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Chapter 1
Nanoengineering and nanoscience: current and emerging trends

Abstract: The study of science at the nanoscale has become one of the most important research topics in recent years. Almost all branches of science are interested in nanotechnology. Metal and metal oxides, carbon family products, polymers, clays and composites are some of the nanomaterials used. Despite their small size, nanomaterials have different properties such as large surface area, different particle shape and size, pore volume, biocompatibility and biodispersibility. For this reason, nanotechnology has also spread to the industry. Due to their unique properties, nanomaterials are widely used in medical, water treatment, sensor and environmental applications. Although nanotechnology research has accelerated especially in recent years, there are still many unexplored materials and application areas. The aim of this study is to investigate the advantages and disadvantages of nanomaterials and nanotechnology applications by examining their usage areas in scientific and industrial fields.

Keywords: Nanoparticles, nanotechnology, materials, metal oxides, particle size

1.1 Introduction

The study of nanoscale materials and the development of associated laws and conceptual information constitute the field of science known as nanoscience. Generally, materials smaller than 100 nm are classified as nanomaterials [1]. Its scientific equivalent is a billionth of a meter [2]. In fact, the existence of nanoparticles (NPs) is not a new phenomenon. Nanoscale materials have been formed in nature for centuries. Some of these are the presence of events that are sources of NPs such as volcanic eruptions and fires and ceramic glazes or stained glass silver NPs for color purposes [3]. The scientific development of NPs for the first time was around 50 years ago for vaccines and cancer treatment [4]. Nanotechnology cannot be limited to any discipline. It is interdisciplinary with natural sciences and various branches of engineering and sciences such as toxicology

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[3]. In recent years, nanotechnology has been used in different disciplines such as engineering, physics, chemistry and medicine. It draws attention with its diagnostic, imaging or therapeutic properties, especially in the biomedical field [5, 6].

The structural properties of nanoparticles (NPs) and the area to be used vary depending on their properties such as size, shape, crystallinity and morphology [7]. An important feature that makes NPs stand out is that they have a larger surface area compared to the raw materials from which they are synthesized. Using many organic and inorganic elements, NPs can be synthesized from natural components such as lipids, proteins, polysaccharides or metals such as Ti, Ag, Au, Zn and Cu by various methods [8, 9]. The use of NPs in the diagnosis and treatment of diseases such as cancer reveals the importance of nanotechnology due to their biocompatibility and biodispersibility properties [7]. As seen in Figure 1.1, a glucose molecule is 1 nm in size, while a water molecule is 0.1 nm. These data indicate that nanomaterials are at the molecular size level [10].

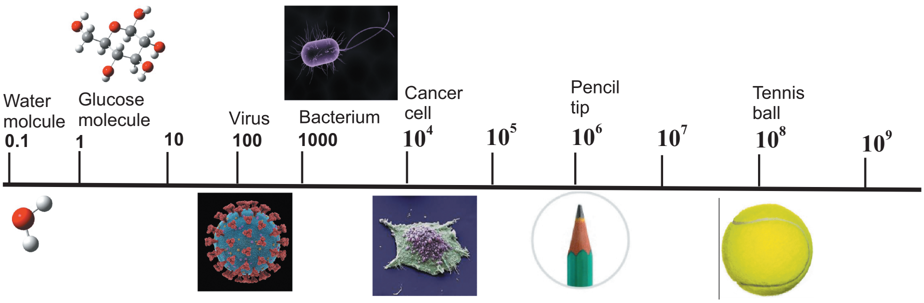

Figure 1.1: Comparison of length scale 10^9.

1.2 Nanomaterials

Nanomaterials with a high surface/volume ratio form the basis of nanotechnology due to their many superior properties. Researches have reported that there are over 1,000 nanoproducts due to their wide usage areas [11]. Today, many material groups such as NPs, nanotubes, nanomembranes and nanofibers are investigated [12]. Numerous distinct metallic NPs have recently been developed and applied. Titanium dioxide (TiO_2), zinc oxide (ZnO), FeO, copper oxide (CuO), bismuth oxide (Bi_2O_3), silica, mesoporous silica and lead oxide (PbO) are some of them [13–15]. Zirconium dioxide (ZrO_2), which is one of the important industrial nanomaterials, has important properties such as catalytic activity, thermal stability and chemically inert structure. Cobalt oxide (Co_3O_4) is another important material in memory storage units, catalytic activity and chemical sensor applications [16]. Zinc NPs are an important semiconductor with optical, piezoelectric and nontoxic properties [7, 17]. Silica and mesoporous silica NPs are nontoxic, biocompatible and biodegradable materials. Thanks to its large surface area and pore volume, it can be used in different applications such as drug release, bone tissue engineering, adsorption, biosensor and solar cell [15]. Various metallic, carbon, polymeric or composite NPs used in recent years and their application areas are given in Table 1.1.

