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Nanomaterials and the interface between nanotechnology and environment

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ABSTRACT

Nanomaterials are the main products of nanotechnology. In this paper we describe some of these nanomaterials, particularly Carbon based systems, their properties, manipulation strategies and applications. History of nanoparticles, as well as the complexity in defining nanomaterials, necessary for regulation and assessment of impacts on society, are also addressed.

KEYWORDS: Nanomaterials; Nanoparticles; Nanotoxicity; History of Nanotechnology

Introduction

Nanotechnology is one of the emerging technologies of the recent decades, along with biotechnology and information technology, and more recently, synthetic biology. Accustomed to a world divided into disciplines and professions that have hardly changed in essence over generations, the sudden advent of a new science or technology causes expectations of all types and sizes; these expectations must also be understood. These discussions raise expectations that can modify the course of development of new technologies and reassess the relationship between society and activities based on older technologies. Apart from the more technical aspects that are the focus of this study, a better understanding of the complexity surrounding a new technology is already an important legacy of nanotechnology[1].

The initially inflated expectations were market forecasts for nanotechnologies, which at the beginning of the twenty-first century were predicting values above $1 trillion for 2015[2]. These figures exclude the semiconductor market, which is a special case because microelectronics, with the continuous reduction of devices in chips, uses components measuring only 22 nm. Returning to nanotechnology and excluding semiconductors, during the last several years, more realistic reviews decrease these numbers to $49 billion in 2017 with nanomaterials being responsible for 37 of the 49 billion, according to the NANO31E research report published by the BBC in September 2012[3].

Therefore, nanomaterials continue to dominate the nanotechnology agenda. To discuss their impact, we start with a definition of nanomaterials recently (2011) agreed by the European Commission[4]:

“A natural, incidental or manufactured material containing particles in an unbound state, as an aggregate, or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1–100 nm.

In specific cases and where warranted by concerns for the environment, health, safety or competitiveness, the threshold size distribution of 50% may be replaced by a value between 1% and 50%.”

The details of this definition surround the whole discussion, and this will be briefly discussed below.

Natural, incidental, and manufactured nanomaterials

Nanomaterials consist of particles or clusters with a size distribution showing a large fraction of particles with one or more dimensions between 1 (1 nm = 1 billionth of a meter) and 100 nm. It is important to note that nanotechnology, i.e., a technology that manipulates matter at this controlled scale, directly relates only to manufactured nanomaterials, designed to have relevant structures for their properties at the nanometer scale. On the other hand, the environment interacts with natural nanoparticles such as soot, volcanic ash, or the webs of some spider species. Human society has also contributed to incidental nanoparticles that are produced as the unintended byproducts of other processes such as those released by car exhaust. Thus, it is important to mention that the development of synthesis, characterization, and control of manufactured nanoparticles also improves the estimate of the presence and impact of natural and incidental nanoparticles.

This controlled manipulation at the nanoscale level probes properties and features that could not be otherwise obtained. This is the aspect that validates nanotechnology as an area of knowledge beyond the pure definition of the object gained by its dimensions.

In the definition given by the European Commission, it is mentioned that the particles or their agglomerates need to have one or more dimensions between 1 and 100 nm, thus including not only particles themselves but also wires with nanometric diameters, films with thicknesses in that range, or surfaces with structures or pores with such dimensions. Therefore, colored glass can be considered a nanomaterial because of the presence of copper nanoparticles, which were already produced in the Bronze Age; so can modern microprocessors of this century, primarily silicon films with structures on a scale of a few tens of nanometers, which include so-called microcircuits.

A bit of history

The story of some emerging technologies has been poorly described for some time, and the same applies to nanotechnology[5]. Some marks are artificially created such as the famous physicist Richard Feynman’s lecture of 1959 at Caltech, entitled “There is plenty of room in the bottom.” It is worth reading the transcript, and in fact, it seems a premonition of genius, but its real influence is disputed. Forgotten for over twenty years, it began to be mentioned as an *a posteriori* validation of a knowledge area still under construction, as discussed by several authors such as Chris Toumey[6] and Richard Jones[7]. Despite this critical review, Feynman’s lecture is still often uncritically cited as the birth of nanotechnology.

