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Selection of Different Nanomaterials and Their Fabrication Techniques in the Defence, Automotive and Computing Sectors

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ABSTRACT
Nanomaterials and nanotechnologies are an emerging field of study. Their peculiar size-dependent properties make nanomaterials extremely useful in a wide variety of applications. This report reviews the potential and existing applications of nanomaterials in 3 such fields- defense, automotive, and computing industries.
Keywords: CNT, fabrication, nanoscience, nanotechnologies, silicon ICs

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I. INTRODUCTION

Before jumping into the applications of nanotechnologies, it is important to define a few terms like "nanoscience", "nanoscale", and "nanomaterials". Owing to the range of dimensions and applications, there is no precise universal definition for any of these nano- terms. However, the following definitions provide the framework around which the study can be centered.

Nanoscience can be defined as the study of objects with size less than 100nm at least in one dimension. It refers to the study, manipulation and engineering of matter, particles, and structures on the nanometer scale.

Nanotechnologies are the design, characterization, production, and application of structures, devices and systems by controlling their shape and size at the nanometer scale. Nanotechnologies basically exploit the unique size-dependent properties of nanomaterials for a wide variety of applications.

Nanomaterials can be defined as the materials which have at least one of their dimensions in the range of 1-100 nm.

Nanoscale is defined as one-billionth of a meter. That is to say, 1 nanometer equals 0.0000000001 meter.

1.1 The Unique Behavior of the Peculiar Scale

What makes this scale of length unique? Why do nanomaterials possess properties different than those of bulk materials or atomic scaled materials? The answer lies in Quantum Mechanical Effects.

At nanoscale, the properties of materials- mechanical, electrical, thermal, and optical- are influenced by the quantum effects; that is to say, at nanoscale, the classical laws applicable to the macroscale fail. Various effects that are unique to the quantum laws of mechanics are observed at the nanoscale. This has significant impact on the properties of nanomaterials, making them different from the bulk materials at the macroscale. Moreover, the nano-dimensions are still bigger than the atomic or molecular dimensions; this makes the nanoscale a gradient factor between the macro and the atomic worlds. Thus, owing to their gradient mid-position between atomic and macro dimensions, nanomaterials possess unique properties, rendering them useful for a wide variety of applications.

II. PROPERTIES RELEVANT AT NANOSCALE

1. Due to their smallness, the mass of nanomaterials is extremely small. This makes gravitational forces negligible; electromagnetic forces are dominant in determining the behavior of nanomaterials.
2. An important phenomenon dominant at the quantum scale is the wave-particle duality. [1]

2.1 EFFECTIVE SCREENING MASS PARAMETER

ESMP, denoted by α, is related to the mass density ρ of a particle by the
following relation:

$$\alpha=1-(1-\rho)^3$$

This implies that the size of a nanoparticle determines whether classical behaviors will be dominant or quantum effects. The greater the size of a nanoparticle, the closer it is to a classical particle.

2.2 UNCERTAINTY PRINCIPLE FOR NANOPARTICLES

The famous Heisenberg uncertainty principle is given by the relation:

$$\Delta p \cdot \Delta x \geq \frac{\hbar}{2}$$

For nanoparticles with ESMP α, the uncertainty principle is modified as follows:

$$\Delta p_x \alpha \cdot \Delta x \geq \frac{\alpha\hbar}{2}$$

Thus, the uncertainty principle is dependent on α applicable to nanoparticles, and completely inapplicable to materials at the macro scale.

3. A significant role in impacting properties of nanomaterials is played by Quantum-Confinement Effect. Quantum confinement effect is essentially the restructuring of discrete energy levels of electrons due to reduction geometric parameters. When the size of a nanoparticle approaches the Bohr exciton radius, the energy gap between its conduction and valence band increases. Thus, it can be said that quantum-confinement effect plays a major role in making the properties of nanoparticles size-dependent.

4. Another very important characteristic of nanomaterials is the increase in their surface area-to-volume ratio. The large surface area-to-volume ratio of nanoparticles signifies that their surface area is maximized, and hence, so is their reactivity and ability to cover a larger surface area in a single coating. This has important applications in the automotive industry, as we shall see in the later sections.

These properties of nanoparticles have important roles to play in various applications, as we shall see in the sections ahead.

III. NANOTECHNOLOGIES IN THE DEFENCE SECTOR

The defense sector, especially in India, is in need of radical technological advancements. An Indian soldier today faces numerous problems- from bullet injuries and biohazards to strenuous travel through remote and inhospitable places with heavily loaded backpacks. While largescale modernization in terms of anti-aircraft missiles and advanced launchers is extremely important, it is equally important to focus on the smaller scaled developments in terms of textiles and small arms. Nanotechnology has the potential to solve many of these small scaled issues.

