

Engineering Materials ENGR 220

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Abstract

Nanotechnology is becoming a crucial driving force behind innovation in medicine and healthcare, with a range of advances including nanoscale therapeutics, biosensors, implantable devices, drug delivery systems, and imaging technologies. Universities also have begun to offer dedicated nanomedicine degree programs (example: MSc program in Nanotechnology for Medicine and Health Care). A nanotechnology-based system, for instance to eradicate cancer, needs four elements: 1) Molecular imaging at the cellular level so that even the slightest overexpression's can be monitored; 2) effective molecular targeting after identifying specific surface or nucleic acid markers; 3) a technique to kill the cells, that are identified as cancerous based on molecular imaging, simultaneously by photodynamic therapy or drug delivery, and 4) a post molecular imaging technique to monitor the therapeutic efficacy. This paper introduces the many healthcare advances that may be possible through nanotechnology, ranging from fitness monitoring, prevention, diagnosis to therapy, and everything in between, as well as the problems existing in present research and a proposal for future studies.

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Introduction

There is beginning to become a large range of ways to aide in health monitoring, with new technology and discoveries through the years. A new and upcoming way is to use nanomaterials, such as carbon nanotubes (CNTs) for health monitoring. In the recent years, nanoscience has developed very rapidly. Reducing the particle size from micro to nano allows for many unique properties and helps in many different applications [31]. There are still many active studies about this type of health care, however it seems to have to potential to cure many diseases that are defined as 'uncurable' at this time. The reason for the use of nanomaterials over other materials is due to the large surface-to-volume ratio and quantum confinement effect [31]. It also has the potential to solve issues such as environmental pollution, which has become a vital issue in the world today, including air pollution, water pollution, and soil contamination [12]. Another positive potential is the detection of toxic metal ions in these environmental pollutants. With the many positive potential effects. These are all options to discuss and consider while studying the future of medicine using nanomaterials.

Motivation

My motivation to learn about this topic is the overall health aspect. It is truly fascinating to me to see the improvements in health care over the years, and the fact that a material studied in this class contributes to this is very interesting to me. I love learning and reading about new ways being studied to solve medical mysteries such as Alzheimer's, which currently has no cure. The fact that a material such as nanotubes has the potential ability to cure uncurable diseases is truly amazing.

Applications

1. Definition

There is no single type of nanomaterial; in theory they can be engineered from minerals and nearly any chemical substance, and can therefore differ with respect to composition, particle size, shape, surface coatings and strength. However, the overall definition is that a nanomaterial must have at least one dimension that is less than approximately 100 nanometers [31].



Figure 1. Structure of nanomaterials [31]



Figure 2. Types of nanomaterials in our environment [16]

1.1 The Class of Materials

Nanomaterials can be categorized into four different groups. The first group is carbon-based nanomaterials; which are carbons with varying morphology; hollow tubes, spheres, ellipsoids. Examples of carbon-based nanomaterials include Graphene, CNTs, and Fullerenes. The second group of nanomaterials includes the inorganic-based nanomaterials, which involves metals, metal oxide nanoparticles, and semiconductors. The third group of nanomaterials is the organic-based nanomaterials, which are a nanomaterial made from organic materials such as dendrimers, micelles, and polymer NPs. The last group of nanomaterials is the composite-based nanomaterials, which are multi-phased nanoparticles with one phase on the nanoscale size. This can then combine with other nanomaterials, or bulk-type materials. The composites of this can be any combination of carbon-based, metal-based, or organic-based nanomaterials [26].

1.2 The Structure of Atoms

In the sciences of nanotechnology, the structure and placement of each single atom can make a huge difference in whether the nanomaterial is a semiconductor or insulator, whether it triggers or stops a chemical reaction, and/or the properties and behavior of the nanomaterial [35].

1.2.1. The Electrons in an Atom

The electrons in the atoms are simply not enough in nanotechnology and nanoengineering. This is because the electrons do not provide a precise mathematical coordinate of every atom needed for studying [35]. As stated before, the precise destinations of the atoms are critical in nanoengineering because a single atom can make all the difference in a material.

