwear additives, enhanced adsorbents, drug-carriers, and specialized diagnostic tools.

From a different point of view, the control of matter at the nano-size level could permit the realization of miniaturized devices with specific functionalities like nano-carriers, sensors, nano-machines, and high density data storage cells. Moreover, given their intrinsic smallness, a huge number of nano-components could be rationally assembled to build very highly complex man-size machines.

Further, more sophisticated applications can be devised, looking at biological systems where out of equilibrium nanostructures direct the synthesis, blending, and assembling of a wide range of molecules, their auto-replication and inter-connection; affording in such way the existence and evolution of living beings and the expression of their astonishing capabilities. From this prospect, the production of "artificial" nanostructures far from chemical equilibrium and/or self-assembling and/or self-replicating could greatly amplify the actual potentialities of nanotechnologies allowing the realization of supra-nanodevices with high density of component elements and characterized by complex and interconnected functionalities.

It can be reasonably expected that the realization of nanotechnologic products and their introduction in the market will deeply affect the human quality of life, reducing drastically the waste of raw materials and energy and leading to a planetary revolution of social relations. Moreover, some of these products could enhance and amplify the actual capability of the scientific world to explore the universe and to investigate physico-chemical phenomena with fast computing machines and advanced research instruments.

Together with the benefits that can be expected by the development of nanotechnological products, it is helpful to consider also the potential risks for living beings, cultural heritages, and ecosystems arising from the introduction of nanotechnology in the environment. Being so small, nanoparticles can easily penetrate inside whatever system, while, being so reactive, they could trigger off very dangerous reactions. This implies that, together with the development of synthetic methods and applications of nanomaterials, investigations on their effects and the exploitation of suitable procedures for their safe manipulation must be carried out. From a more general point of view, it must be also stressed that nanotechnology has its inherent limits so that it will disappoint those who believe to have found the panacea to all the ills of our society.

Nanoscience is not a new discipline, but, rather, it can be viewed as a network of knowledge taken from some well-established sciences: physics, chemistry, biology, and engineering. Many of the theoretical foundations needed to build up nanoscience have been developed in the past so that most of the future work is the untrivial application of these principles aiming to the realization of a broad range of technological products.

Obviously, the first necessary step to develop novel nanotechnologies is the production of nanoparticles. A wide variety of physico-chemical phenomena have been used to set up an enormous number of efficient protocols to synthesize nanomaterials of technological and biotechnological interest.

These protocols can be distinguished according to the starting point of the synthetic route:

- From macroscopic bodies through their subsequent subdivision in ever smaller particles by the input of external energy (top-down methods). Typical top-down methods are the grinding of solids by ball milling or the high-temperature vaporization.
- From atomic and molecular precursors, through spontaneous chemical reaction and/or self-assembling processes (bottom-up methods). Examples are those based on the preparation of colloidal solutions and the use of mesoporous materials.

or to their capability to allow:

- the mere synthesis of nanoparticles
- the spatial control of nanoparticles to obtain a more or less ordered arrangement within a suitable matrix or upon a surface to obtain the so-called nanomaterials

or to the degree of matter dimensionality restriction reached:

- quasi-zero-dimensional particles (quantum dots)
- one-dimensional structures (quantum wires)
- two-dimensional structures (quantum wells)
- three-dimensional fractal-like structures

or to their ability to generate mixed nanoparticles formed by two or more components or nanoparticles with peculiar shape:

- core-shell nanoparticles
- doped nanoparticles
- sandwich nanoparticles
- hollow nanoparticles
- spherical, rod-like, and multifaceted nanoparticles

or to the physicochemical phenomenon employed to stabilize nanoparticles against their spontaneous unlimited growth:

- charging of nanoparticles
- coating of nanoparticles with anisotropic molecules
- spatial segregation of nanoparticles on solid surfaces or embedded into appropriate supporting matrixes

These distinctions also delineate the questions that should be posed in order to plan the better synthetic method suitable for a given nanomaterial and its specific applications.

