Nanomaterial's and the interface between nanotechnology and the environment

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Abstract

Nanomaterials are the main products of nanotechnology. In this article, some of these materials are described, in particular carbon compounds, their properties, handling strategies and applications. It also discusses the history of nanoparticles and the complexity in classifying these materials, necessary for their regulation and assessment of impacts on society.

Keywords: nanomaterials, nanoparticles, nanotoxicity, history of nanotechnology.

1. Introduction

Nanotechnology is one of the emerging technologies of the last few decades, along with biotechnology, information technologies and, more recently, synthetic biology. Accustomed to a world divided into disciplines and professions, which have changed little in essence over generations, the sudden advent of a new science or technology raises expectations of all kinds and calibers, which also need to be understood as much as its cause. These expectations raise discussions that can modify the course of the development of new technology, as well as reassess society's relationship with activities based on older technologies. Apart from the more technical aspects that will be the subject of this article, a better perception of the complexity surrounding a new technology is already an important legacy of nanotechnology 1.

Among the initially exaggerated expectations were market forecasts for nanotechnologies, which at the turn of the 21st century predicted values in excess of 1 trillion dollars for 2015 2. These values exclude the semiconductor market, which is a case in point. part, because microelectronics, which is already nanoelectronics with the continuous reduction of devices on chips, today already has components with only 22 nanometers. Returning to nanotechnologies and excluding semiconductors, over the last few years more realistic revisions have lowered these figures to 49 billion dollars for 2017, with nanomaterials responsible for 37 billion of these billions, according to the NANO31E report presented by BBC research in September 2017. 2012 3.

Thus, nanomaterials continue to dominate the nanotechnology agenda; To discuss this legacy, we will start with a definition of nanomaterials recently agreed (2011) by the European Commission 4:

"A natural, incidental or manufactured material containing particles not bound together or in aggregates or forming agglomerates in which the size distribution shows 50% or more of such particles with one or more external dimensions in the range of 1 nm and 100 nm. In specific cases and justified by environmental, health, safety or competitiveness concerns, the 50% threshold in the size distribution may be replaced by a threshold between 1% and 50%".The detailing of this definition is in itself a summary of the whole theme, as will be briefly discussed below.

2. Natural, incidental and manufactured nanomaterials

Nanomaterials are those consisting of particles or agglomerates of them with a size distribution that presents a considerable fraction of particles with one or more dimensions in the range between 1 nanometer (1 nm = 1 billionth of a meter) and 100 nm. It is important to note that nanotechnology, that is, a technology that manipulates matter in a controlled manner at this scale, is directly related only to manufactured nanomaterials, designed to rem structures relevant to their properties on the nanometer scale. On the other hand, the environment has always interacted with natural nanoparticles (soot, volcanic ash or strands of webs from some spider species), and human society has also long contributed with incidental nanoparticles, produced as unintentional by-products of other species. processes (such as those released by car exhaust). Thus, it is relevant to mention that the development of the synthesis, control and characterization of manufactured nanoparticles also allows improving the estimation of the presence and impact of natural and incidental nanoparticles.

This controlled manipulation at the nanometer scale seeks properties and characteristics that could not be obtained in any other way. This aspect is what seeks to validate nanotechnology as an area of knowledge beyond the pure definition of the object based on its dimensions.

In the definition given by the European Commission it is mentioned that the particles or their agglomerates would need to have one or more dimensions between 1 nm and 100 nm, including, therefore, not only particles themselves, but also threads with nanometric diameters, films with thicknesses in that scale or surfaces with structures or pores with these dimensions. In this way, nanomaterials range from colored glass due to the presence of copper nanoparticles, produced in the Bronze Age, to the modern microprocessors of this century, basically silicon films with structures on a scale of a few tens of nanometers composing the so-called microcircuits.

3. A little of history

The story of an emerging technology is, for a while, barely told, and with nanotechnology it was not (is not) different 5. Some historic milestones are artificially created, such as the now famous lecture by physicist Richard Feynman, given in 1959 , at Caltech, entitled “There is plenty of room at the bottom”. The transcript is worth reading, and indeed it sounds like the premonition of genius, but its real influence is disputed; forgotten for more than twenty years, it began to be mentioned as an a posteriori validation of an area of knowledge still under construction, as discussed by several authors, such as Chris Toumey 6 and Richard Jones 7. Despite this critical review, the Feynman's lecture is still often referred to uncritically as the birth of nanotechnology.