1.2.2. The electronic structure of the solid: energy bands and chemical bonds

There are many different kinds of nanomaterials, hence many different electronic structures. However, to find good descriptions and geometrical features of specific nanomaterials, it is necessary to find the core basis of each atom. For example, for $(In_{12}N_{12})_n$, one can use the PBE (Perdew-Burke-Ernzerh) exchange-correlation functional with the basis set for In atoms and the basis set functional for N atoms is reliable to show and describe the properties of cage-like $(InN)_{2n}$ structures. Another way that can be used is the full relativistic calculation, however this is very expensive and the energy difference may cause errors due to the neglect of the spin-orbit coupling effect. However, both of these methods are good ways to find the chemical bonds and geometric properties of a specific nanomaterial [42].

2. Physical Properties

There are many different physical properties of nanomaterials. The high ratio of surface to volume of nanoparticles leads to the influence of surface atoms on these physical and chemical properties. Nanoparticles have diverse sizes, and therefore have different T_m . T_m states the phenomenon of T_m reduction of particles in small dimensions [6].

Equation 1. (The Gibbs-Thomson equation) [6]

$$\Delta T_m = \frac{2\sigma_{st}T_m}{r\Delta H\rho_s}$$

 $\begin{array}{l} \Delta T_m = \text{melting point depression} \\ T_m = \text{bulk system melting point} \\ \rho_s = \text{solid phase number density} \\ r = \text{nanoparticle radius} \\ \Delta H = \text{melting latent heat} \\ \sigma_{st} = \text{solid} - \text{liquid interfacial energy} \end{array}$

2.1 Density

As stated before, there are many different nanomaterials, all with different properties. However, the density of a nanomaterial can be calculated by directly measuring the inelastic scattering probability in a thin sample [32]. Core-less EELS are able to, with a quantitive model, extract the atomic density. The knowledge of one of the parameters (such as sample thickness) will give a measurement of the other parameter [32]. The average absolute error with this type of measurement was only 4 percent. Another way scientists have figured out how to measure the density of nanomaterials is by using a temperature versus pressure curve [32]. One could graph the density of a specific nanomaterial by using size-dependent density (i.e., Size versus Density) to show the changes in density dependent on the size.



2.2 Thermal conductivity

Thermal conductivity is a very important property of nanomaterials and directly influences the application of them. Nanomaterials have low thermal conductivity due to their interatomic bonding and intrinsic atomic structure [25]. The relationship between thermal conductivity of nanomaterials and their particle size is as follows:

Equation 2. The relationship between thermal conductivity and partical size [25]

$$k_{\rho} = k_b \left(1 - \frac{2d}{3h} \right)^{\frac{3}{2}}$$

d = diameter of nanofilm

h = height of nanofilm

Table 1. Common thermal analysis techniques used for the evaluation of nanomaterial [25]

Main Measured	Technique	Accepted acronym	Common
Property			hyphenated
			technique
Change of mass	Thermogravimetry	TGA	TGA-MS
			TGA-FTIR
			TGA-GC-MS
Heat flux	Differential scanning	DSC	DSC-TGA
	calorimetry		DSC-DTA
Change of	Differential thermal	DTA	DTA-DSC
temperature	analysis		DTA-TGA
Volatiles	Evolved gas analysis	EGA	EGA-MS
			EGA-FTIR
Mechanical	Thermomechanical	TMA	N/A
Properties	analysis		

2.3 Electrical conductivity

Electrical properties, like many other properties of nanomaterials, varies by the geometrical property of that material. By optimizing the distribution of nanocomposites using Lennard-Jones potential model in the boundary conditions according to external strain, and then counting the

average attachment among nanomaterials by strain using the voter model. Using this method, the effect of geometrical properties of nanomaterials can be accurately estimated with a much lower simulation cost. From this measurement, it shows that the diameter of nanoparticle is a primary factor for the sensor. Therefore, the electrical conductivity according to the strain is the largest at small and uniform nanomaterials [17]. The electrical conductivity between nanomaterials can be calculated as shown in equations (3), (4).

