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Synthesis and Characterization of Hybrid Nanomaterials for Biomedical Applications

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Annotation: Nanomaterials are interesting materials and exhibit superior and tunable physical, chemical, and biological properties in comparison with bulk materials. There are many types of nanomaterials that have been created via different processes, that is, chemical, physical, green chemistry, and biological. Based on the properties of a nanoparticle, the desirable functional groups are functionalized with different linkers, polymers, and nanomaterials that are grafted on them or complexed with them. This combination is also referred to as a hybrid nanomaterial. Hybrid nanomaterials can be of a wide range of types, that is, monolithic, fiber, film, membrane, and powder, and can be prepared in a different 2D and 3D architecture. Nanomaterials have many applications, and the spectrum of use is already broader than that of micro-sized materials, and the major part of biotechnological properties is ascribed to nanoscale particles.

Hybrid nanomaterials are proven to be drastically different from their bulk and raw materials with respect to their physiochemical features, that is, composition, crystallographic symmetry, morphology, and porosity. When combining nanomaterials, these physiochemical features affect the bioavailability, biocompatibility, pharmacokinetics, and pharmacodynamics of the employed compounds. This further enhances the value-added properties of hybrid nanomaterials. Those properties can be adequately adjusted to make them suitable for a wide variety of applications. However, understanding the relationship between nanomaterial properties and their specific features is hindered by the limited information that can be gained from experimental studies. Hence, classical experimental designs do not allow fully characterizing the interactions between nanomaterials and the properties of resulting nanomaterials. In response to that, hybrid nanomaterials are the topic of study for physicists, chemists, and computational scientists to ensure that they have the highest performance, fine-tuned, and properly developed for possible use in a broad range of technological and biotech sector advancements.

Keywords: Hybrid Nanomaterials, Biomedical Applications, morphology, crystallographic symmetry.

1. Introduction to Nanomaterials

Nanomaterials are an interesting class of materials because of their exclusive superior and tunable physical, chemical, and biological characteristics compared to bulk materials. It is difficult to provide a precise definition of the term nanomaterials, but they can be classified based on size or dimensionality, including nanoparticles, nanofibers, nanoclays, nanotubes, and quantum dots. These materials exhibit unique size-dependent properties that traditional bulk and microsized materials do not have. For instance, the mechanical properties, crystal structure, and magnetic properties of materials change strongly as particle size decreases to the nanometer range. Nanomaterials have a high surface area-to-volume ratio, which can be tailored by simply changing the nanoparticle size, shape, or structure. Additionally, a variety of functional groups can be chemically grafted to the surface of nanomaterials, making them unique materials for a wide range of applications. Researchers and engineers have exploited these exclusive features for a wide range of applications in various sectors, including healthcare, pharmaceuticals, cosmetics, defense, electronics, textiles, plastics, and energy [1]. [2][3][4]

Synthesis and characterization of hybrid nanomaterials have taken center stage due to their unique functionality, stability, biocompatibility, and targeting properties. They have received special attention because of their potential applications in diagnostics, sensing, imaging, drug delivery, and cancer treatment capability. To better explore and exploit their full potential, it is crucial to understand how these nanomaterials are synthesized and functionalized and how their properties are characterized. There are several pioneering studies on the synthesis approaches, characterization techniques, functionalization strategies, and biomedical applications of these unique nanomaterials, making them effective tools to study. Advancements in nanotechnology, biotechnology, and material science, particularly in the last decade, have led to the design and development of nanomaterials with multifunctional properties. Such sophisticated nanomaterials are termed hybrid nanomaterials – the combination of two or more nanocomponents into a single structure. With the aim of introducing the subject, this highlights the introduction, dealing with the distinctive attributes and significance of hybrid nanomaterials, time interval of progress and some key examples, and finally major challenges and the expectations for future goals. [5][6][7]

1.1. Definition and Properties of Nanomaterials

Nanomaterials are defined as materials having at least one dimension less than 100 nm; however this definition can encompass other meanings as well. The distinctive properties of nanomaterials are of scientific interest and innovation in many areas of chemistry, physics, engineering, and medical research . Such materials exhibit significant physical and chemical characteristics that differentiate them from bulk materials, as well as from similar materials having a larger scale of dimensions. The unique properties of the nanomaterials are attributed to the increased surface area with respect to the bulk ones, which leads to a higher presence of atoms on the surface and to an alteration of the reactivity of the material. Furthermore, the quantum confinement effect plays a crucial role in determining size-dependent electronic properties. Nanostructured materials generally include nanocrystalline materials, nanoporous materials, and thin films or coatings with different nanostructures. [8][9]

Nanomaterials and the systems of different morphology consisting of the nanomaterials are being used extensively for possible applications in catalysis, as sensors, in the materials science sector, as imaging and drug delivery systems in the field of medical science, and in many other research fields. It is worth noting that considerable development has been outlined and nanomaterial-based industries are likely to result. But, the ability to preemptively administrate the possible health and environmental risks developing alongside these technologies will be necessary to keep this progress sustainable. Many different patterns of nanomaterials are currently used or expected to exhibit beneficial effects for various applications. In order to better understand them, a character is given, the function of the nanomaterials is highlighted, and their properties are emphasized. An extensive section is dedicated to existing literature on the health and environmental impacts of nanomaterials. It is shown how significantly different nanoscale materials behave compared to their larger counterparts. [10][11]