Carbon is a rich and important family for nanoscale systems and exhibits broad functionalities with structural arrangements [18]. sp^2 carbon materials can generally be thought of as zero-dimensional fullerene, one-dimensional carbon nanotube (CNT) and two-dimensional graphene [19]. Graphene has unique electronic, optical, catalytic, mechanical and magnetic properties, thermal conductivity and gas barrier properties. Thanks to these properties, graphene has uses in different applications from energy storage to biomedical materials [20, 21]. Graphene oxide (GO) and reduced graphene oxide (RGO) are known as several-layer graphene oxide materials [22]. In addition, carbon-based nanomaterials such as fullerene and CNT are used in different applications from medicine to electronics such as metal NPs [23]. Figure 1.2 shows the molecular structure and shape of fullerene, CNT and graphene.

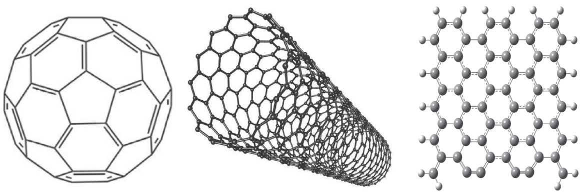

Figure 1.2: Moleculer structure of fullerene, carbon nanotubes and graphene.

Table 1.1: Different nanoparticles and area of applications.

Nanoparticles	Area of application	References
TiO_2	Bone tissue engineering	[24]
TiO_2	Antibacterial, larvicidal and anticancer effects	[8]
CeO_2	Anticancer effect	[25]
ZnO	Antifungal activity	[17]
Chitosan nanoparticles	Antibacterial activity	[26]
Silane-modified Fe_2O_3	Anticorrosion	[27]
CuO NPs	Adsorption	[28]
NiO NPs	Adsorption	[28]
Silver	Catalytic activity	[29]
CuO NPs	Photocatalytic, antimicrobial and anticancer activity	[30]
Fe/Zn bimetallic	Cytotoxicity study	[7]
Mesoporous-ordered silica (MCM-41)	Adsorption	[31]
$ZnO/ZnCr_2O_4$	Photocatalytic degradation	[32]
Graphene	Cytocompatibility effect	[20]
ZrO_2/Co_3O_4/RGO	Electrochemical sensor	[16]
PEGlyted nanographene	Photothermal therapy Targeted chemotherapy	[21]

In addition, nano-sized materials of clays have come to the fore in recent years. Nanoclays can be used in drug carrier systems, catalyst or adsorbent, food packaging in different areas. The nanosize of the clay affects the thermodynamic, physical and chemical properties of the composites synthesized with polymers. It provides benefits such as increasing the stability of the drug or increasing the biodegradability of the polymer in drug release applications [33]. Polymer nanoparticles can be obtained both from natural polymers and synthetically by synthesis. They can be functionalized with polysaccharide, protein or amino acid molecules. In this way, they become more effective for drug release [34]. Polymeric nanoparticles with high drug loading capacity can be easily sterilized and dispersed [35]. Poly-hydroxyethyl methacrylate (p(HEMA)), which can be synthesized in nanosize, is an important polymer in this field and is used in biomedical and pharmaceutical fields such as soft contact lenses [34]. Chitosan NPs, on the other hand, have high zeta potential and large surface area. The use of chitosan nanoparticles, which are used in the treatment of agricultural diseases, in many areas such as drugs, vaccines and gene release is being investigated [26].

Nanofibers are very fine yarns with a diameter between 50 and 500 nm, which are light, porous and have a high activity. They are unique materials for dressings, protective clothing, membrane and tissue engineering. They are obtained by different methods such as phase separation, interfacial polymerization, freeze-drying synthesis, especially electrospinning method [36]. In addition, the production of nano-based cellulose fibers and their applications in composite materials has increased interest due to important properties such as high stiffness, biodegradability and low weight. The application of cellulose nanofibers in polymer reinforcement is a topic of recent interest [37].

