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NANOMATERIALS: CLASSIFICATION, ORIGINS, HISTORY, TOXICITY, AND REGULATION

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ABSTRACT

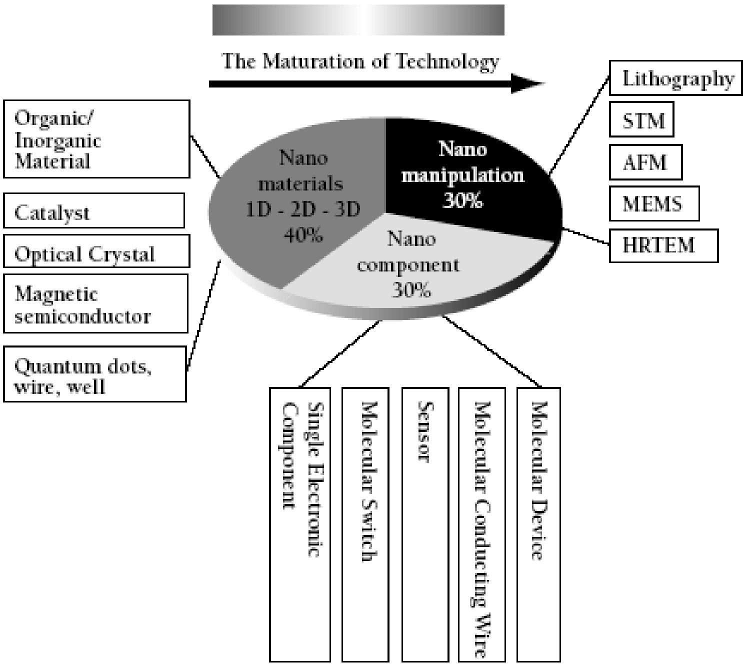
Synthesis, characterization, investigation, and utilization of nanostructured materials (NSMs) are the main topics of nanoscience. These materials have at least one dimension that is in the nanoscale range. A nanometer, or 10^{-9}m, is one billionth of a meter. A nanometer is about the length of ten hydrogen atoms or five silicon atoms arranged in a straight line.

In recent years, there has been a great deal of interest in the processing, structure, and properties of materials whose grain sizes range from tens to many hundreds of nanometers. The ability to pattern and describe materials at the nanoscale length scale is driving a revolution in materials science and engineering. Innovative materials possessing exceptional electrical, optical, magnetic, and mechanical characteristics are being created at a swift pace for applications in bioengineering, information technology, energy, and the environment.

The essay provides a summary of the origins of NPs and NSMs, both natural and manufactured, as well as their harmful effects on tissue. It also covers the history and classifications of NMs. Also covered are the laws that various nations have put in place to lessen the risks involved.

1.0 Introduction

The ability to accurately construct materials at the nanoscale was originally referred to as "nanotechnology" in 1974 by the late Norio Taniguchi. This is indeed how the term is currently used; it now refers to the design, characterization, manufacture, and application of materials, with the scope having expanded to include devices and systems in addition to materials. Hence, the design and manufacture of materials, tools, and systems with control at nanoscale dimensions is referred to as nanotechnology. Thus, size and control are the fundamentals of nanotechnology. Because of the diversity of applications, figure (1), the plural term 'nanotechnologies' is preferred by some; nevertheless, they all share the common feature of control at the nanometre scale (Ramsden, 2005, P.3).



Source: Data provided by Prof. Chung-Yuan Mou, Department of Chemistry, National Taiwan University.

Figure 1. Nanotechnologies: Areas of application and level of maturity

2.0 Nanoscience

There is occasionally a distinction drawn between nanotechnology and nanoscience, with the latter concentrating on the study and observation of phenomena at the nanoscale and methods of modifying matter at that size, where numerous properties of matter are different from those known at higher scales. Nonetheless, the distinction is not really significant because the activity of a nanotechnologist will inevitably require them to examine, analyse, and engage with matter. The term "nanoscience" alludes to a strong body of theory that could serve as the foundation for a technology; this theory is still in its infancy, and both nanoscientists and nanotechnologists are likely to contribute to it.