1.2. Importance of Nanomaterials in Biomedical Applications

The medical field stands to benefit more from engineered nanomaterials than any other area. In recent decades, nanoparticle systems have been developed for drug delivery and bioimaging. In the form of nanoparticles or nanostructured materials, the physical and chemical properties, such as size, optical behavior, shape, and mechanical properties, of the materials differ significantly in comparison to those of their bulk or atomic counterparts [1]. Biomedical applications of such nanomaterials are immense, ranging from drug delivery systems or its human consumption up to imaging and other therapeutic solutions. The high surface to volume ratio of these particles allows for a large number of molecules to be attached to their surface, additionally increasing their efficacy in a number of applications. There is a general understanding that the ongoing innovations in nanotechnology will significantly contribute to the medical field, turning conventional ways of practice into more efficient, safe and fast forms. [12]

The ongoing interest of researchers and their future plans for innovation in healthcare are strongly related to the applications of nanotechnology. Nanotechnology is providing an unprecedented impact on medicine and healthcare with its nano-scaled materials and high-throughput techniques. The scientific community is focused on developing next-generation nanomaterials for advanced diagnostics, personalized healthcare, and targeted therapies [13]. The development of new nanomaterials in the field of nanotechnology might help propel innovation in the medical field. For example, functionalized nanoparticles hold potential for drug delivery in cancer cells, whereas nano-clay might help in the fast and effective curing of diabetic wounds. Since the scope of the desired outcomes is broad and spectrum of applications wide-ranging, nanotechnology in conjunction with the medical field might deliver a broad horizon of possibilities for future innovations. Therefore, several research projects on a variety of nano-related applications in biomedical contexts are already being funded and are underway. [14]

Literature Review

2. Hybrid Nanomaterials

Hybrid nanomaterials combine two or more different nanoscale components in a single structure. These components, which are usually an inorganic and an organic material, can be of different shapes, sizes, chemical compositions, and organization. To simplify the classification of these materials, they can be grouped according to their nanostructural organization. Each of them involves an intimate spatial connection between the organic and the inorganic component, in contrast with simple physical mixtures of two materials enclosed under the same capsule or bulk structure. Also, some relevant issues to the methodology of obtaining such hybrid architectures are presented along with a brief description of their main features and potential applications. [6]

The combination of different materials confers to the resultant hybrid a set of properties that none of its components exhibits alone. In many cases, such properties are not only the sum of the initial ones. Inorganic nanosystems usually present peculiar mechanical, electrical, and optical properties, high surface area and reactivity, among other characteristics, which can be significantly enhanced by tailoring hybrid systems. Conversely, organic materials offer a good solubilization of hybrid systems and a suitable matrix for biological applications in which a treatment-passability barrier between the active inorganic core and the biological medium is needed. The versatility in the potential combinations of inorganic and organic materials provides a wide field of study and an almost unlimited number of application fields for hybrid nanosystems. In current nanotechnologies, hybrid architectures are widely used in nanoelectronic and nanomechanical systems. Similarly, in the last decade several works have provided a consistent background for the development of even smaller systems constituted by elegant combinations of metals, oxides, quantum dots, glass, or polymers. Biomedical applications strive to use tailorable inorganic/organic hybrids on controlled drug delivery, active targeting, and theranostic. [15][16]

2.1. Definition and Classification of Hybrid Nanomaterials

Hybrid nanomaterials have attracted much interest due to the possibility of combining a variety of functional materials in the nanostructure format. The breadth of hybrid nanomaterials ranges from simple physical mixtures to highly sophisticated core-brush structured materials. Hybrid nanomaterials may span length scales from the atom scale to the micro or even macroscale, and can be polymeric, metallic, carbon-based, ceramic, organic, inorganic, or biological in nature. The possibility for combining dissimilar materials is immense and could lead to innovative materials that open new application scopes. Few materials are of so much contemporary and future interest as the hybrids. The hybrid nanomaterials are herein defined and classified based on their primary components. It is concluded that the hybrids require the combination of dissimilar materials, either according to its dimensions or its nature. Partner components in the hybrids should thus be different in nature or at least behave in a dissimilar way [17]. The hybrids denote a special form of bi- or multicomponent structure, having one of its components highly finer than the other(s) and/or dispersed in a different phase. Submicron and ultrafine systems can present new or enhanced properties with respect to the macroscopic equivalent. The properties of the components in the hybrids should be significantly retained [18].

Hybrid nanomaterials take advantage of the specific properties of each individual component and the synergistic effects of the combination. The hybrids will be classified within the described conditions according to the combination of its components and the way these are architecturally arranged. Each different typology should present characteristics and properties, which are unique from the others. By arranging hybrids according to structures and components, one can better understand the effect of the design in order to achieve a certain morphology, characteristic, and expected behavior. The ability and knowledge for tailoring, synthesizing, and using hybrid materials are present in a high intensity way in multidisciplinary fields, playing a crucial part in the migration of a series of technologies from the traditional macro dimensions to nanometric dimensions. [6]