Because below specific critical threshold values, nanoparticle properties are generally strongly size and shape dependent, the judgement of the merit of each preparation methodology is related to its ability to finely control these structural parameters and the corresponding polydispersity degree. Moreover, taking into account that bare nanoparticles are thermodynamically unstable against an unlimited growth and very often display an enhanced chemical reactivity, every good synthetic protocol should allow not only reproducible size and shape control but also appropriate structural and chemical stability.

As a consideration of general validity, it is important to point out that there is not any best synthetic method for all nanomaterials and their specific applications, but each one can be efficient for some substances and unsuitable for others. This implies that the choice of the most convenient route for the synthesis of a specific nanomaterial requires the knowledge of the advantages and disadvantages of each synthetic strategy including its cheapness.

Here will be described one of the most powerful synthetic bottom-up methods based on the use of some surfactant-containing microheterogeneous systems (liquid crystals, monolayers and multilayers, solutions of direct and reversed micelles, direct and reversed vesicles, water-in-oil and oil-in-water microemulsions) as peculiar solvent and reaction media. Thanks to the nano-sized microheterogeneities characterizing the microstructure of these systems, appropriate species can be hosted in spatially separated domains that, as a consequence of specific diffusion processes, can come in contact and react, forming the precursors of the nanoparticles. The accumulation of these precursors in confined space leads to the formation of nanoparticles shaped by their boundaries, whereas their dispersion in the medium and surfactant adsorption on the nanoparticle surface could prevent nuclei agglomeration and precipitation, providing size and shape control. The advantages of such strategy are

- Nanoparticles synthesis can be performed at mild conditions implying a low cost technology and unnecessary expensive apparatus.
- The synthetic method can be easily scaled up for high-volume production of nanomaterials.
- Nanoparticles of a wide class of substances (metals, semiconductors, superconductors, magnetic materials, biomaterials, polymers, water soluble inorganic and organic compounds, etc.) can be produced.
- The synthesis can be easily modulated to obtain coated, doped, mixed, onion or hollow nanoparticles. This capability is of particular industrial importance because the physico-chemical properties of these nanoparticles are frequently found to be very different from those of the single components, showing significant changes in the electronic structure and enhanced catalytic activity.

- Good control of nanoparticle composition, size, shape, polydispersity, and stability of these parameters with time is generally achieved by appropriate selection of the experimental conditions.
- Specific physico-chemical properties can be conferred to nanoparticles by confinement and surface effects, and enhanced potentialities can be given by their random or ordered dispersion in microheterogeneous systems.
- By changing the nature and/or the composition of the microheterogeneous system, different local structures and dynamics can be achieved leading to the production of a great variety of nanomaterials.
- Microheterogeneous systems represent not only the media where nanoparticles can be synthesized but also can be considered suitable for their transport, preservation, and application. They possess also potentials to realize specialized out-of-equilibrium nanoparticle containing systems to model or minic biological processes.
- By simple evaporation of the volatile components of nanoparticle-containing surfactant solutions, it is possible to prepare mono-, bi-, and three-dimensional spatial configurations of nanoparticles in surfactant matrixes, the so-called nanoparticle/surfactant composites, showing very interesting collective properties. By changing the experimental conditions, nanoparticle size and internanoparticle distance can be easily regulated. It is worth noting that at present, the major efforts are directed to establish suitable techniques to assemble nanoparticles in 1D, 2D, and 3D architectures that have important applications in photonics, biotechnology, and microelectronics.
- Nanoparticle/surfactant composites can be easily manipulated, layered on suitable supports, transferred, and resuspended.
- Being some microheterogeneous systems composed of biocompatible, biodegradable, and/or ecocompatible substances, the nanoparticle synthesis in such media is particularly adapted to pollution-free productions. Moreover, interesting nanomaterials for pharmacological and environmental applications can be exploited
- Since microheterogeneous systems share many of the fundamental properties of biomembranes, nanoparticle synthesis in these environments allows a realistic simulation of important biological functions such as the formation and reconstruction of solid constituents of the human body.
- Considering the huge value of the numerical density of nanosized domains contained in microheterogeneous systems, in principle, a relevant number of identical nanoparticles can be synthesized and hosted in such systems. As a quantitative estimate, it can be easily calculated that, in a litre of a 0.1 mol dm^{-3} micellar solution of a typical surfactant having a head group area of 50 $Å^2$, about 10^{20} nearly identical nanoparticles with a size of 50 Å can be synthesized and hosted.