The word "nanotechnology" will be used broadly in this study (Ramsden, 2005, P. 3). In numerous application fields, nanoparticles (NPs) and nanostructured materials (NSMs) are a rapidly expanding techno-economic sector and an active research subject. Because their tunable physicochemical properties—such as melting point, wettability, electrical and thermal conductivity, catalytic activity, light absorption, and scattering—allow them to perform better than their bulk counterparts, NPs and NSMs have become more and more important in technological advancements (Vanadam, et al., 2018, P.1050).

2.1 Classification of Nanomaterials

Four material-based categories can be used to classify the majority of contemporary NPs and NSMs (references to recent reviews on these various types of NMs are provided):

(i) Nanomaterials based on carbon: These NMs often consist of carbon and have geometries like spheres, ellipsoids, and hollow tubes. The category of carbon-based NMs includes fullerenes (C60), carbon nanotubes (CNTs), carbon nanofibers, carbon black, graphene (Gr), and carbon onions. With the exception of carbon black, the main production techniques for these carbon-based compounds include chemical vapour deposition (CVD), arc discharge, and laser ablation. (P.189, Kumar & Kumbhat, 2016).

(ii) Inorganic-based nanomaterials (NMs): These comprise NSMs and NPs made of metal and metal oxide. Metals like Au or Ag NPs, metal oxides like TiO2 and ZnO NPs, and semiconductors like silicon and ceramics can all be created with these NMs.

(iii) Organic-based nanomaterials: These comprise nanomaterials derived primarily from organic matter; they do not include NMs derived from carbon or inorganic substances. In order to convert organic NMs into desired structures as dendrimers, micelles, liposomes, and polymer NPs, non-covalent (weak) interactions are used for the self-assembly and molecular design.

(iv) Nanomaterials based on composites: Composite nanostructures (NMs) are single-phase, multiphase nanoparticles and NSMs that can be joined with other nanoparticles, larger, bulkier materials (like hybrid nanofibers), or more intricate structures (like metal-organic frameworks). The composites can consist of any mix of metal, ceramic, or polymer bulk components with metal, organic, or carbon-based nanometer particles. As shown in Figure (2), NMs are synthesized in various morphologies based on the qualities needed for the intended use (Vanadam, et al., 2018, P.1051).

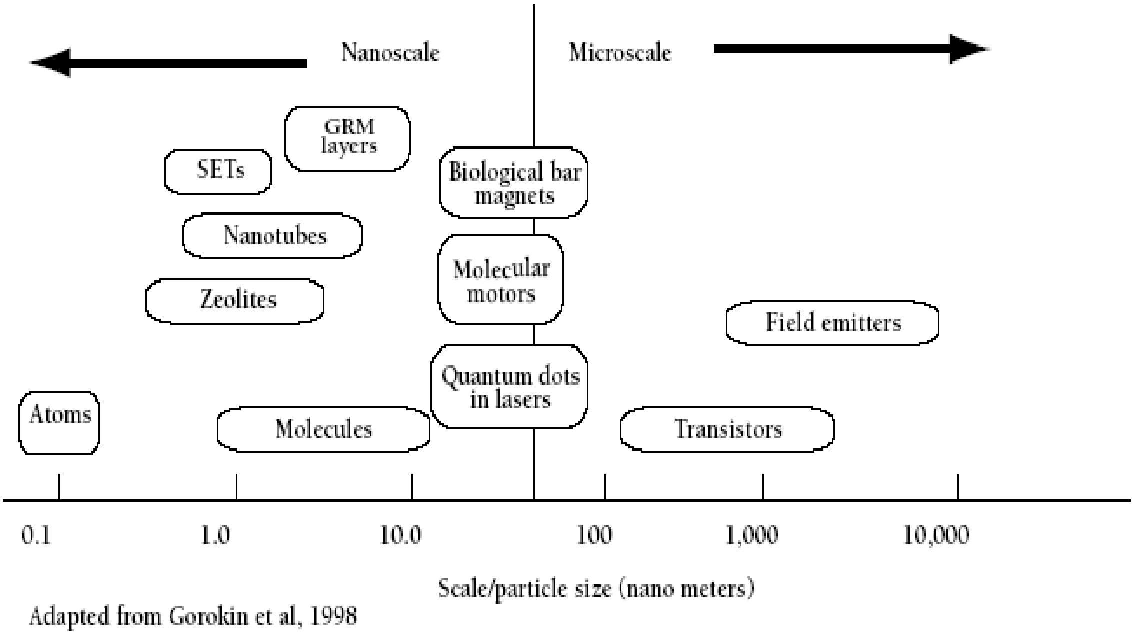


Figure 2. Scale of some nano-scale products and applications

2.2 Nanomaterials based on their origin

In addition to categories based on dimensions and materials, NPs and NSMs can also be categorized as natural or synthetic according to where they came from:

(i) Natural nanomaterials are created in the environment by biological species or by humans. Natural sources can easily be used to create artificial surfaces with unique micro- and nanoscale templates and features for technological applications. Regardless of human activity, naturally occurring NMs can be found in all of the Earth's spheres, including the hydrosphere, atmosphere, lithosphere, and biosphere. Earth is made up of naturally occurring new materials (NMs) that are found in all of the planet's spheres, including the biosphere, which is made up of microorganisms and higher organisms like humans, the hydrosphere, which is made up of lakes, rivers, seas, and groundwater as well as hydrothermal vents, and the lithosphere, which is made up of rocks, soils, magma, and lava at different stages of evolution (Hochella, et al., 2015, P. 2).

(ii) Synthetic (designed) nanomaterials can be created through physical, chemical, biological, or hybrid synthesis processes, mechanical grinding, engine exhaust, and smoke. The issue of risk assessment techniques has come up recently due to the surge in the production and subsequent release of engineered nanoparticles (NMs) as well as their use in consumer goods and industrial settings. When predicting the behaviour and eventual fate of manufactured nanoparticles (NMs) in diverse environmental environments, these risk assessment techniques are very beneficial. The main question with designed NMs is whether their behaviour can be predicted using the knowledge that is now available, or if they behave differently from natural NMs in relation to their surroundings. At the moment, several sources pertaining to prospective uses are employed in the creation of tailored nanomedicines (Wagner et al., 2014, P. 53).

3.0 History and development of nanomaterials

More than 4,500 years ago, humans began to take advantage of the reinforcement that natural asbestos nanofibers might provide for ceramic matrixes (Heiligtage & Miederberger, 2013, P. 16). More than 4,000 years ago, the Ancient Egyptians used NMs in a synthetic chemical procedure to create PbS NPs with a diameter of about 5 nm for hair dye. Similarly, in the third century BC, the Egyptians created and employed "Egyptian blue," the first synthetic pigment, by sintered combining quartz and glass particles that were as small as nanometers (Johnson, et al., 2013, P.135).

Egyptian blue is a complex combination of SiO2 and CaCuSi4O10 (both in glass and quartz). Archaeological research has revealed the widespread usage of Egyptian blue as a decorative material in several ancient Roman Empire countries, including Egypt, Mesopotamia, and Greece. The metallic nanoparticle era began when Egyptians and Mesopotamians began employing metals to make glass in the 14th and 13th centuries BC, which can be considered the beginning of the synthesis of metallic NPs using chemical means (Schaming & Remita, 2015, P.17).

These substances might be the first synthetic NMs used in a useful application. Red glass tinted by surface plasmon excitation of Cu NPs has been discovered at Frattesina di Rovigo, Italy, dating back to the late Bronze Age (1200–1000 BC) (Artioli, et al., 2009, P.81). Similarly, it has been observed that Cu NPs and cuprous oxide (cuprite Cu2O) are present in Celtic red enamels that date back to the 400–100 BC period. Yet, the most well-known instance of the use of metallic NPs in antiquity is found in a Roman glass work piece. The Lycurgus Cups are a type of dichroic glass from the fourth century that changes colour depending on the direction of light. It shows green when light is coming from the front and red when light is coming from the back. According to recent research, the Lycurgus Cups have roughly 10% Cu and Ag–Au alloy NPs in a ratio of 7:3. (Freestone, et al., 2009, P.40). Later, colloidal Au and Ag NPs were added to create the red and yellow stained glass prevalent in churches built during the Middle Ages. Mesopotamians began decorating their glazed ceramics with metallic lusters around the ninth century. Because of the unique Ag and/or Cu NPs that were separated inside the outermost glaze layers, these decorations displayed incredible optical qualities. These ornaments are an example of metal nanoparticles that, in specific reflection settings, exhibit iridescent vivid green and blue colours. A double layer of Ag NPs (5–10 nm) in the outer layer and larger ones (5–20 nm) in the inner layer was discovered by TEM investigation of these ceramics. Interference effects resulted from the continuous distance between the two layers, which was measured to be around 430 nm. Because of the first layer's light scattering, the phase shift is caused by the dispersed light from the second layer. When scattering, this incoming light wavelength-dependent phase shift results in a new wavelength. Later, this method was used all over the world to produce red glass. A comparable method was employed in Japan in the middle of the 1800s to create the well-known Satsuma glass. The ruby hue of the Satsuma glass was enhanced by the absorption qualities of Cu NPs (Nakai, et al., 1999, P.82). Furthermore, the best examples of natural NM utilization since antiquity are clay minerals with a thickness of a few nanometers. According to reports, wool and clothing in Cyprus were bleached with clay as early as 5000 BC.