Equation 3. Electrical Conductivity of nanomaterials [17]

 $\sigma_{ij} = \delta_{ij\sigma}$ Equation 4. Electrical Conductivity of nanomaterials [17]

$$\delta_{ij} = \begin{cases} 1 \text{ if } d_{ij} \leq r_i + r_j \\ 0 \text{ if } rd_{ij} > r_i + r_j \end{cases}$$

 $\begin{aligned} d_{ij} &= distance \ between \ nanomaterials \\ j &= \begin{cases} distance \ between \ centers \ of \ two \ NPs \\ perpendicular \ distance \ between \ the \ centers \ of \ the \ NP \ and \ the \ CNT \\ minimum \ distance \ between \ two \ CNTs \\ \delta_{ij} &= attachment \ indicator \\ d_{ij}, r_i, \ and \ r_j &= geometrical \ properties \ of \ nanomaterials \end{aligned}$

2.4 Superconductivity

Superconductivity of many materials is actually measured at the nanoscale. Nanotechnology is the source used by researchers to increase the superconductivity temperature of many materials [28]. From researchers, it is known that Nb, Pb, and Bi are all superconductive nanomaterials.

Nanoparticle	Reference Size (nm)	$\mathbf{T}_{\mathbf{c}}(\infty)(\mathbf{K})$	$\frac{\mathrm{H_m}}{(\infty) \left(\frac{J}{mol}\right)}$	T _{mb} (K)	Atomic diameter (nm)
Nb	1.20	9.2	26,359	2740	0.2859
Pb	3.79	7.2	4774	600.58	0.3500
Bi	1.65	5.6	11,297	544	0.3071

Table 2. The physical parameters of calculated materials (nanoparticles) [28]

2.5 Specific heat

Shape and size of nanomaterials is dependent on the specific heat. The specific heat of nanomaterials can be measured at constant pressure. Specific heat is found to increase with decreasing size of nanocrystals, which indicates that the specific heat varies inversely with particle size [29]. The cause for increased specific heat at small sizes is the high atomic thermal vibration energies of the surface atoms [29].



Equation 5. Relationship between specific heat and constant pressure of nanomaterials [29]

$$C_{pn} = \infty \frac{1}{\theta_{Dn}^2}$$

2.6 Melting range

It is found that melting entropy and melting enthalpy decrease with a decrease in size of the nanomaterial. It is also found that the Qi model and Guisbiers model are both good applications when studying the melting range of a nanomaterial [4].



Figure 5. Melting entropy vs. size using Qi model for Cu [4]

Figure 6. Melting enthalpy vs. size using Qi model for Cu [4]

Equation 6. Melting temperature and melting enthalpy relationship [4]

$$\frac{Tnm}{Tbm} = \frac{Hnm}{Hbm}$$

2.7 Thermal properties

There are many thermal properties of nanomaterials. These include but are not limited to melting point, thermal conductivity, specific heat, and thermal expansion. Generally, the thermal properties of nanomaterials differ greatly from bulk materials [41]. For example, the melting point and melting entropy and enthalpy of nanomaterials are lower than those of bulk materials [41].

2.7.1 Thermal Behavior

The thermal behavior is an imperative property for many applications due to the changes in viscosity and viscoelastic behavior of nanomaterials. The thermal properties of nanocomposites

were inspected by DTA (a method that the physical property of nanomaterial is investigated as a function of temperature) and displayed DTA curves that show the degradation point (Figure 3) [25].



2.8 Magnetic properties

Each nanomaterial has different magnetic properties and structures. Ferrite shows the cubic structure, and has low hysteresis loss, therefore having a variety of applications in various sectors of Science and Technology, such as the core of a transformer, microwave devices, biomedical imaging, and hydroelectric cell [13]. Additionally, it has been reported that the substitution of a non-magnetic particle gives a change in magnetic, structural, optical, and electrical properties [13]. Due to these special properties at the nanoscale, soft magnetic materials are now used for applications in top quality filters, the head of digital tapes, and high upgrade sensors [13].

2.9 Optical properties

Like many other properties of nanomaterials, optical properties vary on the material as well. The material being discussed and studied in this section is graphene. Graphene is a zero-bandgap semiconductor, so optical properties in its pure form are unlikely [1]. The sp³/sp² ratio is considered a key factor for linear and nonlinear optical properties of graphene-based materials [1]. The optical properties in graphene are adjustable in terms of oxidation/reduction level and edge size, which could be beneficial in future studies. The technique used to find the optical properties in nanomaterials thus far is the Z-scan technique.



2.10 Corrosion resistance

Corrosion resistance of nanomaterials was measured in steel reinforced concrete. Concrete is the most widely used construction material due to its low cost. However, it deteriorates quickly [39]. The study found that the introduction of nanomaterials in the concrete could increase both its strength and durability. Many different nanomaterials were tested, and many were found to provide better corrosion resistance to the concrete [39].