But the history of effective approaches to instituting a nanotechnology is strongly related to the development of nanomaterials 8. Two milestones are relevant here: the science of colloids and molecular engineering, the first from the mid-19th century and the second from the mid-20th century. XX. Starting with the science of colloids, it is worth remembering that colloids are systems in which one or more components have dimensions within the range of 1 nm to 1 µm. In other words: basically nanoparticle systems. A part in-An interesting part of this story was constructed by silver nanoparticles, as discussed by Nowack, Krug and Height in the thought-provoking article “120 years of nanosilver history: implications for policy makers” 9. In this work, the authors state and document that silver nanoparticles “they were commercially available 100 years ago, having been used in products with applications as diverse as pigments, photography, wound care, conductive composites, catalysts and germicides”. In that same work, it was raised that already in 1889 the synthesis of colloidal silver had been reported by a method that produced particles with diameters between 7 nm and 9 nm, as well as the first patent with “nansilver”, which dates back to 1954.

The second relevant milestone is two years younger than this pioneering patent in nanotechnology. The MIT (Massachusetts Insitute of Technology) physicist Arthur Von Hippel published in 1956 the article Molecular Engineering, in which he suggests that “instead of taking prefabricated materials and trying to find engineering applications for them, consistent with their macroscopic properties , we can construct materials from atoms and molecules for a desired end... [the engineer] can play chess with elementary particles according to pre-established rules, until new engineering solutions become apparent” . It is the very definition of nanotechnology, but Von Hippel goes further, proposing its institutional realization: “what we are trying to create as an answer to this situation are truly interdepartmental laboratories (that is, interdisciplinary, a word still little used at the time) for the molecular science and engineering”. This proposal by Von Hippel is part of what was suggestively called by Hyungsub Cchoi and Cyrus Mody “The long history of molecular electronics: the microelectronic origin of nanotechnology” 10.

4. Some nanomaterials and their properties

The example of the history of silver nanoparticles and their uses is an interesting case to discuss obtaining and some properties of nanomaterials. The action of a given amount of material is increased if it is divided into smaller and smaller portions, increasing the ratio between the area and volume of the material. A cube with an edge of 1 cm has a volume of 1 cm3 and an area of 6 cm2. If the material that constitutes the cube is divided into small cubes with an edge of 100 nm, we will have the same total volume, but the total area of exposure, adding all the nanocubes, will be 60 m2, which represents an area of contact with the environment of the same amount of material 100,000 times larger. Nanoparticles 10 nm in diameter have 30% of their atoms on the surface! If this material is a germicide like silver, for example, when divided into nanoparticles, the action will be much more effective than the same amount of material distributed in larger particles. Physical processes and chemical reactions become faster and more efficient. In addition, phenomena that do not occur in larger portions can pass sar to happen in nano dimensions, called emergent phenomena. Some of these emergent phenomena originate in the manifestation of quantum phenomena in these dimensions, but this aspect, often overvalued, will be left aside in this article. Gold, for example, when divided into nanoparticles, changes color (the color change of materials in the form of nanoparticles is sometimes due to quantum effects, but often it is a purely classical phenomenon) and binds chemically with biological materials. This ability to bond chemically, mainly to organic compounds, constitutes one of the key elements in the nanotechnology of materials, the so-called functionalization of nanoparticles.

A nanoparticle can be functionalized when it is attached to a molecule that performs a certain function, such as recognizing other molecules. A proposal that has become known is the functionalization of iron nanoparticles with biocompatible molecules that recognize cancerous tissues, causing iron nanoparticles placed inside the body to bind to these tissues, allowing diagnostic and therapeutic actions in the presence of fields magnetic 11.

Nanoparticles are generally obtained by chemical synthesis, and some important examples were initially obtained almost by accident. This is the case of fullerenes, molecules formed by a few dozen carbon atoms forming cages, the best known being the one in the shape of a soccer ball made up of 60 carbon atoms. These molecules were identified for the first time in 1985 in an experiment involving the combustion of a graphite surface by means of an intense laser beam. A review of this history, as well as a description of fullerene applications, can be appreciated in a recent review article 12. These molecules are one of the great icons of nanotechnology and nanomaterials, the pretext of an enormous initial expectation that, over more than twenty years, turned into a better known and still very interesting panorama.