Enhancing Earth-based astronomical telescopes using adaptive optics and magnetic mirrors composed of ferrofluids that may change form have been the subject of recent research. Commercial solar cells with dye-sensitization capabilities employ TiO2 NPs. An external iPad keyboard driven by light was introduced by Logitech in the summer of 2012, marking the first significant application of dye-sensitized solar cells in a commercial setting. The human serum albumin NP substance AbraxaneTM containing paclitaxel was produced, marketed, and introduced to the pharmaceutical industry in 2005. In 2014, there were about 1814 nanotechnology-based consumer products that are commercially available in over 20 countries (Vance, et al., 2015, P.6).

4.0 Nanotechnology in future

Here, we tackle the subject of why it is so frequently claimed that nanotechnology is revolutionary. Let's look at three different aspects: indirect, direct, and conceptual (Figure 3).

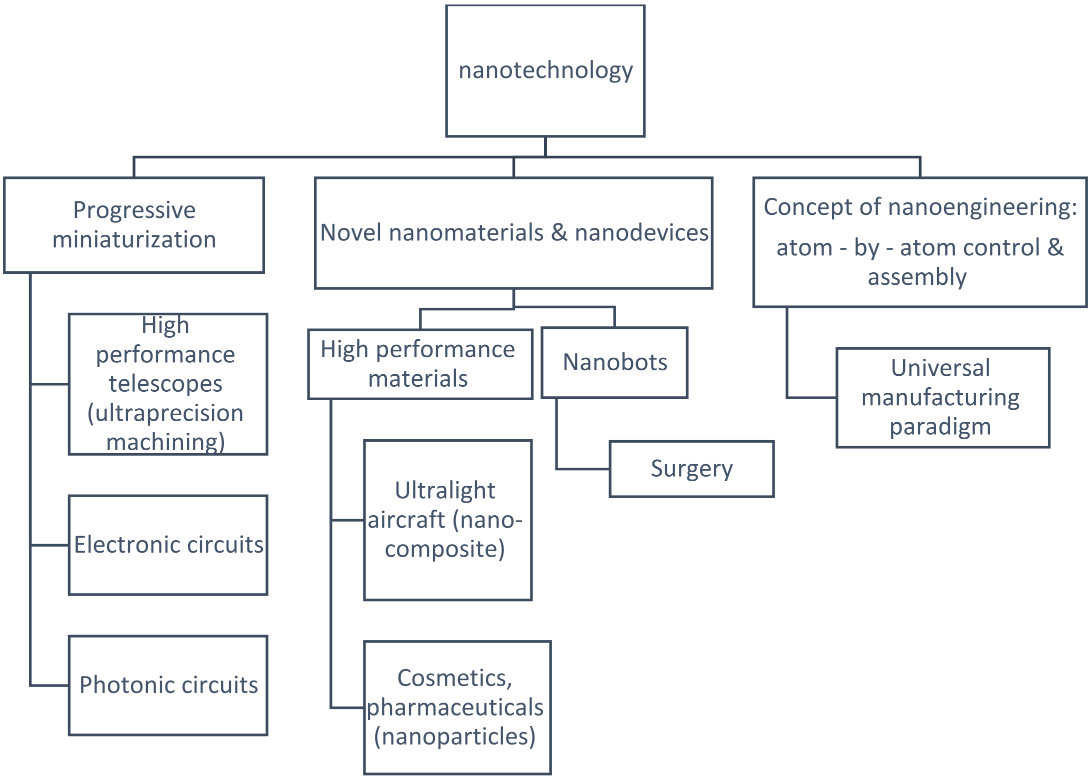


Figure 3. From left to right , the indirect, direct and conceptual branches of nanotechnology , with examples. (Ramsden, 2005, P.8).