2.11 Phase transformations

In a study of ZrO₂:Eu:Li (1-11%) nanomaterials, it confirms the phase transformation from a mixed phase to a cubic phase [23]. SEM analysis was used to confirm the porous nature of the samples and the variation in the pore length [23]. Phase transformation is different for each nanomaterial; however, it is possible for most.



Figure 9. LFP stained by ZrO2:Eu:Li (7% mol) nanomaterial [23]

3. Mechanical Properties

Nanomaterials have very good mechanical properties due to many factors, such as their volume and surface and quantum effects of nanoparticles [36]. As nanoparticles are added to a common material, the particles refine the grain forming an intragranular structure or an intergranular structure. Both of these improve the grain boundary and therefore promote the mechanical properties of materials [36]. For example, adding 3 wt% nano-SiO₂ to concrete can improve the concrete's compressive, bending, and splitting tensile strength [36]. As another example, adding 3% nano-oil palm empty fruit string filler into kenaf epoxy composites can improve their tensile strength, elongation at break, and impact strength [24].

3.1 Yield strength

The yield strength of nanocomposites depends on various parameters, such as the content of nanoparticles, and dispersion [40]. The best strength in polymer nanocomposites was founds by the smallest nanoparticles and the thickest interphase [40]. Therefore, the strength of the interphase was directly related to the yield strength of nanocomposites [40]. Using the Nicolais-Narkis model for yield strength, the equation is:

Equation 7. Original Nicolais-Narkis model for yield strength [40]

$$\sigma_R = 1 - a \emptyset_f^{\frac{2}{3}}$$

a = 1.21 $\sigma = yield strength of composite$ $\phi_f = volume fraction of nanoparticles (n³)$

3.2 Tensile strength

According to a study of the effect of the use of nanoparticles to modify the binder of asphalt mixtures using the tensile strength test, the tensile strength of the mixtures increases when nanoparticles are added, especially when the binder is modified with nano clay [15]. This study shows that when nanomaterials are introduced, the tensile strength of the material increases. Therefore, tensile strength and nanomaterials in a material have a direct relationship. The equation used for the indirect tensile strength test is defined as:

Equation 8. Indirect tensile strength test equation [15]

$$ITS = \frac{2P}{\pi DH}$$

P = peak load (kN) D = diameter H = height

Equation 9. Indirect tensile strength ratio equation [15]

$$ITSR = \frac{ITS_{wet}}{ITS_{dry}} x \ 100$$

3.2.1 Phase Diagrams

Knowledge of size and shape is dependent for the phase diagram of nanoparticles [34]. However, not all nanoparticles are spherical, so another route must be taken. The phase diagram of non-spherical particles can be calculated from the spherical case, at the corresponding value of (A/V) [34].



Figure 10. Size and temperature-dependent phase diagram of silver nanoparticles [9]

3.2.2 Elastic Deformation

The elastic deformation of nanoparticles can differ between different materials. The elastic deformation and fracture of materials has attracted a lot of attention due to stress-distribution, and therefore show promising application to advanced stress sensing techniques [3]. Due to this, mechanoluminescent materials have been reported to be suitable for real-time sensing of strength and location of damages caused by dynamic events [3]. Additionally, the elastic deformation in ZnS crystals may give rise to the light emission [3]. Nano-indentation tests can be done on elastic nanoparticles to show the graphs of them at different deformations and rigidity [27].





3.2.3 Plastic Deformation

Contamination and porosity-free bulk nanostructured materials can be processed from coarsegrained workpieces by severe plastic deformation [10]. During severe plastic deformation procedures, the grain refinement is usually associated with the formation of a large amount of lattice defect, such as dislocations, grain boundaries, and vacancies [10]. The higher the dislocation density, the smaller the grain and crystallite [10]. The high pressure used during severe plastic deformation has a strong influence on the defect structure, and the lattice defects formed during severe plastic deformation facilitate precipitation, therefore influencing the phase composition of the alloys [10]. Due to the Gibbs-Thomson effect, the volume fraction of secondary phase nanoparticles is influenced by the energy of interfaces and the size of the particles [10].