Indeed, the history of effective approaches to establish nanotechnology is strongly related to the development of nanomaterials[8]. Two points are relevant here the science of colloids and molecular engineering, the first in the mid-nineteenth century and the second in mid-twentieth century. Starting with the science of colloids, it is worth remembering that colloids are systems in which one or more components have dimensions from 1 nm to 1 μm. This basically denotes nanoparticle systems. An interesting part of this story involves silver nanoparticles, as discussed by Nowack, Krug, and Height in their provocative study “120 years of nanosilver history: implications for policy makers”[9]. In this paper, the authors argue and document that silver nanoparticles “were already commercially available for 100 years, and used in products with diverse applications such as pigments, photography, treatment of wounds, composite conductors, catalysts, and germicides.” This study reported the synthesis of colloidal silver back in 1889 through a method producing particles with diameters between 7 and 9 nm, and the first "nanosilver" patent dated back to 1954.

The second important historical mark was two years before the nanotechnology patent. A physicist at Massachusetts Institute of Technology, Arthur Von Hippel, published the article *Molecular Engineering* in 1956 suggesting "instead of using prefabricated materials and trying to find engineering applications for them, consistent with their macroscopic properties, we can build materials from atoms and molecules to a desired end... [engineers] can play chess with elementary particles according to predefined rules, until new engineering solutions become apparent." It is the very definition of nanotechnology, and Von Hippel even proposes their institutional accomplishment: "What we are trying to create as an answer to this situation is truly interdepartmental laboratories, i.e., interdisciplinary, still a rarely used word at the time of science and molecular engineering." This proposal by Von Hippel is a part of what was suggestively called by Hyungsub Cchoi and Cyrus Mody as "The long history of molecular electronics: the microelectronics origin of nanotechnology"[10].

Examples of Nanomaterials and their Properties

In the example of the history of silver nanoparticles and their use, it is interesting to discuss some applications and properties of nanomaterials. The reactivity of a given quantity of material increases after being divided into increasingly small portions, thus increasing the ratio between the area and volume of the material. A cube with a 1 cm edge has a volume of 1 cm^3 and an area of 6 cm^2. If the material constituting the cube is divided into small cubes with 100 nm edges, we obtain the same total volume; however, the total exposed area of all nanocubes will be 60 m^2, which represents a contact area with the environment of 100 thousand times greater for the same quantity of material. Nanoparticles with a diameter of 10 nm have 30% of their atoms at the surface.

If such a material is a germicide like silver, for example, when divided into nanoparticles, the reactivity will be more effective than for the same amount of material divided into larger particles. Physical processes and chemical reactions become faster and more efficient. Moreover, phenomena that do not occur at larger scales can occur at nanoscale dimensions, which are known as emergent phenomena. Some of these emerging phenomena originate as the result of quantum effects at these dimensions; however, this aspect is not considered in this study. For example, gold changes color if divided into nanoparticles. The color change of materials in nanoparticle form is sometimes because of quantum effects; however, it is often a purely classical phenomenon and chemically bonds with biological materials. This chemical bonding capability, especially with organic compounds, is one of the key elements of nanotechnology materials, the so-called functionalization of nanoparticles.

A nanoparticle can be functionalized if it is attached to a molecule that performs a particular function such as recognizing other molecules. One known proposal is the functionalization of iron nanoparticles with biocompatible molecules that recognize cancerous tissues through magnetic induction of iron nanoparticles placed inside the body that bind to these tissues and facilitate diagnostic and therapeutic actions in the presence of magnetic fields[11].

In general, nanoparticles are obtained by chemical synthesis, and some important examples were initially discovered almost by accident. This is the case of fullerene molecules consisting of a few tens of carbon atoms forming cages. The soccer ball-shaped fullerene is well known and composed of 60 carbon atoms. These molecules were first identified 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 applications of fullerenes can be assessed in a recent study[12]. These molecules are one of the great icons of nanotechnology and nanomaterials, leading to a significant initial expectation that, over more than twenty years, has become a well-known outlook and still very interesting.