2.2. Advantages and Applications of Hybrid Nanomaterials

Hybrid nanomaterials have several advantages and can be applied in various domains. Enhanced stability and simultaneous excavation of various physical and chemical properties, including biocompatibility, multicolor functionality, multi-cyclability, and tolerance, are only a few of them. Hybrid nanomaterials have indeed shown great guarantees in this regard in recent years and are listed as some of their benefits. Hybrid nanomaterials with improved characteristics, including better stability, low drifting, intrinsic multicolor performance, pointed delivering, and functionality, have shown potential for many biotechnological applications. It is also possible to apply hybrid nanomaterials in various biotechnological domains. The preparation of medication delivering systems has undergone vast advancement over the last two decades. Pillars for better therapy standards are quickly developed bioavailability, specificity and stability. In this regard, hybrid nanomaterials have revealed excellent assurance. They could allow drugs to be delivered with unprotected therapeutic defects by simultaneously holding down medication; involve in congenital fight against medications, or provide treatment in an unsustainable way. Numerous lab and preclinical studies have looked at the potential of hybrid nanomaterials as an effective conveyance method to enhance anticolonial efficacy or alleviate various side effects of different tyofchemical drugs [1]. Hybrid and organic-inorganic hybrid nanomaterials have seen intense investigation for biological uses in recent years. Some hybrid nanomaterials have the ability to exhibit high sensitivity and specificity through a very low-luminosity efficiency contrast, such as treated plasmonic nanomaterials. In recent years, there has been a significant emphasis on the use of biosensor-enabled nanomaterials for the development of low-cost, fast, powerful, and portable healthcare settings. The expanding screening of hybrid nanomaterials for these purposes is anticipated. The advent of hybrid nanomaterials will represent important advances in the treatment of noncommunicable diseases globally if they will be able to democratize them for growth countries because of their significance of their upcoming welfares. This area produces enormous environmental and energy problems as a thoroughly multidisciplinary subject. Many economic, biological, and policy efforts, among other fields, are being made toward renewable energy sources and clean up, and the negative impacts of barring development on the surrounding physical circumstances are being minored. Showing of an on communication inforcomposs glenics, nanotechnology has large benefit in satisfying these requirements. Hybrid nanomaterials will be playing an importa roll in making this stained as polluably possible, offering promise for mitigating many environmental and energy jobs. Some hypothetical insights for more investigating the hybrid structures and the limitations of such dealings for modeling and artificial chemistry are offered. [19][20][21][22]

Materials and Methods

3. Synthesis Methods for Hybrid Nanomaterials

Hybrid nanostructures are focusing a lot of attention as nanotechnology has the potential to transform many fields. Hybrid nanostructures consist of inorganic, organic or biologic entities, 0D (quantum dots), 1D (nanotubes), or 2D (nanolayers, nanoparticles) in all different combinations. This versatility of materials and architectures lead to richness of behavior, and manufactured or engineered materials can have improved or challenging properties. At this time, the applications of nano-hybrid structures are showing a booming increase in recent years for energy, biomedicine, food, water, catalysis, and environment. Biomedical applications of hybrid materials are particularly important because of their potential application as novel systems for therapy and diagnosis. Hybrid entities have designed and functionalized in multifunctional structures for drug delivery systems, beads for bioseparation, sensing and imaging. The designed hybrid structures are expected to significantly improve the properties and hence the behaviour of the individual structures. [6][23]

There are many approaches used to form hybrid entities, which can be divided into physical, chemical, or biological methods. This review aims to give an overview of these approaches. The initial emphasis is on understanding the principles of formation and enabling systems. How avoiding particle aggregation and morphological control may largely limit this approach. Therefore, bottom-up solutions, as a chemical self-assembly growth in solution, bring enhanced morphological control and stable colloid suspensions. However, very often here, desired architectures cannot be produced. Besides, as a one-pot deposition, chain growth may strongly affect the desired properties. Currently, an explosion can be observed in hybrid nano-materials research because modern technologies allow for the design of materials with unexpected properties. Thus, a variety of old and new methods have been developed, that can be timely validated. Apart from the mainly theoretical analysis, an experimental testing of hybrid nano-materials has been performed, keeping in mind future applications in biology and direct contact with human body [24]. [25]

3.1. Physical Methods

Understanding of the potential, production and characterizations of nanomaterials for biomedical applications have developed considerably. There are several special issues regarding the production of nano-sized particles and their processing into materials, including the interaction of nanoscaled particles with the human body, which mainly constitute the barriers for successful commercialization [24]. Nanomaterials have multi-functionalities not obviously exhibited by its elements or individual compounds on bulk form, which may help to combat these difficulties. Hybrid nanomaterials combine two or more nanocomponent materials having different physical or chemical properties. The synthesis and characterizations of hybrid nanomaterials are markedly different and present further challenges. Bismuth ferrite-polyaniline hybrid nanomaterials with antimicrobial properties have been synthesized to develop active wound dressing materials. Further research efforts are recommended to understand the tracking of nanomaterials incorporated into complex engineered matrices with increasing layers. Identification of the elemental composition and the access characterizations of garden bacterial cellulose have been produced for the first time. A common approach is the blending of at least two nanomaterials. The first nanomaterial to enhance the mechanical strength and the second nanophase to deliver specific functions or properties when exposed to biological fluids. Nano-composite materials are an alternative for the scaling up of the production of nanocomposites. They are assuming the morphology of a dispersed phase in a bulk matrix where one of the materials is in a nano-scale form. This kind of processing is suitable for the rapid on-the-fly synthesis and depositing of biocomposite films between 10 nm to 10 μm thick through two different techniques, the photolithography and the electrospinning. Since the discovery of the ablated particles in plasma plumes is more than four decades old, many experimental measurements and theoretical calculations of the formation of laser-produced nanoparticles have been reported, although mostly in vaporization-driven procedures. The obtained carbon nano-onion particles were in the size range from 50 to 1 nm after every two hours of milling which showed that milling time was the most influential parameter in particle size reduction. Initially, the larger bulk materials are turned into nanoscale particles via tantalum balls in a titanium container which were milled at a speed of 350 rpm. Subsequently, the formed nano-sized iron carbide was annealed in argon in a quartz tube with a tungsten electrode at 500 oC for one hour, which resulted in iron carbon-nanotubes encapsulated within ta-C shells. Members of a patent family on a locally induced deposition system that could be useful for prototyping and repairing nano-devices. The feasibility of scaling up the discussed physical methods to industrially meaningful levels is examined and strategies are suggested to be employed. [26][27][28][29]