One of the first steps was the development of an efficient synthesis method for producing "macroscopic quantities" of these molecules. Most application proposals are still speculative, including improvement of photovoltaic cells and germicidal action, such as the veteran silver nanoparticles. Several of these applications involve the functionalization of these fullerenes.

An illustrious relative of fullerenes are carbon nanotubes, layers of carbon atoms rolled up in tubes with diameters of a few nanometers, discovered in 1991 13. The possibility of applications for these nanotubes is more promising and their production is more intense, with several products already available on the market. In fact, the role of carbon nanotubes can be followed, unlike other promises of nanomaterials, by following the publicity material of companies for products based on nanotubes. The sequence of discoveries of allotropic varieties of carbon was again disturbed for the synthesis of sheets of carbon atoms, called graphene, Andre Geim and Konstantin Novoselov in 2004, who received the Nobel Prize in Physics in 2010 for this discovery 14. This, at the moment, is the big new bet, with prototypes of touch screens, battery electrodes, electronic devices and solar cells already available.

Graphene is a layer only one atom thick, in which the carbon atoms are arranged as if they formed a hive composed of hexagons, which led to a supplementation of the definition of nanomaterials by the European Commission: "derogating from the text above, fullerenes , graphene flakes and carbon nanotubes, with one or more external dimensions less than 1 nm should be considered nanomaterials". This layer of atoms has some surprising properties, such as excellent electrical conductivity. Its synthesis is relatively simple, and can be obtained by purely mechanical means of exfoliation of these layers, from ultrapure graphite. Nanolithography techniques, developed in the context of the microelectronics industry, make it possible to "design" different devices and circuits on these sheets of carbon atoms. It is already possible to speak of an emerging market for graphene with production centers in various regions of the world, as can be seen in searches on the web 15. Despite this promising scenario, it is important to emphasize that it is not yet clear how much this material will expand. impose on applications that in fact dominate the market, as the reviews of this market, mentioned at the beginning of this article, prudently suggest. On the other hand, it is also interesting to observe the mechanisms that motivate research in view of an intrinsic limit of graphene: the absence of a gap of allowed energies, a fundamental characteristic of semiconductor materials, cornerstones of nanoelectronics. Thus, the use of graphene in electronic devices is only possible in more complex and costly arrangements. The solution is to try to generate this gap through geometric structuring, exploring quantum effects or, alternatively, to look for a new material that has the same characteristics as graphene, plus this fundamental property of semiconductors: the energy gap. And such material exists; this is molybdenum disulphide, which can be present in these layers one atom thick and is intrinsically a semiconductor. In 2011, a research group presented a transistor based on a molybdenum 16 disulfide monolayer.

5. The interface between nanomaterial's and the environment

The purpose of this article is not to exhaust a vast topic such as the development of nanomaterials, but rather to show some examples that expose certain fundamental aspects to understand this area of research, development and innovation. The examples highlight, in particular, the importance of the chemical synthesis of these materials, often overlooked in view of the emphasis given to tools for direct manipulation of matter on an atomic scale, such as scanning test microscopes, but which do not “produce” nanomaterials. . The functionalization of nanoparticles is an important tool for self-assembly of nanostructures, one of the “bottom up” strategies, while the miniaturization of “conventional nanoelectronics” is a “top-down” strategy. Details on these strategies can be found in books 1.

It is important to return once more to the European Commission regarding nanomaterials, which defines them according to the presence of particles with dimensions between 1 nm and 100 nm. This is certainly an arbitrary definition, as particles with a characteristic size of, for example, 200 nm can also be considered nano. And in the scientific literature, in fact, systems with dimensions greater than 100 nm are often named nano, overlapping with other nomenclatures such as submicron or, in the case of particles, with the more traditional name of colloidal particles. , dating back to the 19th century. For the scientific community, such ambiguity usually has no greater consequences than relativizing the objectivity of scientific discourse. However, regulatory frameworks, such as the European Commission's definition, mean that products can escape restrictions. In this context, it is worth mentioning the proposal formulated in a scientific article from 2009 that the fundamental criterion for defining nanoparticles in environmental, health and safety regulations is not size, but “new (emerging) size-dependent properties” . According to the authors of this work, according to the proposed criterion, only those with dimensions smaller than 30 nm should be considered nanoparticles (that is, they would need an additional regulation to the existing regulations for materials in macroscopic volumes) 17.