A first step was the development of an efficient synthesis method for producing these molecules in "macroscopic quantities." Most of the application proposals are still speculative, including the improvement in photovoltaic cells and germicides, such as the well-established silver nanoparticles. Many of these applications involve the functionalization of these fullerenes.

A distinguished relative of fullerenes is carbon nanotubes, layers of carbon atoms rolled into tubes having diameters of a few nanometers, discovered in 1991[13]. The application possibility of these nanotubes is more promising, and their production is more robust with various products already available in markets. Indeed, the role of carbon nanotubes can be differently tracked from other promised nanomaterials by monitoring the distribution of commercial applications based on nanotubes. The sequential discovery of allotropic varieties of carbon materials was again affected by the synthesis of carbon atom leaves called graphene by Andre Geim and Konstantin Novoselov in 2004, who received the 2010 Nobel Prize in Physics for this discovery[14]. This is the big new achievement, with prototype "touch screens," battery electrodes, electronic devices, and solar cells already available.

Graphene is a layer with a thickness of only one atom, where the carbon atoms are placed in a honeycomb arrangement composed of hexagons, which led to a more complete definition of nanomaterials by the European Commission: "derogating from the above, fullerenes, graphene flakes, and carbon nanotubes having one or more external dimensions below 1 nm should be considered as nanomaterials." This layer of atoms shows some spectacular properties such as an excellent electrical conductivity. Its synthesis is relatively simple and can be achieved by purely mechanical means by peeling these layers from ultra-pure graphite. The developed nanolithography techniques in the context of the microelectronics industry allow "drawing" diverse circuits in these carbon atom sheets.

One can already see an emerging market for graphene with production centers in various regions of the world, as can be seen while searching the web[15]. Despite this promising scenario, it is important to note that it is unclear how this material will be used in applications that actually dominate the market such as the market review mentioned earlier in this study, and this suggests prudence. Moreover, it is interesting to observe the research motivation mechanisms in view of an intrinsic limit for graphene: the absence of a gap allowed energy bands, which is a fundamental characteristic of semiconductor materials, the cornerstone of nanoelectronics.

Therefore, the use of graphene in electronic devices is only possible in more complex and costly arrangements. The solution is to generate these gaps by means of geometric structuring, exploiting quantum effects, or seeking a new material with the same characteristics as graphene, along with a fundamental property of semiconductors: the energy gaps. Such materials in fact exist, such as molybdenum disulfide, which can be present in these one-atom-thick layers and is inherently a semiconductor. In 2011, a research group showed a transistor based on a monolayer of molybdenum disulfide[16].

The interface between the environment and nanomaterials

This study does not explore a broad topic such as the development of nanomaterials, but instead consider some examples that show certain fundamental aspects to understand this research area: development and innovation. In particular, examples highlight the importance of the chemical synthesis of these materials often forgotten in the shadow of the prominence given to the direct manipulation of matter at the atomic scale, such as scanning microscopes that do not “produce” nanomaterials. The functionalization of nanoparticles is an important tool for the self-arrangement of nanostructures, a “bottom-up” strategy, while the miniaturization of “conventional nanoelectronics” is a “top-down” strategy. Details of these strategies can be found in references[1].

It is important to return again to the European Commission definition regarding nanomaterials, which defines them as a function of the presence of particles with dimensions between 1 and 100 nm. Certainly, this is an arbitrary definition because particles having a characteristic size (for example, 200 nm) can also be regarded as nano. In addition, in the scientific literature, systems larger than 100 nm are often considered as nano, overlapping with other nomenclatures such as submicron, or in the case of particles, the more traditionally named colloidal particles, which is dated back to the nineteenth century. To the scientific community, such ambiguity usually does not result in greater consequences than to relativize the objectivity of the scientific discourse.

However, regulatory frameworks such as the definition given by the European Commission mean that products can circumvent restrictions. In this context, it is worth mentioning the proposal that the fundamental criterion to set nanoparticles in environmental regulations, health, and safety is not the size but the “new (emerging) size-dependent properties” published in a scientific study in 2009. According to the authors of this study, following the proposed criteria, nanoparticles should be considered (i.e., for macroscopic volume regulations, these would need additional regulations in addition to existing materials) as only those with dimensions less than 30 nm[17].