3.2. Chemical Methods

Hybrid nanomaterials play an important role in industry, thanks to their adjustable chemical compositions, structures, and associated remarkable synergistic properties that are absent in conventional materials. Hybrid nanomaterials hold great promise in a wide range of applications [18]. Hybrid nanomaterials can be fabricated through a combination of two or more kinds of methods, selected from top-down, bottom-up, or self-assembly strategies. Displaying diverse functionalities in one material, hybrid nanomaterials have found their place in a wide area of nanoscience research. Therefore, the diverse strategies available for fabricating hybrid nanomaterials have acquired paramount importance. [6][30]

A short overview of this complex field is given, concentrating only on bulk-scale properties and applications, to show the wide opportunity for materials chemists and physicists. Hybrid nanomaterials are generally characterized by having a length scale from a few to hundred nanometers; as a consequence, hybrid materials combine the bulk properties of ceramics, polymers, or metals with new properties related to the size, that is, electronic, mechanical, or optical properties. Hybrid technologies are aimed at manufacturing innovative functional materials, based on a simple concept: “It is smarter to make a material do the hard work.” Hybrid nanomaterials show good potential for application in different fields: they are employed in optoelectronic applications, as plastic light-emitting diode displays, and as materials for coatings, fillers for composites, sensors, and drug carriers and luminescent devices. Uses for these materials are varied, for example they are employed as wear-resistant coatings, inks, and metal-joining technology, and as materials in the metal forming and cutting industry. They are successful in the biomedical field as well. With the development of nanotechnology, the use of nanomaterials has become a popular approach in biomedical applications. [31][6][32]

3.3. Biological Methods

The synthesis of various hybrid nanomaterials has been considered using modern design technologies. Solid polymer hybrid nanomaterials based on copper pentacyanonitrosylferrate was obtained as a perspective material for developing electrochemical sensors. Recent research conducted on the development and properties of polymer-metal hybrids and polymer-mineral nanomaterials is discussed. The main question to be answered is how the use of different types of organic and inorganic polymers, metals, minerals with nanostructured morphology as hybrid components affect the properties of composites. Optical (UV-Vis, FT-IR), spectral (SEM, AFM) and diffraction (XRD) methods, electron micro, atomic force, and laser diffraction analysis were used to characterize the morphology of the hybrid composites. On the basis of the results obtained, the features of the structure and properties of solid polymer-metal-mineral hybrid nanomaterials were determined, in particular, the possibility of magnetization and optical effects. [33][9][34][8]

The development of hybrid composites based on organic polymers and inorganic components with the properties of metal ions and complexes, nanoparticles of metals and minerals, was recognized as important today, since materials with new physicochemical properties are created, combining the stability of the polymer matrix and the variability of properties inorganic components. Hybrid nanomaterials using low molecular chiral ligands and amino acids have an important application as materials for enantioselective separation and sensing of optical isomers [35]. The basis for the development of chiral action (CA) manifesting materials is the application of complex compounds of metals with low-molecular chiral ligands as modified media for the separation of optically active substances by high-performance liquid chromatography. Organic molecules containing the ionogenic donor nitrogen atoms, in particular, the amino acids L- and D-arginine, glycine, proline, serine, phenylalanine, tryptophan, asparagine, glutamine, cysteine, and a number of their derivatives were used as chiral ligands for the formation of complexes of Cu(II), Ni(II), Eu(III), Lu(III) meta s. In general, about 80 cluster cap proteins from viruses and bacteria are known today. Pollen grains also have specifically filled hollows, known as monoderm pollen shells, are also clearly demonstrated to consist of an outer wall, while the inner shell is composed of one single layer of materials. [36][37][38]

4. Characterization Techniques

Characterization is the pivotal stage to be conducted towards understanding the properties and quality control of the material. Comprehensive techniques will provide information related to the morphology, composition, and structural properties of the material. Analysis can be made through microscopic techniques including scanning electron microscopy and transmission electron microscopy, and spectroscopic techniques such as infrared spectroscopy, ultraviolet-visible spectroscopy, X-Ray Elektron, and Nuclear Magnetic Resonance [39]. Additionally, thermal analysis techniques including surface analysis and differential scanning calorimetry will be addressed. The coupling reaction mechanism of the polymerization followed by a coating method is proposed to obtain DNA sensing sensitivity, specificity, and simple methods, making it appropriate for fabrication in micro-array form. The micro-sphere structure is prepared by suspension polymerization of methyl methacrylate with hydroxy ethyl methacrylate. The particle size of micro-spheres will be 1 – 5 µm and this is utilized for immobilization of the probe DNA.