Nanocomposites with organic or inorganic properties are functional materials that do not form a mixture with each other and contain organic and inorganic components in their structures. Complex nanometer-based structures can be formed from them [38].

1.2.1 Synthesis methods and structure analyses

There are two different approaches to synthesis methods in nanotechnology. One of them is the "top-down" approach. In this approach, nano-based materials are made using the smallest structures. This is photonic applications in nanoelectricity and nanoengineering. The "bottom-up" approach, on the other hand, can be called molecular nanotechnology. Science is concerned with the production of different nanoparticles and nanomaterials with extraordinary properties [39].

With the increase in research on the subject, the synthesis methods of nanoparticles have also been developed by scientists. Green synthesis, which has become popular in recent years, is frequently preferred because it is environmentally friendly, inexpensive, efficient and easy. Plant, fruit and vegetable extracts, bacteria and various microorganisms are used as reducing agents. Various phytochemical substances such as polyphenols, especially in plant extracts, reduce metal ions and provide nanoparticle synthesis [9]. Some of the commonly used methods are given in Figure 1.3.

After synthesis, the chemical structure of nanoparticles can be analyzed by techniques such as

- ultraviolet spectroscopy (UV/vis),
- Fourier transform spectroscopy,
- x-ray diffraction,
- energy-dispersive X-ray spectroscopy.

Properties such as size and particle shape in the morphological structure can be determined using

- scanning electron microscope,
- transmmison electron microscope (TEM),
- atomic force microscope,
- selected field electron diffraction techniques [9, 32, 40].

TEM images are given for superparamagnetic Fe_3O_4 NPs in Figure 1.4a and for hydroxyapatite NPs in Figure 1.4b. When the morphological structure of nanoparticles is examined, it is seen that the shape of Fe_3O_4 is spherical and hydroxyapatite is needle-like [41].

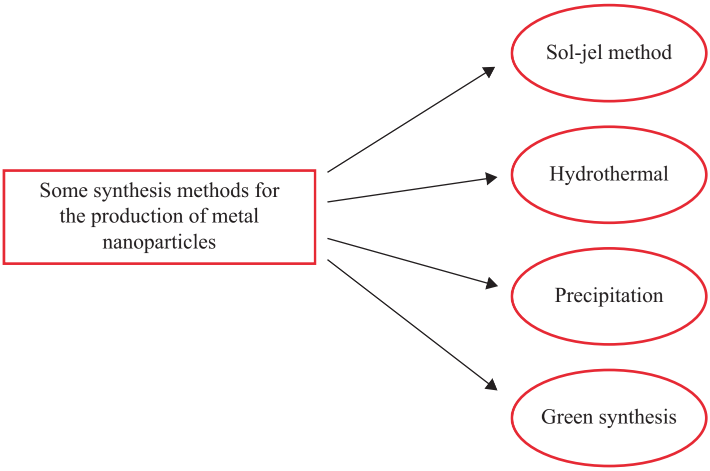

Figure 1.3: Some of the common methods used in metal nanoparticle production in recent years.

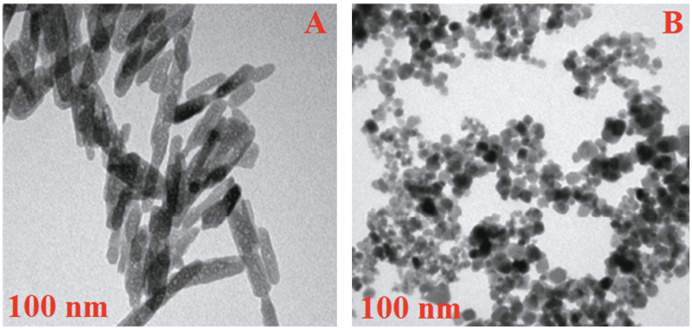

Figure 1.4: (a) Superparamagnetic Fe_3O_4 nanoparticles and (b) hydroxyapatite.

1.3 Scope of application

Nanoparticles obtained in organic, inorganic, metal or hybrid form have very good electronic, optical, physical or biological properties. Therefore, the use of nanoparticles has spread to various fields such as [3, 30, 39, 41]
- electronics,
- medicine (controlled drug delivery, anticancer activity, tissue repair, hemolytic activity),
- biomedical (pharmacy, detecing pathogen, antigen diagnosis),
- catalysis,
- fluid,
- agriculture.

