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Introductory Chapter: Hybrid Nanomaterials

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1. Introduction

One of the most exciting research fields in recent decades in the area of materials engineering is that of hybrid nanomaterials. These materials possess extraordinary physical and chemical properties derived from their size in the nanoscale. Among the reasons for this technological and scientific trend are its multidisciplinary and the combination of the best attributes of both inorganic and organic chemistry, which give rise to multifunctional materials based on an approximation of building blocks. In addition, there is the possibility of incorporating the physical and biological sciences to produce biomimetic approaches to create unique materials derived from the requirements of emerging technologies that lead to the development of a current driving force to perform unprecedented research of materials, devices, and applications. So far, although many reviews, articles, and books are being continuously published, the scientific literature continues to surprise with new contributions and different views of researchers around the world. The purpose of this chapter is to present an updated introduction of hybrid nanomaterials and their recent advances of this decade.

2. Basic concepts

Hybrid nanomaterials are defined as unique chemical conjugates of organic and/or inorganic materials [1]. That is, these are mixtures of two or more inorganic components, two or more organic components, or at least one of both types of components. The resulting material is not a simple mixture of its components but a synergistic material with properties and performance to develop applications with unique properties, which are determined by the interface of the components at the molecular or supramolecular level. Its functionality is associated with the improvement of physicochemical properties. For the electrochemical or biochemical properties through the optimization mainly of magnetic, electronic, optical, and thermal properties or a combination of them, since the mechanical properties are rather directing towards flexibility, which is not considered as a demand [1], see **Figure 1**. The inclusion of nano-sized materials has further expanded the extraordinary properties of hybrid materials thanks to the challenge of having greater options for multifunctional materials. In the last two decades, the development of multifunctional applications is receiving a lot of attention thanks to the chemical and physical properties of the materials, which are giving rise to developments of high adding value. These materials are classified as innovative advanced materials applicable to a huge diversity of applications including optics, electronics, sensors, ionics, energy conversion and storage, mechanics, membranes, protective coatings, catalysis, etc. [1].

The unique versatility of these materials allows designing materials with tunable properties, with improved performance and properties to their long-established counterparts in the market. The diversity of organic and inorganic components that can be incorporated into these materials is from sizes of a few angstroms to thousands of angstroms, so these can be categorized among molecular species, in nano- and/or supramolecular sizes, or with extended structure. Some of the illustrative examples of hybrid materials are [1]:

- Donor-acceptor perovskites
- Intergrowth organic–inorganic perovskites
- Sol–gel silica modified with organic molecules
- Active organic molecules doped into conductive polymers
- Organically grafted inorganic phases
- Organically modified mesoporous materials
- Poly-oligo-silsesquixane-loaded polymers
- Active organic molecules intercalated into layered silicates, oxides, chalcogenides, and 2D materials
- Mixed organic–inorganic polymers
- Silica plus organic polymer
- Polymer-supported inorganic clusters or nanoparticles
- Polymers intercalated in layered silicates, oxides, chalcogenides, and 2D materials
- Polymer-clay composites
- Polymer-magnetic nanoparticle composites
- Biomineral-type composites

- Organically substituted polysiloxanes and polysilsesquioxanes
- Polymer-coated inorganic nanoparticles
- Silica-embedded bioactive species
- Fiber-reinforced nanocomposites, etc.

In the range of nanomaterials and supramolecular materials, there is a greater variety of possible cases, which leads to a wide continuous set, whose size ranges from molecules to solid-state materials. Moreover, the chemical nature of the components as well as the interaction between them leads to different possibilities of structure, degree of organization, and properties. In the design of this type of materials, it is transcendent to tune the nature, extent, and accessibility of internal surfaces [2–4]. Globally, the trend most used for the application of new materials is to predict and control their chemical and physical properties. In particular, the manipulation of atoms and molecules in nano-sized materials is related to nano-chemistry and molecular engineering.

3. Classification

In accordance with the chemical origin of the interface or links established between the components in a hybrid material, these materials can be categorized as is shown in **Figure 2** [1, 2]. A first class of hybrid materials are those based on the synergy of the phases through weak chemical interactions based on Coulomb forces, London dispersion forces, hydrogen bonds, and dipole–dipole forces. A second class of hybrid materials are those based on the synergy of the phases through strong chemical bonds such as Lewis acid–base, covalent, or ionic-covalent bonds. The latter class of materials depends on the relative stability of the synergy between its components, since it determines the types of organic functionalization or the type of complex organic ligatures based on transition metal cations required to anchor the organic components to inorganic components.