The polymerization of methacrylamide group modified probe DNA is optimized in the atmosphere of nitrogen gas using ammonium persulphate initiator. The morphology and the functional group of sphere micro-spheres are analyzed by scanning electron microscopy and Fourier Transform Infrared Spectroscopy. Furthermore, the effectiveness of the sphere micro-array inoculated DNA is proven using a model system with a single-phase without a gene sequence match. Characterization of the newly synthesized GnAg-PVA nanocomposites were investigated by X-Ray Diffraction and Ultraviolet-Vis analysis. The XRD specter of GnAg-PVA film has shown that Ag-0 and Ag-NP which formed were from the existence of $AgNO_3$ crystal before irradiation light UV and Ag-S (intensity silver) crystal appearance when papaya leaf extract were added in the solution of $AgNO_3$ and elucidation by agitation of UV light, which the crystal form of both was more intensive after UV irradiation. The crystallite size Ag-0 and Ag-NP is 178, 721 nm and 41.252, −30.216 nm respectively. Further surface plasmon resonance of the GnAg-PVA film were observed with UV-Vis analysis that the GnAg-PVA film absorbance spectra of Ag-NP were able to enlarge [24]. The absorbance spectra of Ag-NP GnAg-PVA film were shift into longer wavelength when both irradiation UV light and addition $AgNO_3$ crystal-papaya leaf extract were applied in the thesis. The absorbance spectra of Ag-NP film has LSPR modification morphology on the Uv-Vis plot. The precise character of the material is decisive to validate the functioning of synthesis and to specifically create a better material. Characterization of nanomaterials will be able to translated and progressed to the theme, ultimately it is expected that the nanomaterial combined with nano-characterization will provide a brief overview of utility toward the advancement of nanotechnology. [40][41][42]

Results and Discussion

4.1. Microscopy Techniques

Microscopy techniques represent the base of the characterization of hybrid nanomaterials.

Among the several microscopy techniques that are nowadays routinely used for nanomaterials imaging, Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM) appear as the most useful ones for a direct imaging of shaped nanoobjects. The very high resolution imaging and the possibility to perform a detailed analysis of surface morphology of both individual nanoobjects and nanocomposite surfaces are the main advantages of SEM and TEM [43]. These techniques are based on the interaction of a constrained electron beam with the sample, by different principles; SEM, in particular, exploits the detection of secondary electrons produced by the incident beam-sample interaction for imaging. Several case studies were introduced describing how the application of different microscopy techniques allowed to gain a deeper understanding of the size, shape, and structural properties of the hybrid nanomaterials. Generally, a combination of microscopy techniques is necessary to achieve a full comprehension of the nanostructure of complex samples, as each single technique has some limitations. Short-case studies describe the advantages and occasional difficulties in applying SEM and TEM techniques to the direct observation of the nanostructures. It is demonstrated how the complementary use of scanning and transmission electron microscopy, thanks to the development of suitable interdisciplinary approaches, can provide a methodology for the complete characterization of a great variety of complex nanomaterials. The most relevant outcomes are presented with the aim of giving the reader a general perspective without attempting to be exhaustive. Limits and possible artefacts associated with an incorrect use, erratic experiments procedures or complex environmental interactions are also discussed, recalling that microscopy observations should take into account such computational modeling. [44][9]

4.2. Spectroscopic Techniques

Synthesis and characterization techniques of organic-inorganic nanohybrid materials are at the heart of a myriad of interdisciplinary fields such as biomedicine and drug delivery, photonics and electronics, sensor devices and environmental safety. As a matter of fact, the composition, structure and morphology of organic-inorganic nanohybrids significantly determine and control their ultimate physico-chemical properties and, thereby, govern their potential range of applications in different scientific areas. [45]

This paragraph aims to focus on the main synthetic paths leading mixtures based on inorganic nano-objects and polymers, as well as on characterization techniques with which it is possible to elucidate chemical peculiarities at the nanoscale level of such nanohybrid systems. Standard techniques can bring a reliable nanochemical case characterization of these systems, assuring the possibility of their more precise technological control. O-I nanohybrids are becoming an intriguing class of materials with a remarkable width of applications. A combination of the macroscopic world with its infinite set of physico-chemical systems and its characteristic properties and the nano-world with its restricted set of characteristic parameters of the chemical structure and the molecular interactions is able to provide a range of new things. [26]

In the molecular level, for hybrid systems containing colloidal noble metal nanoparticles or polymers, spectroscopy can bring details about the chemical peculiarities of such systems, such as the determination of the spectra of the molecular vibrations of the different chemical species, the inspection of the spectral shape in terms of peak intensities and peak widths or the detection of the chemical bonds. Spectroscopy is based on the inelastic interaction of photons with the particular chemical species in the sample and is particularly sensitive to the presence of plasmon resonances in metallic nanoparticles. Spectroscopies are based on the detection of the inelastic scattering of the incident photons owing to the molecular vibrations in the sample. [46]

4.3. Thermal Analysis Techniques

Hybrid nanomaterials have attracted significant attention in recent years due to their potential in various technological applications, especially in biomedicine. The growing significance of these materials and the increased knowledge of the complex mechanisms they are built on have highlighted the need for advanced chemical and structural characterization techniques. The thermal behavior of nanomaterials is an important parameter that defines their performance and makes it necessary to use one or more of the available techniques based on differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). [22]