In this section, popular applications and research areas in which nanomaterials are used today will be examined.

1.3.1 Medicine, health and biomedical areas

The use of nanotechnology in medicine has paved the way for the use of nanomaterials for the diagnosis of diseases or for various therapeutic purposes [42]. For example, cancer is a disease that has been affecting human beings for many years and whose treatment has been investigated. Cancer is the uncontrolled division and proliferation of cells. Sometimes it can occur in a certain organ and sometimes in a spread [43]. Especially for cancer treatment, many nanomaterials such as Ag NPs and TiO_2 NPs are used as drug delivery systems or for their therapeutic effects [8, 42].

The use of nanoparticles in bone tissue engineering has increased in recent years. Superparamagnetic iron oxide and hydroxyapatite nanoparticles were observed to improve mineralization and osteogenic differentiation of bone tissue [41]. Superparamagnetic iron oxide nanoparticles are used against brain tumor. It is shown in Figure 1.5 that the composite material synthesized in small nanoscale, modified with silica nanoparticles and CNTs passes through the blood-brain barrier (BBB). Even in a low magnetic field, nanoparticles have been reported to provide heat to destroy tumors. It has been reported that superparamagnetic iron oxide/silica/carbon nanoparticles (earthicles) pass through the BBB from the blood to the brain and reach the brain tumor (glioblastoma) and brain cells (astrocyte) [44].

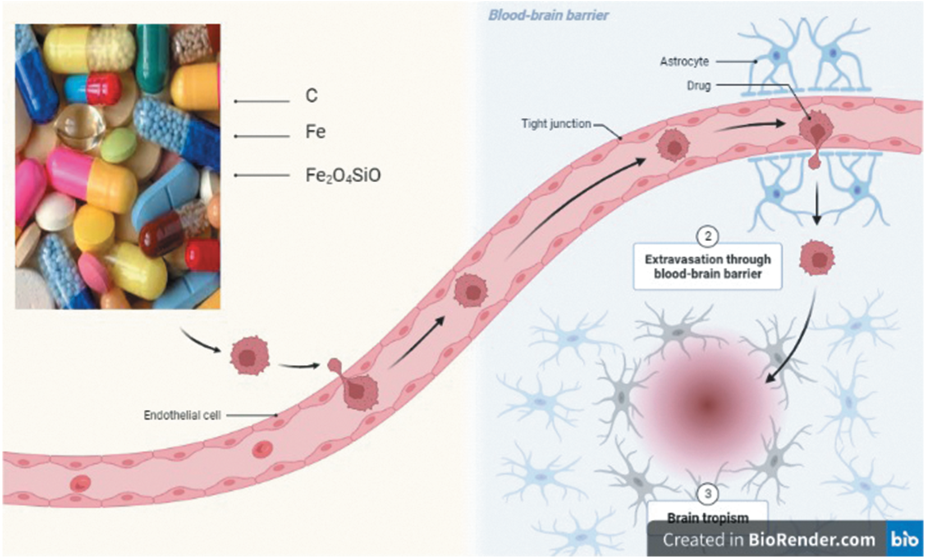

Figure 1.5: Passage of superparamagnetic iron oxide nanoparticles through the BBB and reaching the brain from the blood.

Nanoparticles are widely used as drug delivery agents. Nanoparticles, which can be used as both a lubricant and a drug delivery system, are used instead of surgical procedures in joint diseases such as osteoarthritis [45]. Nanotechnological methods are used in various surgical procedures. There are sensors used to accurately determine blood pressure in the balloon inflation method, which is a technique used to unclog the arteries [46].

Biocidal properties of various nanoparticles are being studied to remove bacteria that threaten public health. NiO nanoparticles, a semiconductor material with magnetic, catalytic and photocatalytic properties, are known to have significant antibacterial properties even at low concentrations. In addition, NiO/chitosan nanocomposites have reported superior antibacterial effects against Gram-negative (*Escherichia coli*) and Gram-positive (*Saccharomyces cerevisiae* and *Bacillus subtilis*) bacteria [47]. ZnO

NPs have antifungal properties and are effective against pathogens such as *Erythricium salmonicolor* [17].