- From a theoretical point of view, the encapsulation of nanoparticles within the peculiar microheterogeneities characterizing surfactant-based systems gives the opportunity to investigate a wide spectrum of quite intriguing and unexplored phenomena such as reaction and crystallization in confined space, preferential adsorption of surfactant molecules on certain nanoparticle crystallographic facets, growth inhibition, and structural organization within self-assembled structures

In the past few decades, many investigations have been carried out with the aim to synthesize nanoparticles in microheterogeneous systems and to control their physico-chemical properties. All these studies have confirmed the great potentials and versatility of the inherent synthetic methods. Besides, starting from an initial tendency to use microheterogeneous systems for the mere control of the nanoparticle size, now it is increasingly becoming the tendency to realize specialized nanoparticle containing microheterogeneous systems with specific structural and dynamical peculiarities for technological or biological applications. A lot of supra-nanoparticular assemblies with peculiar architectures have been prepared to date.

Even if these studies have not produced a general theory enabling the selection a priori of the optimal conditions for the synthesis of nanoparticles of a given material with the wanted properties, nevertheless, some general criteria and pivotal external parameters governing their synthesis have been underlined. Here, an attempt to collect together theoretical and experimental results and to furnish a unified approach is addressed. However, given the huge amount of knowledge accumulated in this field, the account of the contributions of all the researchers working in this area is practically impossible due to time and space constraints of both the writer and the readers. For this reason, this book has been written with the intention to be suggestive more than comprehensive. From a different prospect, the strict content of this book is not the most important thing but rather the interaction between the mind and imagination of the readers with its physical content. I think and hope that, from some of these interactions, new discoveries and interesting interconnections will be triggered.

This book was intended to furnish a systematic but introductory-level treatment of the basic topics necessary to the neophytes for the preparation of nanomaterials through surfactant-based media. It should help them avoid the need to go into the jungle of the bibliographic world to achieve a panoramic view of this specific research field.

Because the correct use of microheterogeneous systems aiming at nanoparticle synthesis requires the knowledge of their structural and dynamical properties, an overview of these aspects will first be presented. Besides, it must be emphasized that a preliminary and unavoidable step of nanoparticle syntheses in these systems is the solubilization of appropriate precursors and reactants. For this reason, general information on the microscopic processes governing the solubilization phenomenon and some guidelines for solute entrapment in such systems will also be given. Taking into account that reaction rates and mechanisms show distinctive features due to the peculiar structure of microheterogeneous systems, some information concerning these aspects, focused on reactive processes leading to nanoparticle formation, will be furnished. All these arguments will be treated in Chapter 1.

Other fundamental subjects are the thermodynamics and kinetics of the nanoparticle formation and growing processes in homogeneous and microheterogeneous systems together with the molecular phenomena responsible for the possible growth inhibition and nanoparticle stabilization. These arguments are helpful to understand the differences and analogies among the various strategies employed to control the nanoparticle size and to obtain stable nanomaterials. They are useful guidelines for nanoparticle synthesis. This matter will be considered in Chapter 2.

An overview of the peculiar properties of nanoparticles and nanomaterials will be considered in Chapter 3 not only to appreciate the potentialities of these systems but also because the knowledge of their exotic properties is also necessary to delineate a successful synthesis. In particular, quantum size and surface effects will be considered.

Finally, some specific recipes for nanoparticle synthesis will be presented in Chapter 4. The intention is to underline the wide variety of the methodologies employed to prepare nanomaterials by microheterogeneous systems that can be easily transposed for the synthesis of other nanomaterials. In particular, the recipe ensemble can also be taken as a container of microheterogeneous systems with well-known structural and dynamical properties. However, to save space, these recipes are not sufficiently detailed, and for the interested reader the direct reference to the reported bibliography is strongly suggested.

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