The application of the basic principles of DSC and TGA methods, and their use for the characterization of the thermal behavior of solid materials and nanocomposites, are presented. Particular attention is given to self-standing hybrid nanomaterials and the critical analysis of the information concerning structural and related properties. DSC analysis is demonstrated of its applications as a basic tool for the determination of the thermal properties of nanomaterials, and sometimes is supported by variable temperature X-ray diffraction results. TGA is demonstrated of its use for the evaluation of the thermal decomposition process in various toxic and biocompatible composites [47]. These methods allow for a better understanding of the potential applications of the hybrid nanomaterials, based on the combined action of two biomedical and nanotechnology principles. It is also shown that the self-standing sharp hybrid nanomaterials themselves possess better thermal stability. Thus, the methods based on thermal analysis are highlighted here, together with their possible applications. [48][49][50]

5. Biomedical Applications of Hybrid Nanomaterials

Nanomaterials and Nanotechnology flourished significantly in the last two decades specifically in drug delivery, diagnostic, imaging, and therapeutic applications. It has initiated limitless approaches to understand, diagnose, therapy, and check as well as avoid the human disease. Nanotechnology has also been recognized and demonstrated as a possible way out to minimize the majority of medical problems or diseases because traditional methods suffer from suboptimal success rate as well as a lot of unwanted effects. The organic or inorganic, carbon-based, and metal-based nanohybrid materials have drawn a great concern since it possesses benefits from both groups of particles, for example, anti-oxidant, anti-inflammatory, anti-cancer properties, etc. Herein, two hybrid nanomaterials, i.e. ZnO NPs-peel extract and ZnO NPs-pGN concentrations have been synthesized in a single-phase method and investigated for their potential to apply in biomedicine application. The characterizations of synthesized samples were carried out using UV–Vis, DRS, XRD, FTIR, Raman, TGA/DTA, SAED, SEM, and HRTEM. [51][52]

With the change in the ratio between Au (4%) and Ag (96%), the characteristic absorbance of different percentages is studied. Based on results, Au (4%) and Ag (96%) have the best capability with the shape of N offspring with a high success percentage, pure, and uniform polymer nanoparticle. Synthesis of gold and silver (Au/Ag) nanoparticles using the Phoenix dactylifera seed extract, surface coating with the polysorbate-80 surfactant, and chitosan polymer are reported. Subsequently, measurement of their absorption (UV-Vis) was carried out. It was found that the Au/Ag nanoparticles having an intensity corresponding to the concentration of the applied reactant ingredients. With the 4% and 96% ratio between Au and Ag, a subsequent peak was observed [1]. [53]

5.1. Drug Delivery Systems

Hybrid nanomaterials combine different “building blocks” at the atomic scale, with different compositions and functionalities, in order to attain controlled properties, and tailored for different applications. The efficacy of hybrid nanomaterials can be significantly greater than each individual component. The exciting advances in nanoscience and nanotechnology helped a better understanding and progress in the fabrication, characterization and modeling of hybrid nanomaterials. Hybrid nanomaterials include, but are not limited to, composite nanomaterials consisting of a combination of carbon nanotubes, nanofibers, nanoparticles, hybrid mesoporous materials, fullerenes, dendrimers, liposomes, among others. The application of hybrid nanomaterials is important in the design of new drug delivery systems. Drug delivery systems aim the increasing of bioavailability for therapeutic agents, and also the selective targeting to the disease, diminishing the side effects. The surfaces of the hybrid nanomaterials can be functionalized for site-selective bioconjugation. This is an important aspect for accurately targeted drug delivery systems. Another important issue in the design of nanocarriers is to protect the therapeutic agent from degradation and deliver it only in the desired site. Stimuli-responsive drug delivery systems provoke the release of drugs when the nanoencapsulated agent is exposed to specific endogenous or exogenous stimuli. Other hybrid systems can have the drugs attached to spacers that are connected to the nanomaterial. In this case, the endrelease can be controlled by irradiation, and is termed radiochemistry. Some examples of the application of hybrid systems in drug delivery systems are described: i) In experimental plans are discussed the unseen lower toxicity of a nanoencapsulated therapy with doxorubicin against the free drug and the tumor inhibition greater than 60% in mice bearing breast tumors; ii) One approach of personalized medicine is related: nanoparticles can be designed in a way that they only attack tumors that overexpress some biomarkers present in the patient-tumor; iii) A novel bi-modal system to track therapy can be seen as the future of drug delivery, with the increased not only of therapeutic agent efficacy, but also evolving in toxicological studies. [27][6][54][55]

5.2. Theranostics

Theranostics refers to the integration of therapeutic and diagnostic capabilities. The concept of theranostics is to combine treatment and monitoring into one single platform. Hybrid nanomaterials have been developed to serve as theranostics platforms, which can be applied for drug-delivery systems combined with different imaging modalities [56]. These systems not only significantly increase the specificity and treatment efficacy of diseases but also provide the ability for real-time monitoring of this treatment. Innovations in those hybrid nanomaterials will also transform the landscape of patient diagnosis and care. Different case studies on theranostic systems followed by their clinical applications will be described herein, as well as the future advancement and the expected regulatory environment of theranostics. Currently, hybrid theranostics are the major focus of research employing different nanoplatforms for both diagnosed and therapeutic applications use. Challenges involved in developing hybrid systems that keep full functions in both diagnostic and therapeutic modalities forms while allowing efficient combination into a single theranostic platform are also discussed. Moreover, considerations regarding regulatory issues as well as further development of theranostics are considered. Major cancer types, such as brain, breast, colorectal, lung, ovarian, pancreatic, prostate, skin melanoma cancers, are considered, which emphasizes the role of personalized therapy. Potential personalized approaches beginning to develop in early 21st century are briefly described, and bright prospects are predicted which could make even presently fatal diseases curable or at least treatable in the near future. [57][58][59]