The cosmetics industry uses nanotechnology effectively to realize people's desire to stay beautiful and young. For this, he resolutely pushes his limits. Nano-based materials are applied in various hair care products such as antiaging and skin rejuvenating cosmetics, sunscreen creams and shampoos. For example, nanoemulsions are used in shampoo, conditioner, nail polish, lotion or antiwrinkle creams because they increase skin penetration. Nanoemulsions can deliver ingredients that may be beneficial for the skin into the skin depending on the concentration [48].

1.3.2 Water treatment

Water is nonrenewable and a vital resource for human survival. Due to the increase in population and industrialization, it has led to the pollution of waters [49]. Dyes are important pollutants arising from the wastes of sectors such as food, automotive, textile or cosmetics that harm human health [29, 50]. As an example of these dyes, methyl orange is a carcinogenic azo dye used in the food and textile industry [29]. Methylene blue, a cationic dye, is a dark blue dye with high water solubility. It causes vomiting, diarrhea, tachycardia, shortness of breath and skin irritation as well as harming the environment [9]. Even very small concentrations of dyes contaminating water systems are visible. Due to the coloration of the water, photosynthesis is reduced and therefore the water flora is adversely affected. Plants, animals, the environment and human health are harmed by the pollution of water [9, 40]. In Figure 1.6, nanomaterials used in water treatment and possible contaminants are shown schematically.

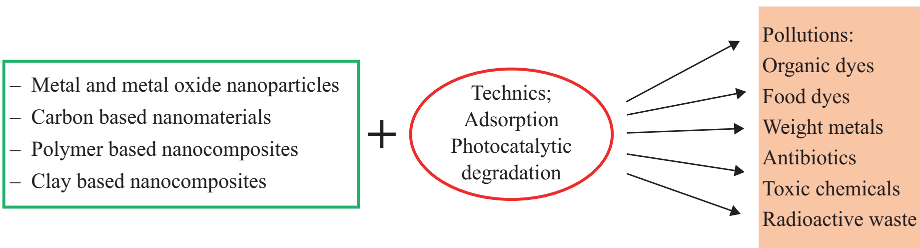

Figure 1.6: Nanoparticles used for cleaning from wastewater and types of pollution in water.

Nanoparticles are widely used in adsorption and photocatalytic degradation applications for water treatment. CuO NPs with large surface area, antibacterial and antifungal properties provide photocatalytic degradation of organic dyes such as methylene blue under UV lamp [9]. Similarly, nanocomposite obtained by using xyloglucan, a biodegradable and nontoxic polysaccharide and magnetic Fe_3O_4, has been reported to be 99% successful in removing cationic dye from aqueous solution when used as a photocatalyst. In order to improve the photocatalyst activity and adsorbent properties of the synthesized nanoparticle, there is a need to continue research with different dyes or pollutants [40].

Mesoporous silica nanoparticles (MSNs) have unique structural properties due to the controllability of their pore diameters. They can also be functionalized with different functional groups. They are used as sorbent in the removal of weight metals such as chromium due to the active sites they have [31]. Materials formed by CNTs containing metal oxide are among the alternatives that can be used to minimize air pollution and solve the water treatment problem [49].

1.3.3 Agriculture

Nanotechnology has the power to change the course of the current food and agriculture industry [39]. The effective use of nanotechnology in agriculture provides benefits in areas such as transport in soil, displacement in plants, and efficient targeting of pests with the use of pesticides at nanoscale, thanks to nanomaterials. New studies such as crop nutrition and smart plant sensors reveal that nanotechnology could be important for sustainable agriculture [51]. Nanobiosensors will help in the fight against undesirable pathogens in the agricultural sector. It is predicted that nanostructured materials that reduce the amount of dose required for crop plants and increase the activity of pesticides will exist in the future [39]. Zinc is beneficial for plant