Equation 10. Gibbs-Thomson equation for particles [10]

$$\Delta T_m(x) = T_{mB} - T_m(x) = T_{mB} \left(\frac{2\sigma_{sl}}{H_{f\rho_s r}} \right)$$

3.3 Shear strength

In a study of interfacial mechanical properties of concrete, nanomaterials were added and the shear strength was then tested. The study showed that low dosages of CNTs can remarkably increase the interfacial shear strength. The maximum improvement was achieved at a dosage of 0.2 wt% [30]. From this study, it was concluded that the maximum tensile and shear strength improvements were 51% and 53% from the use of CNTs, and SEM images indicated that the nanomaterials modified RAC interfaces showed a denser microstructure [30]. Overall, nanomaterials helped this material to have a stronger tensile and shear strength.



Figure 12. Relative interfacial shear strength modified by NS and CNT of various dosages [30]

3.4 Elongation

The shape elongation of nanoparticles was first observed by D'Orleans in 2003 [2]. At this time, large nanoparticles were required because they thought only large nanoparticles had elongation [2]. Elongation differs for every nanoparticle; however it seems that the elongation does not seem to have any positive effect on the mechanical or chemical properties of other materials. At this time, it is very challenging to find the elongation of a nanoparticle, and it requires more studies and research.

Nanomaterial of different dosages

3.5 Young's modulus

Many fundamental properties of nanoparticles are both difficult to understand and are still unknown. Properties such as thermodynamics and elasticity along with temperature dependence determine the stability of nanoscale devices [22]. The variation of Young's modulus and vibrational frequency is computed with the size of the metallic nanostructures of different shapes and have different dimensionality [22]. For studying the size, shape, and dimensionality dependence of Young's modulus, this equation is used:

Equation 11. Expression of Young's modulus [22]

$$\frac{Y_N}{Y_B} = \left(1 - \frac{1}{\frac{12D}{D_0 - 1}}\right) \exp\left(-\frac{2\lambda S_b}{3R} \frac{1}{\frac{12D}{D_0 - 1}}\right)$$

 $Y_N = Young's moduli for nanoparticle$ $Y_B = Young's moduli for bulk particle$ $D_0 = 2(3 - d) * h$ D = diameter $S_b = bulk vibrational entropy$

There may be a positive or negative sign in the expression depending on the orientation.

3.6 Modulus of rigidity

Sliding friction between particles normally occurs when the particle is not spherical in shape and has low adhesion to the tribopair surfaces [11]. In this case, nanoparticles play a role as a spacer to minimize direct contact between two shearing surfaces [11]. The rigidity of the tribopair surfaces and the interaction forces between particles are important for particle motion [11]. Nanoparticles are ultimately very important for lubrication and influencing the tribological particles of lubricated systems.

3.7 Ductility

The ductility of nanomaterials can be enhanced through cooperative dislocation emission from cracks and grain boundaries [8]. Grain size significantly impacts the dislocation emission [8]. Grain boundary sliding can toughen a nanocrystalline material even though it surpresses dislocation emission. With increasing grain size, the main dislocation source can transform from grain boundaries to crack tips [8]. This is where nanomaterials come in to enhance the ductility of these materials

3.8 Impact strength

Nanomaterials can be even used in the dental industry. Nanomaterials were used in resins to reduce the accumulation of bacteria on the surface of dental prostheses, which can ultimately lead to systemic disease [6]. In a study, nanomaterials greatly helped the amount of bacteria, P. aeruginosa, in the resins. However, the nanomaterials had no effect on the impact strength, even sometimes reducing it [6]. Therefore, nanomaterials will most likely not help other materials with their impact strength in the future.

Source of	Sum of Squares	df	F	Р
Variation	_	-		
Corrected	152575.683	5	376.137	< 0.001
model				
Intercept	552000.417	1	6804.086	< 0.001
Concentration	151065.433	2	931.034	< 0.001
Resin	464.817	1	5.729	0.020
Concentration	1045.433	2	6.443	0.003
x Resin				
Error	4380.9800	54		
Total	708957.000	60		
Corrected total	156956.583	59		

Table 3. ANOVA for effects of incorporation of β -AgVO₃ and type of acrylic resin on impact strength [6]

3.9 Fatigue resistance

In a research experiment studying the fatigue of asphalt binders when introduced to CNTs, it is found that a higher content of CNT can improve the fatigue resistance [33]. This is an interesting study because it shows how useful nanomaterials can be for multiple different uses. Overall, nanomaterials were a success when fatigue resistance was testing, and therefore will most likely be helpful with fatigue resistance in other materials in the near future.