This discussion about a definition of nanomaterials based on quantitative criteria of size and composition is a central issue, which also appears in the European Commission's definition. The upper limit of 100 nm seems to be safe above 30 nm, a dimension identified as really problematic, but the issue of composition remains, which is safeguarded by the end of the article: “in specific cases and justified by environmental concerns, health, security or competitiveness, the 50% threshold in the size distribution can be replaced by a threshold between 1% and 50%”. This safeguard is important, as it allows for specific regulations for products that contain nanomaterials.

The subject is literally vital, as nanoparticles, being more reactive than their macroscopic counterpoints, present a toxic potential that needs to be approached differently from traditional protocols. Furthermore, nanoparticles can, in the case of human health, cross any natural barriers within the human body 18. This vast subject of nanotoxicity should be the subject of other articles in this issue, but some aspects deserve a brief consideration here. In the article “Cytotoxicity of Nanoparticles”, published in the journal “Small” in 2008 19, the authors evaluate the action on cells of several groups of nanomaterials: fullerenes, carbon nanotubes, metallic and semiconductor nanoparticles. The conclusions are cautious, acknowledging that “cytotoxicity induced by nanoparticles is reported by different studies”, but that “in vitro tests may not be clinically relevant”. They point to the question of the dose and consider that “it would be premature to declare that nanoparticles are inherently dangerous” and that research needs to continue.

A much more recent study, published in 2013, also covering several types of nanoparticles, better outlines the comparison between test protocols, also drawing attention not to extrapolate results from in vitro tests and to the diversity of actions of different nanoparticles on different types of cells. In any case, research needs to be deepened, but it safely states that the accurate assessment of the bioactivity of manufactured nanomaterials requires multiple and specific tests to avoid false negatives 20.

6. Conclusion

When writing a popularization book on nanotechnology in 2009 1 also calling attention to its risks, the scenario was uncertain about the extent of these risks. Despite systematic advances in the research of these risks, there is still a long way to go, citing the conclusions of the aforementioned article, that is, the panorama remains open. However, it is important to note that health, environmental and safety impacts of nanomaterials were incorporated into the discussion agenda. And this is a phenomenon that is still growing and quite recent.

Scientific activity in nanotechnology continues to grow: when searching for scientific articles in the "Web of Science" database with the word "nanoparticles" as a topic, I obtained more than 220,000 records in July 2013, 37,000 of which in just 2012. The oldest record is from 1981, but the scientific production associated with this keyword began to grow significantly from 1992 onwards. Of this huge set of scientific works, only 1,885 appear under the classification of toxicology and 4,666 are related to environmental sciences. It is interesting to note that works on nanoparticles with these approaches began to be published with more intensity only from the period between 2004 and 2006, more than a decade after the beginning of the "boom" of research in nanoparticles.

In addition, or despite this, at the same time, awareness of the safety and toxicity of nanomaterials is greater than it was a few years ago. A quick search shows that English entries on nanomaterials (nanoparticles, nanotubes and fullerenes) on Wikipedia now incorporate sections on safety and toxicity. The nanotechnology entry has sections on regulation and environmental and health issues. Some milestones that led to increased concern about safety in the use of nanotechnologies are described in the "white-paper on nano safety" (http://www.nano--safety.info/) and coincide with the growth of the literature science in the area in the middle of the last decade.

Finally, I would like to remind you once again that looking more carefully at history can be important. Not only has the history of nanotechnology in general been poorly told or divulged, often omitting its distant roots, but that of nanotoxicology in particular has also been neglected has not received due attention. Toxicological studies of silver nanoparticles date back to the 1930s 9; thus, the identification of the need for adequate protocols to evaluate nanomaterials in opposition to macroscopic quantities is quite old and, apparently, forgotten for a long time. It is a case of what is called in sociology of science the concept of multiple discoveries 21, which addresses the hypothesis that a scientific discovery in general is not a single phenomenon, but a multiple one, carried out independently by different scientists, simultaneously or even at different times, when "rediscoverers" are unaware of precursor scientific information. Usually addressed as a problem internal to the scientific community about the recognition of intellectual priority, here it is clearly a problem with wider social effects.

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