In addition, hybrid materials can be classified as organic-in-inorganic (organic moieties used to modify inorganic materials) or inorganic-in-organic (inorganic constituents used to modify organic materials or matrices), as illustrated in **Figure 3** [3]. Hybrid materials based on the first approach can be subdivided into two types, namely, (1) inorganic materials modified by organic moieties and (2) colloidal polymers stabilized by organic moieties. On the other hand, inorganic materials are

Figure 2.
Basic classification of hybrid materials according to the types of chemical interaction between their components.

Figure 3.

Types of hybrid materials based on the adding of inorganic and organic components and vice versa.

modified via surface charge or functionalization with ligatures. Among the colloidal particles that can be used are nanoparticles, nanobars, nanotubes, nanostars, nanoflowers, etc., which must be electrostatically stabilized to be uniformly distributed throughout the material, preventing the formation of clusters. The incorporated inorganic constituents have small particle or structure morphologies, and these are made of clays, ceramics, minerals, metals, semiconductors, carbon-based nanomaterials, and two-dimensional materials. These materials are integrated into organic materials or matrices of either chemical or biological type. Chemical matrices can be polymers, monomers, synthetic molecules, etc., and the chemical materials derived from them are layers by layers (LbL), hydrogels, brushes, and copolymer blocks, both in the form of vehicles or coatings. The biological matrices used belong to one of the following groups: bacteria, microorganisms, molecules, polysaccharides, proteins, nucleic acids, carbohydrates, and lipids.

A more recent classification of hybrid materials is based on their functionality [1]. Three different types of materials can be identified: (1) structurally hybridized materials, (2) functionally hybridized materials, and (3) hybridized materials in their chemical bond.

4. Applications

Many applications have emerged by taking hybrid materials to the commercialization stage, and another huge amount is in its research and prototype phase to become emerging applications, as shown in **Figure 4** [4]. Among the numerous applications of organic–inorganic hybrid materials are:

- Gas barriers
- Packaging
- Sealants
- Hybrid pigments
- Decorative coatings
- Scratch-resistant coatings
- Anti-corrosion coatings
- Hair care products

Figure 4.
Applications of hybrid nanomaterials to flexible electronics (adapted from [4]).

- Spin-on-glass materials
- Acoustic and thermal insulators
- Electrical insulators
- Smart textiles
- Flame retardants
- Green tires
- Automotive parts
- Dental products
- Controlled-release biocapsules
- Biocatalysts and/or photocatalysts
- Contrast agents for magnetic resonance imaging (MRI)
- Hybrid anti-cancer nanoparticles
- Biosensors
- Supercapacitors
- Fuel cells
- Solar cells
- Actuators
- Optical chemical sensors

- Flexible hybrid batteries
- Microlenses and waveguides
- Organic light-emitting diodes (OLEDs)
- Photochromic and/or electrochromic coatings, etc. [5]

Tag sensors for realizing radiofrequency identification (RFID) based on inkjet printing nanomaterials are easily stamped on textile, plastic, paper, glass, and metallic surfaces [6]. For example, by means of hybrid materials, using titania and silica, it is possible to develop templates onto polymer and/or glass substrates.

Electrochemical energy storage using supercapacitors is an option to power portable and/or wearable electronic devices. For this application, nanomaterials such as metal–organic frameworks (MOFs), metal nitrides, MXenes, and phosphorene are mixed with organic materials to improve electrode performance [7].

A huge variety of hybrid materials has been proposed for implementing electrodes for rechargeable batteries by means of inorganic polymers and materials such as graphene, carbon nanotubes, or their combination [8]. These storage devices are used to power portable applications.

Hybrid materials such as conductive polymers combined with nanostructured transition metal oxides, graphene, and/or carbon nanotubes are being used for the design of electrodes for solar cells [9].

5. Conclusions

Around the world, different research groups are continuously presenting new strategies, studies, and applications related to the technological development of novel hybrid materials. These materials promote continuous innovation in various technological sectors as presented in this chapter. Although there are numerous advances so far, the real possibilities can only be limited by the imagination of engineers and scientists around the world. The contributions of biologists, chemists, physicists, and materials scientists take advantage of both the integration and the miniaturization of electronic devices to develop emerging technologies in various areas of electronics as presented in the chapter. In this way, it can be affirmed that the area of hybrid nanomaterials is experiencing continuous growth as a topic of scientific research, incorporating more and more research groups worldwide thanks to the diversity of approaches that drive technological innovation.

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