3.10 Hardness

Figure 13. The effects of the content of nano-Al₂O₃ on the fracture toughness and hardness of a ceramic tool material [36]



Figure 13 shows the variation law of fracture toughness and hardness with the increase of nano-Al₂O₃ content [36]. The fracture toughness and hardness decrease after the initial increase. However, when the Al₂O₃ content reaches 4 vol. % its fracture toughness and hardness reach the maximum [36]. This figure overall shows that adding a lot of nanoparticles can reduce the mechanical properties. Unfortunately, the introduction of nanomaterials doesn't always make the mechanical properties better.

3.11 Failure Analysis and Prevention

Throughout this report, one can see that nanomaterials can be very good for many reasons. However, there are a few aspects where nanomaterials did not help, and therefore should probably be prevented in further studies. For example, nanomaterials did not influence impact strength in a positive way, actually reducing it. In a certain instance, this could end very bad if it is used for the wrong purpose. Additionally, nanomaterials did not seem to help the hardness of a material in a positive way either, actually reducing the material's mechanical properties. Again, this could end poorly if used in the wrong manner. However, nanomaterials did improve a lot of properties of materials drastically and could be of great help in the future for many purposes, from dental hygiene to building bridges.

4. Manufacturing Process

Manufacturing nanomaterials comes with a lot of prior knowledge including physics, biology, chemistry, materials science, and engineering [5]. The manufacturing of nanomaterials depends on cooperation between academia and industry in order to be informed about current needs and future challenges [5]. A common method for the production of nanoparticles is the aerosol based processes. An aerosol is a system of solid or liquid particles suspended in air or other gaseous environments [5]. These particles can range in size. As an example of this type of manufacturing, pigments as carbon black particles and titania were used as reinforcements for car tires and for the production of paints and plastics [5]. Another way to manufacture nanoparticles is by molecular or atomic condensation, which has been around since the 1930's (mfr). For this type of manufacturing, the main parts are a vacuum chamber consisting of a heating element, the metal to be vaporized, powder collection equipment, and a pumping system [5]. A bulk material is heated in a vacuum chamber and produces steam, which is directed to a chamber filled with inert or reactive gas (mfr). The pressure of the gas is high enough to then promote particle formation (mfr). After this, rapid cooling of these particles leads to the formation of nanoparticles [5].

5. Materials and Environment

Natural nanomaterials are in 97% of our environment, and they do no harm to humans [16]. However, synthetic nanomaterials are considered to have a horrible effect on the environment as a whole [16]. The extensive use of synthetic nanomaterials in all aspects make them more likely to be in our atmosphere, water sources, soil, and landfill waste [16]. Therefore, it is crucial that researchers understand the effects and behavior of each nanomaterial before use, as it is just recently studied. It is also important to understand the effects of nanomaterials on human beings before use, as they are beginning to be used in the medical field. Nanomaterials can have a very positive effect on medicine and medical studies; however it must be made sure that they are safe first.

6. Cost Analysis

Since nanomaterials are a new study, there are going to be more expensive than materials scientists and researchers already know everything about. As discussed in the previous section, it is important to note that one must know the effects and safety of the material to the environment and to human beings before use of it. Because of this, the use of nanomaterials at this point in time is going to be more expensive. The cost will mostly go towards the study of it, however, as of right now, there is not a cost analysis on the use of it due to it being such a new thing. After research and studies, it may be found that nanomaterials are not very costly to make, or it may be found that they are very expensive. The complex manufacturing process of nanoparticles and then nanomaterials may lead one to believe that it could be a costly process.

Summary

Overall, nanomaterials could be very beneficial to many different platforms, ranging from the medical field to construction. Nanomaterials deem to be very helpful towards many aspects, such as mechanical to chemical properties of materials. There is still a lot of unknown with nanomaterials, which is or will be studied in the future. One of the most important aspects I believe that should be studied is the effect on the environment and human beings, as there is still not very much information on that aspect. It will be very interesting to see how nanomaterials evolve over the next few years through research and studies.

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