This discussion about the definition of nanomaterials based on quantitative criteria of size and composition is a central issue, which also appears in the definition given by the European Commission. The upper limit of 100 nm appears to be safe above 30 nm, in which size is identified as problematic; there remains the question of the composition, which is assured by the end of the article: “in special cases, justified by environmental concerns, health, safety, or competitiveness cases, the 50% threshold size distribution can be replaced by a threshold between 1% and 50%.” This safeguard is important because it allows specific regulations for products containing nanomaterials.

The subject is literally vital because nanoparticles are more reactive than their macroscopic counterpoints and show a toxic potential that needs to be addressed in a different way from traditional protocols. Furthermore, regarding human health, nanoparticles can cross any natural barriers inside the human body[18]. This vast subject of nanotoxicity should be the subject of other studies, and some aspects deserve a brief consideration here. In the study “Cytotoxicity of Nanoparticles,” published in 2008 in the journal “Small”[19], the authors evaluate the action on cells of various groups of nanomaterials: fullerenes, carbon nanotubes, metal nanoparticles, and semiconductors. The conclusions are cautious, recognizing that “nanoparticles-induced cytotoxicity is reported by different studies,” and “*in vitro* tests may not be relevant clinically.” They point to the dosage question and consider that “it would be premature to declare that nanoparticles are inherently dangerous,” and more research is needed.

A more recent study, published in 2013, covering several types of nanoparticles better delineates the comparison between test protocols and gains attention to not extrapolate *in vitro* results and the diversity of actions of different nanoparticles on different cell types. In any case, more research is needed, although they safely demonstrate that the accurate assessment of bioactivity of manufactured nanomaterials requires multiple and specific tests to avoid false negatives[20].

A non-conclusion

After writing an introductory book on nanotechnology in 2009[1], while also drawing attention to its risks, the scenario about the extent of these risks was uncertain. Despite the systematic advances in research of these risks, the conclusions of the study mentioned the point that there is still a long way to go, i.e., the outlook remains open. However, it is important to note that impacts of nanomaterials on health, environment, and safety have been incorporated into discussions, and this is still a growing and very recent phenomenon.

Scientific activity in nanotechnology continues to grow. While seeking scientific studies in the “Web of Science” database using the word “nanoparticles” as a search term, I received over 220 thousand hits in July 2013, and 37.000 in 2012. The earliest record is dated from 1981; however, the scientific literature associated with this key word began to significantly grow in 1992 and after. From this enormous body of scientific study, only 1.885 results are shown under the classification of toxicology, and 4.666 are related to the environmental sciences. Interestingly, studies on nanoparticles with these approaches began to be published with more intensity only between 2004 and 2006, more than a decade after the start of the "boom" in the research on nanoparticles.

Moreover, awareness regarding the safety and toxicity of nanomaterials is greater than a few years ago. A quick research shows that English entries on nanomaterials (nanoparticles, nanotubes, and fullerenes) in Wikipedia now incorporate sections about safety and toxicity. The nanotechnology entry features sections about regulation and environmental and health issues. Some milestones that led to increasing concerns about security in the use of nanotechnologies are described in the "white paper on nanosafety" (http://www.nano-safety.info/) and coincide with the increase in specific scientific literature in the middle of the last decade.

Finally, I again remind that it may be important to more carefully address history. Not only has the nanotechnological history been "poorly explained" or disclosed, as is often the case, omitting their origins such as toxicology, in particular, also has not received due attention. Toxicological studies of silver nanoparticles date back to the 1930s[9]; hence, the identification of the need for appropriate mechanisms to assess nanomaterials, as opposed to macroscopic quantities, is very old and seemingly forgotten over time. It is a case called, in scientific sociology, the concept of multiple discoveries[21], which states the hypothesis that a scientific discovery, in general, is not a single phenomenon but involves multiple steps independently performed by different scientists, simultaneously or even at different times, when "rediscoverers" are unaware of previous scientific information. This is usually regarded as a problem internal to the scientific community regarding the recognition of intellectual priority and is clearly a problem with wider social ramifications.

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