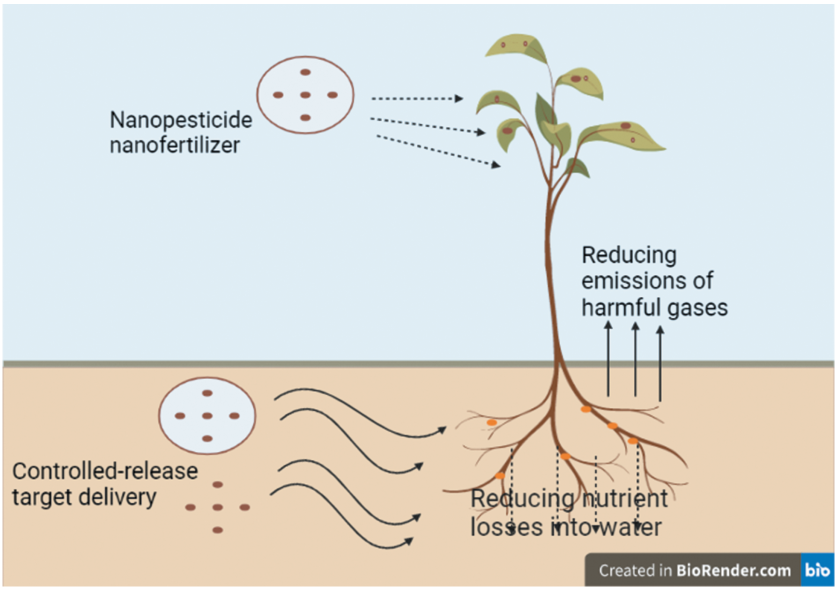

Figure 1.7: The path that nanofertilizers follow in the soil after they affect the plant.

growth and a metabolic regulatory element. In some plants, its deficiency may have consequences such as yellowing and shrinking of the leaves. Processing ZnO nanoparticles into plants by using them in biofertilizers is one of the important studies [52]. Scientific reports report that gold, CeO_2, ZnO, CuO, FeO, Fe/SiO_2, Mg, TiO_2 and calcium nanoparticles are used as nanofertilizers.

The use of nanobiotechnology is very important in terms of minimizing agricultural waste and sustainable development [53]. There are still issues that are not clear. For example, copper, silver and zinc-based nanoparticles have the potential to be used as pesticides and fungicides. However, it is known how this potential will affect the soil quality in the long term. There is a need for the formation of new agricultural models and the development of the obtained data by processing [51]. In Figure 1.7, the effect of the use of nanofertilizers on plants and soil is given visually.

1.3.4 Industrial area

Another use of nanoparticles is as a lubricant. Lubricants have functions such as removing excessive heat, preventing friction, wear and corrosion, and resistance to degradation. It has been reported to provide benefits such as reducing friction and increasing brightness. Properties of nanoparticles such as concentration, size, shape and structure affect tribological properties when added to the lubricant. The movement of CNTs in the lubricant medium is shown in Figure 1.8 [54].

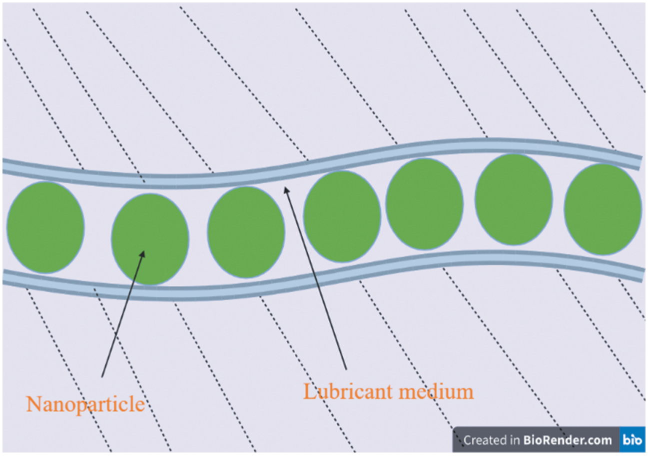

Figure 1.8: Carbon nanoparticles as lubricant.

Corrosion is the irreversible self-damage and destruction of metal [55]. Nanomaterials are unique materials that can show anticorrosive properties due to their surface and volume ratios [1]. The surface/volume ratio of nanoparticles causes them to be effective in corrosion. Despite their small size, they preserve the amount of active site by increasing the surface of a given mass. During inhibition, nanomaterials are subjected to physical or chemical sorption on the metal surface. This result reveals the structure that prevents corrosion [55]. The solubility and sorption abilities of nanomaterials in aqueous electrolytes are important in terms of corrosion [1]. Nanoparticles can increase the corrosion resistance of organic coatings by extending electrolyte paths due to their large surface area. However, if the nanoparticle agglomerates, its efficiency against corrosion may decrease [27]. Silver, silica, iron and copper, ZnO and TiO_2 nanoparticles have anticorrosion ability [55].