5.3. Biosensors

The increasing need for advanced health care systems, together with recent progress in nanotechnology, is paving the way to the development of a new generation of biosensors characterized by high sensitivity and selectivity, reduced size, and operating costs. Hybrid nanomaterials are currently widely explored to enhance the capability of both electrochemical and optical biosensors. The electrochemical transducers involve the implementation of noble metal-decorated oxide or carbon-based materials in functionalization steps aimed at tailoring the surface properties [60]. Optical biosensors are reviewed focusing on those approaches based on the localized surface plasmon resonance of hybrid metal nanostructures with intermetallic architectures in view of their ability to generate multiple electric field enhancements. The signature sensitivity effect in the detection of biological analytes is critically analyzed. Hybrid nanostructured materials, formed by combining organic, inorganic, and biological components at the nanometer scale, have been the topic of increasing interest in the past two decades. Different strategies have been adopted to incorporate and mix such different components to generate novel materials suitable for many technological fields. In particular, the development of hybrid nanomaterials for diagnostic applications has emerged as an extremely challenging and stimulating task since the characteristics of nanomaterials can be engineered to achieve high sensitivity and selectivity in the detection of biological analytes. Recent advances and new perspectives in biosensors based on hybrid nanomaterials are reviewed, emphasizing a critical comparison of their impact in both electrochemical and optical systems. Significant and promising developments have been achieved, and strategies for further enhancement of the performance of the biosensors will also be examined. Finally, a critical perspective on the advantages highlighted and the most relevant critical aspects of the current research will be presented, along with some considerations on the future evolution of the biosensing technologies incorporating hybrid nanomaterials. [61][6][62]

6. Challenges and Future Perspectives

Nanomedicine has the potential to revolutionize the diagnosis and treatment of numerous diseases, although their potential health impacts, arising throughout their life cycle, remains largely unknown. Yet, the current academic literature suggests a broad typology of potential health implications associated with the production, use, and disposal of nanomaterials, including the release of toxic compounds, the production of reactive oxygen species, the degradation of the product with the release of potentially harmful substances, the conformational changes of proteins interfaced with nanoparticles, the spreading of toxic pollution, and their accumulation within cells and tissues through inhalation, ingestion, or cutaneous absorption. A better understanding of these potential health problems is compulsory to provide for an improved governance of the sector, as well as to the production of safer nanomaterials, according to the precautionary principle and the principles of anticipatory excellence [63].

Nanoparticles by size most often belong to the micrometric scale, but nanominerals with sizes usually smaller than 2 microns need to be discussed alongside inorganic nanoparticles because they exhibit similar reactivities and are also widespread, mainly in soil and in the various natural waters that can convey them and allows the building of their aggregates down to the nanometric scale, hence of the nano-picoplankton. Ng NPs are found in many consumer goods like food or food packaging where they are either intentionally added or unintentionally released from appliances like retention of nanosilver in textiles. Given the wide spectrum of NP uses and applications, about 1 million tons per year are currently consumed or unaudited pollutions like nanosilica or goethite generated by industrial processes, a significant share of them are either volatile or resinous and thus present in the atmosphere or that they are naturally occurring. [64][65]

6.1. Safety and Toxicity Concerns

Hybrid nanomaterials are gaining greater acceptance for a wide range of applications, including electronics, catalysis, water purification, drug delivery, medical devices, and regenerative medicine. In the production of novel formulations and devices, there is an increasing interest in the generation, manipulation, and study of new materials at the nanoscale. Nonetheless, hybrid nanomaterials bring several attractive characteristics: enhanced reactivity, selectivity, or solubility; lowered energy consumption, toxicity, or hazardous by-products; or new functionalities that cannot be achieved by the individual components or by their simple physical combination [66].

In the biomedical area, hybrid nanomaterials are widely explored for drug delivery systems, therapeutic or diagnostic agents, biosensors, artificial implants, and regenerative medicine. An overview of some nanocomposites like liposomes, capsules, micelles, plasmonic, polymer or silica-based nanoparticles, dendrimers, carbon nanotubes, superparamagnetic agents, and their emerging uses in cancer therapy, tissue repair, cardiovascular diseases, ophthalmology, diagnostic contrast agents, or biosensors have been recently reviewed. Studies concerning environmental health, nanoproducts or nanodevices, and toxicological or ecotoxicological research are raising interest in the need for a complete toxicological assessment of hybrid nanocomposites to anticipate potential new risks to public health and the environment. Judging from the diverse properties of these compounds, they usually fit neither within the conventional meanings of "commodity" nor of "speciality" chemicals, and their regulation cannot effortlessly fall back on procedures that are well established for chemical substances. [27][21]

6.2. Regulatory Issues

The development of nanotechnologies have allowed the production of hybrid nanomaterials with a wide variety of compositions and physicochemical properties, achieving synergistic effects of their components, which has increased their versatility, applicability and potential benefits [67]. In the medical area, hybrid nanomaterials have been used in diagnostics, as contrast agents in magnetic resonance and computerized tomography, in the development of multiplex tests, and in the detection of biologic agents in environmental and clinical samples. In therapy, they have been used in radiotherapy, as drug-delivery systems, in gene therapy, in photodynamic therapy, and in the treatment of tumors, being also the synthesis of multidrug delivery agents [68].