By indirect, we mean that current technologies are gradually becoming smaller, which allows them to be used in new contexts. The term "direct" describes the use of new, nanoengineered objects for entirely new uses or to improve the functionality of already-existing materials and processes. Lastly, there is the conceptual side of nanotechnology, where all substances and procedures are viewed from a molecular or even atomic perspective. This is similar to how complex molecules, like proteins, are disassembled into their component amino acids in living systems, which are then utilized as templates to synthesise new proteins. This process has an artificial counterpart that is still mostly unexplored.

Novel integrated manufacturing life cycles are yet to be developed, with a focus on extreme energy efficiency and the elimination of unwanted waste products. Moreover, a fresh perspective on the universe, its structures, and its processes is possible with the conceptual nano-viewpoint (Ramsden, 2005, P. 8).

5.0 The Toxicity of Nanomaterials

Since NPs are created by natural processes, humans are exposed to them. The main factors causing the release of nanoparticles in their original or modified forms into the environment are the production, use, disposal, and waste treatment of items containing Nano products. Human skin often blocks foreign chemicals, although the lungs and digestive system are among the organs that are vulnerable to them. In terms of size, NPs are similar to viruses. The human immunodeficiency virus (HIV), for example, has a diameter of about 100 nm. When breathed, nanoparticles (NPs) can easily enter the bloodstream and travel to many parts of the human body, such as the liver, heart, or blood cells.

It is important to note that the origin of NPs affects their toxicity. Numerous of them appear to be safe, and some even seem to improve health (Gnach, et al., 2015, P. 44). The transfer of active chemical species from organism barriers such the skin, lungs, body tissues, and organs is facilitated by the tiny size of NPs. Thus, depending on their composition, NPs may induce asthma, cancer, irreversible oxidative stress, and damage to organelles. Exposure to nanostructured materials and NPs can have a variety of acute harmful effects, such as the production of reactive oxygen species, denaturation of proteins, disruption of mitochondrial activities, and disruption of phagocytic processes. Common chronic harmful consequences of NPs include uptake by the nucleus, neuronal tissue, reticuloendothelial system, and the production of neoantigens that may cause organ malfunction and hypertrophy. Agglomeration, uniformity, morphology, composition, and dimensionality are the general characteristics of NPs that are used to categorize them. Similar to free NPs, nanostructured thin films or fixed nanoscale circuits found in computer microprocessors have important distinctions that make it easier to classify them according to their applications.

Since there are no restrictions on free NP movement, they can spread more easily across the environment and represent a risk to human health when exposed to it. On the other hand, there is no health danger associated with handling fixed nanoparticles (NPs) properly, where the nanostructured pieces are affixed to a sizable object. In this instance, where their main states are safe, asbestos is an excellent illustration. Subsequently, asbestos mining produces fibrous particles at the nanoscale, which when inhaled by the lungs turn into an airborne aerosol that is carcinogenic and poses a serious health risk. The toxicity of NMs is dependent on multiple parameters, as per toxicological data:

- **Effect of dose and exposure duration:** The quantity of NMs that enter the cells is directly influenced by the exposure duration multiplied by the molar concentration of NPs in the surrounding media. Aggregation and concentration effect: The toxicity of NPs at various concentrations has been the subject of numerous conflicting reports. Aggregation is encouraged by increasing the NP concentration. Since the majority of NP aggregates are micrometer in size, a sizable portion of the aggregated NPs may not enter cells and hence lose their toxicity.