Today, many nanoparticles are used to take advantage of the gas sensor properties [56]. Volatile organic compounds (VOC), known to be canserogens, adversely affect human and environmental health. For example, formaldehyde, polycyclic hydrocarbons and some organic waste gases are highly carcinogenic. They can even lead to death from excessive inhalation. Various metal oxide semiconductor nanoparticles and carbon-based materials such as ZnO, SnO_2 and WO_3 show gas sensor properties [57]. Nanocomposite synthesized using ZnO and polyaniline has superior sensor properties for NO_2 gas [56].

Nanotechnology has made progress in electronic applications as well as in all fields. Thanks to their large surface areas, they are candidate materials for flexible electronics. There are many uses such as energy devices, optical and electronic devices, wearable heaters for thermal therapy, sensors, soft electronics and field effect transistors [58, 59]. Copper is an important and inexpensive alternative to noble metals for use in soft electronic circuits. It has high electrical conductivity and is easily available [59].

1.4 The future of nanomaterials

Technological developments in the world now point to the existence of nanotechnology and nanoscience. Scientific data show that when microtechnology is typed into the Google search engine, 130,000 results are obtained, while nanotechnology is written more than 20 million search results [60].

It is expected that the areas affected by developing nanoscience and nanotechnology will increase. Wear-resistant tires, nano-based particles with the best performance of paint pigments, lasers with enhanced performance with new features, nanoparticles to be used in medicine with the ability to deliver the drug to the target, designs of innovative biosensors, production of nano-based traps to eliminate environmental pollution are some of them (Figure 1.9) [61].

As can be seen, the use of nanotechnology and nanomaterials is a subject that develops and comes to the fore in contemporary life. The number of nanoparticles and nanocomposites synthesized by different methods is increasing day by day and their properties are being examined.

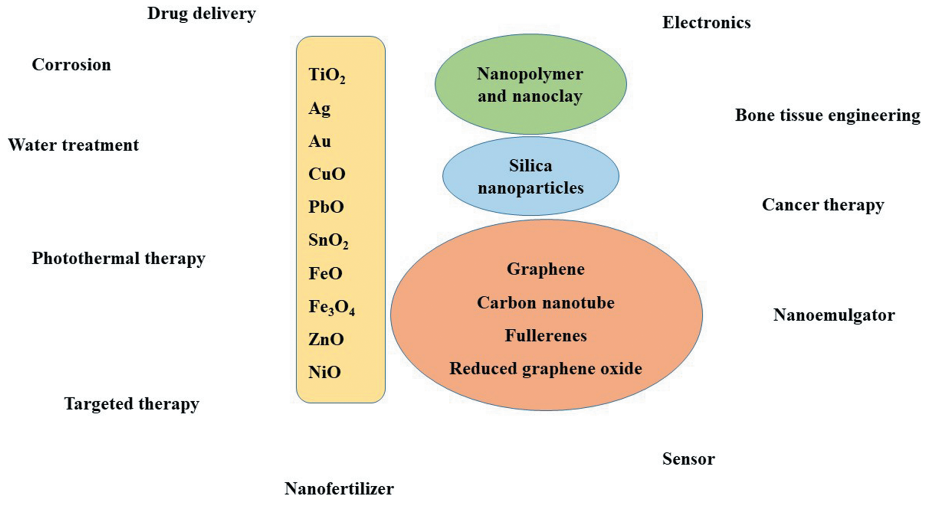

Figure 1.9: Different nanomaterials and applications.

In line with these results,

- it is necessary to understand the physical and chemical structures of many nanomaterials;
- it is important to choose the right application area by investigating its cytotoxic and antibacterial properties as well as its electronic and magnetic properties;
- in addition, the efficient and cost-effective development of synthesis methods is necessary for sustainability.

The fact that nanotechnology can be used in almost all fields is an indication that the scientific studies and industrial applications on this subject will continue rapidly.

Finally, in the next 10 years, nanoscience and nanotechnological applications have been accepted as the most promising scientific and technological development among the technological fields that exist today. Every country in the world has made a large investment in nanotechnological applications. National governments have also led to the emergence of the National Nanotechnology Initiative due to the financing activities in Europe. The major future consequences of nanotechnology on issues such as privacy or the emergence of a common language are alarming. Every society must be prepared for the changes that come with nanoscience and its nanotechnological applications.

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