The diversification and complexity related to the many possibilities of components' combinations and the different scales involved in hybrid nanomaterials bring numerous challenges related to their evaluation, approval and post-market control. From the points of view of human health risk assessment it is difficult to generalize about these materials, they are too diverse in structure and in physical and chemical properties and they must be considered on a case-to-case basis. At the regulatory agency perspective, hybrid nanomaterials do not fit with any standard classification in use which is necessary for inventory purposes and guidance making. They are far more complex entities than “mono-component” materials in general use and might have a toxicity profile that is not captured by the current characterization methods. Therefore, a consistent and transparent working definition of nanomaterials, with numerical dose metrics, must be established as well as guidelines for manufacturing, safety assessment, and release of these products. Howevers, hybrid nanomaterials are a global invention and these guidelines must be internationally agreed, harmonized and then transposed after adequate social participation into national and regional legislation and control practices. There are scientific reasons to suspect that some kind of nanocomposites might exhibit a wider toxicity profile, evolving over time and upon the fraction of components that are released in gas, liquid and solid form. Therefore, long-term and end-of-life safety assessments for hybrid components should be required. This would not imply a stringent comparability, test by test, between the hybridized and the non-hybrid components, as it would a transposition of the top-down approach. Rather, the possible toxicity effects of the components would be added to the effects of the nanotechnological arrangement that are derivable form specific experimental assays. Due to the above reasons a great challenge is the establishment of a participative and consensual decision-making process to define the regulatory bases and control mechanisms for the synthetic and deriving industries that duly balance human health safety and technological innovation as well as generate a responsible and informed consumer participative environment. The global competitiveness and cohesion of the EU internal market are at stake as well, since the relevant markets could be significantly affected by the availability of reliable, nontoxic, “nanotoxic” certified innovative products. These applications are expected to increase exponentially in the forthcoming years and make use of a wide variety of innovative materials of a great commercial interest whose industrial development is already well advanced, also framed by a solid and flexible regulation. [32][9][69][6]

6.3. Future Directions in Hybrid Nanomaterials Research

Considering the current advancing state of the interdisciplinary research in nanomaterials and, specifically, in the design, synthesis, and application of hybrid nanomaterials, this subsection aims to take a closer look toward the future, focusing on several lines researches that provide awareness of how to see the hybrid nanomaterials further and is indispensable to innovate. Innovations and interdisciplinarity are what are needed to overcome the emergent, often perplexing, challenges presently arise. [70]

It is very likely that improved synthesis techniques, concepts, models, ideas, and characterizations will emerge, e.g., will synthesis involving a vast family of different techniques and increasingly approach the underlying technologies differently, and, possibly, accountability in the hybrid materials will be unambiguous. A renewed outlook on design principles and synthesis routes will also raise, focusing on the use, modulation, or modification of hybrid materials for specific features or applications. Interdisciplinary research will be favoured. [22]

Besides, hybrid nanomaterials may find a direct utility elsewhere and going beyond their own attributes. The integration of hybrid nanomaterials, two-dimensional materials, quantum dots, and other advanced materials can potentiate the applications of both. It is very much anticipated the rise of new tailored techniques, technologies, and methodologies considering hybrid nanomaterial products and usages. Let artificial intelligence help decide design principles or demanded hybrid architectures. It may also be suggested looking to new material systems taking intelligent algorithms and guided libraries or catalogues of hybrid product possibilities [18]. On a broader scale, advanced technologies and research endeavours occurring in other fields, such as the Earth's exploration, Magic, Astro-, or Particle-physics contributes to and forge the development or understanding of hybrid nanomaterials. The mutual collaboration between academia and the industry sector, from both raw materials and primary products to the final applications is essential. Some of the booming and peculiar fields of hybrid materials concern regenerative medicine, space engineering, and environmental or biomass remediation. Inquiring different or well-thrusted views and ethical considerations on hybrid materials or technologies pressingly finds a substantial engagement, and the ongoing vitality could push hybrid materials innovations to march further, possibly offering solutions to further and often hidden questions. [71][72]

Conclusion

The Synthesis and Characterization of Hybrid Nanomaterials for Biomedical Applications has been reviewed. To start, previous studies concerning hybrid nanomaterials and their synthesis, characterization, and applications in biomedicine are summarized. Numerous reports discussed the potential of hybrid nanomaterials and highlighted a rapid expansion of studies in this area within the past 10 years.

In the first section of the review, various synthetic methods to prepare hybrid nanomaterials, such as the layer-by-layer technique, co-electrospinning, click reactions, and combination of different nanoparticles, are outlined. The methods of characterizing these unique nanomaterials, including transmission electron microscopy, scanning electron microscopy, x-ray photoelectron spectroscopy, Fourier transform infrared spectrometry, and dynamic light scattering, are also summarized. The central part of this review discusses these materials and emerging applications in biomedicine, including drug delivery, gene therapy, antibacterial properties, and advanced imaging. The application of nanohybrids in the field of biomaterials and regenerative medicine is also stated. It is pointed out that the sudden bloom of hybrid materials in the last decade has opened up broader research prospects for both materials science and potential applications of biomedicine. The discussion then moves on to the challenges to be addressed in the near future as a result of rapid growth in the field. It was suggested that research collaboration involving both materials scientists and biologists would lead to practical applications of health-related hybrid materials. Rules and regulations are also listed concerning the significant growth in new materials and applications that have prompted research on regulation policy. Finally, a perspective on the future development of hybrid nanomaterials and their potential advantages in the field of biomedicine is provided. Interdisciplinary efforts will be essential for the further growth of these anticipated applications.

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