- **Particle size effect:** The toxicity of NPs is size-dependent. Compared to Ag^+ ions and Ag NPs with larger diameters (20–100 nm), Ag NPs with a diameter of less than 10 nm have a greater ability to enter and disrupt the cellular systems of several creatures (Ivask, et al., 2014, P.9).
- **Particle shape effect:** Different toxicity levels at various aspect ratios are exhibited by NPs due to their shape-dependent toxicity. According to Lippmann (1990), asbestosis can be caused by 2 µm length fibers, mesothelioma can be caused by shorter asbestos fibers (5–10µm), and lung cancer can be caused by 10 µm length asbestos fibers (P.88).
- **Surface area effect:** Generally speaking, as surface area and particle size decrease, so does the toxicological effect of NPs. Furthermore, it should be emphasized that human cells respond differently to nano and microparticles at the same mass dose.
- **Crystal structure effect:** NPs may show distinct cellular absorption, oxidative processes, and subcellular localization depending on their crystal structure. For instance, the toxicity of the two crystalline polymorphs of TiO_2, rutile and anatase, varies. Anatase NPs (200 nm) do not cause DNA damage in the dark, while rutile NPs (200 nm) cause DNA damage by oxidation (Gurr, et al.,2005, P.213).
- **Surface functionalization effect:** According to Sayes et al. (2004), P.4, the surface characteristics of NPs have demonstrated dramatic effects pertaining to translocation and subsequent oxidation processes.

- **Pre-exposure effect:** Shorter exposure times or pre-exposure to lower NP concentrations can both increase cellular phagocytic activity. The human body becomes somewhat more adaptive to NPs as a result of this pre-exposure (Johnston et al., 2000, P. 168).

6.0 Regulations pertaining to nanomaterials

Nanomaterials have high levels of chemical bioactivity and reactivity, can penetrate cells, tissues, and organs, and have higher bioavailability. NMs excel in biomedical applications because of these special qualities. These advantages do provide some risk for toxicity, though. Therefore, various government agencies have put laws, rules, and regulations into place to reduce or eliminate the risks connected to NMs.

However, there isn't a single international law, procedure that has been accepted globally, or legal definitions for the creation, processing, labeling, toxicity testing, or assessing the effects of NPs on the environment. To address the potential hazards of NMs and Nano products, US regulatory bodies including the Institute for Food and Agricultural Standards (IFAS), the United States Environmental Protection Agency (USEPA), and the Food and Drug Administration (FDA) have started to implement protocols. The FDA has been investigating the origins of non-metalloids (NMs), their potential effects on humans, animals, and plants, as well as ways to reduce or eliminate these hazards, since 2006. (Thomas, et al.,2006, P.91).

7.0 CONCLUSIONS

Although nanotechnology is still relatively new, there are many other fields that deal with atoms and molecules. The study of atoms and molecules, their behaviour, and manipulation has long been a focus of the fields of physics, chemistry, and biology, in various ways. Quantum mechanics is already well-established as the science of the extremely small.

Nanotechnology is already impacting a very wide range of human technological activity. It is characterized as both a method for creating ultrasmall materials and gadgets and a concept in which everything in the world is considered from the viewpoint of atomic or molecular building blocks. What effects does nanotechnology have on systems, devices, and materials? The massive increase in surface area is the most obvious effect of materials becoming smaller.

Therefore, nanoparticles provide an instant and automatic advantage for any material whose performance depends on a particular surface area. Another benefit that could arise from finely dividing the material is that its intrinsic qualities could be improved. This is especially true for electronic and photonic devices, where small enough devices allow energy levels to become discrete, enabling size-dependent output energy tuning and other useful features (which are lost in devices that require arrays of particles if they are not uniform in size). Interestingly, if silicon is produced in chunks smaller than 5 nm, its band gap becomes direct instead of indirect, having important implications for monolithic polyfunctional optoelectronic devices. Last but not least, material downsizing may make it possible to effectively combine a variety of qualities into a single composite material—a combination that might not be possible at the macro scale.

Strictly speaking, the majority of the displayed tiny devices are still micro devices. Single-electron devices, the building blocks of ultraminiature electronic circuits for computing and other uses, are the subject of extensive research at the actual nanoscale. Considerable research is being done on biological molecular motors as a potential source of really nanoscale motor design inspiration. The active field of integrated optics, where light is guided and controlled in structures whose dimension is significantly less than the wavelength of light, is currently referred to as "nano-optics."

One of the main characteristics of nanotechnology is that it is a perspective where issues related to the comprehension of fundamental mechanisms are resolved at the nanoscale level. This frequently results in a unique understanding of how a process functions, making it possible to design significantly better controls and produce output of far higher quality.

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