3.1 Nanotechnological Textiles

Nanomaterials are known to have properties like:

1. Increased surface area-to-volume ratio
2. High tensile strength
3. Improved wear resistance
4. Light weight
5. Enhanced flexibility

All these properties make it a potential material for textiles. The following could be the enhanced features of nanomaterial-textiles:

1. Micro body and environment sensors embedded in the uniform could enhance the environmental and situational awareness of soldiers.
2. Nano-sensors with thermal adjustability and sensing integrated in a smart-suit or smart-helmet can enhance the thermal imaging capabilities; replacing thermal imagers with such smart-suits or smart-helmets reduces the load carried by a soldier in recon and CASO operations.
3. Quantum Dots are well-known for their ability to change the color (wavelength) of light emitted by changing their dimensions. A quantum dot of a material X emits larger wavelengths at higher dimensions. As the dimensions of the same QD made of material X is reduced, the wavelength of light emitted, and thus the color of light emitted, changes. This ability of QDs can be used to make smart-suits with the capability to change colors, thereby providing an enhanced switchable camouflaging ability for day- and night-time operations.
4. Nanomaterials can be used to make textiles that provide enhanced protection from micro-sized viral and chemical elements, thus providing smart-suits with biological and chemical protection.
5. Nanomaterials can be used to make flexible antiballistic textiles that provide better protection from bullets than the current bullet proof vests being made of Kevlar.
6. Additionally, nanomaterials can be used to bring about functionalities like breathability, water repellence and UV protection.

Properties of nano textiles	Nanomaterials
electro conductive/antistatic	• „Carbon black" • Carbon nanotubes (CNT) • Cu • Polypyrrole • Polyaniline
increased durability	• Al_2O_3 • CNT • Polybutylacrylate • SiO_2 • ZnO
antibacterial	• Ag • Chitosan • SiO_2 (as matrix) • TiO_2 • ZnO
self-cleaning/ dirt and water repellent	• CNT • Fluoroacrylate • SiO_2 (as matrix) • TiO_2
moisture-absorbing	• TiO_2
improved staining/ reduced fade	• „Carbon black" • Nanoporous hydrocarbon-nitrogen coating • SiO_2 (as matrix)
UV protection	• TiO_2 • ZnO
fireproof	• CNT • Boroxosiloxane • Montmorillonite (Nano-clay) • Sb_2O_3
controlled release of active agents, medicinal products or fragrances	• Montmorillonite (Nano-clay) • SiO_2 (as matrix)
Luminescence	• no information
heat conductive/isolating	• CNT

Fig 1: Nanomaterials and associated properties

As can be seen from Fig 1, there are various nanomaterials that can be used in nano-textiles with enhanced and new functionalities. As a matter of fact, there are currently bullet proof vests being made which consist of Carbon Nanotubes, because the tensile strength of CNT is known to be ~100 times that of steel!

In this report, we will only look at the fabrication of CNT for textiles that have enhanced functionality.

1.2 CNT-based Nano-Textiles: Properties and Fabrication

Carbon nanotubes can produce textiles with the following properties:

1. Fireproof behavior, making them suitable as bullet-proof and operational overalls.
2. Increased durability, which will improve the lifetime of overalls.
3. Water and dirt-repellence, which is necessary for hygiene and sanitation of soldiers, as they often spend months together in remote, potentially hazardous conditions.
4. Heat conductive and isolating materials to keep the fabrics breathable and comfortable with respect to seasonal and daily weather changes.

CNTs are fabricated by the following methods:

1. Electric arc discharge method: a DC electric charge is established between a pair of water-cooled graphite electrodes in an inert helium atmosphere at approximately 66.66 kilo pascal. The anode gets consumed and produces sublimated material that gets deposited onto the cathode and the surface walls.

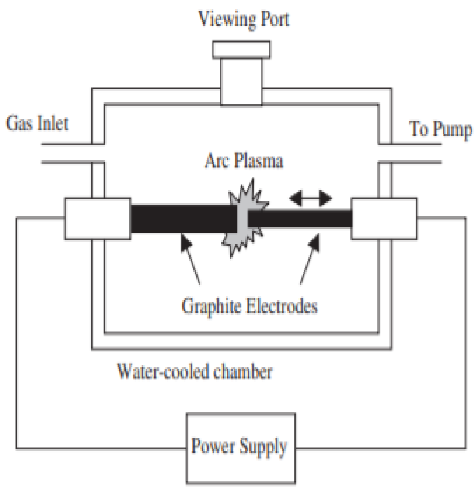

Fig 2: Schematic representation of arc deposition method

2. Laser vaporization: a solid graphite target is mounted on a quartz tube and placed in a temperature-controlled oven. The target is then subjected to an incident single- or double-pulsed Nd:YAG laser. A carbon-based soot is obtained, along with well-graphitized MWNTs. This method can also be used to fabricate SWNTs by using graphite target doped with appropriate transition metal catalyst.

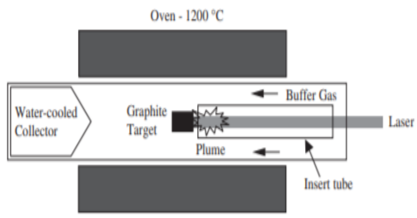

Fig 3: Schematic representation of laser vaporization method

3. Catalytic decomposition of hydrocarbons: often known as Chemical Vapor Deposition, or CVD, this technique has an upper hand over the other 2 methods in the sense that CVD allows continuous operations while laser-vaporization and arc methods are batch processes. Thus, CVD allows

faster production of CNTs. The basic procedure involved in CVD is: Gas-phased hydrocarbons undergo pyrolysis to obtain carbon molecules in vapor phase. These carbon-rich vapors are transported to a substrate onto which the layer needs to be deposited. Finally, either by mechanical or chemical means, the vapor is condensed such that it gets deposited on the substrate.

Fabricating CNT-Fibers (CNTF)

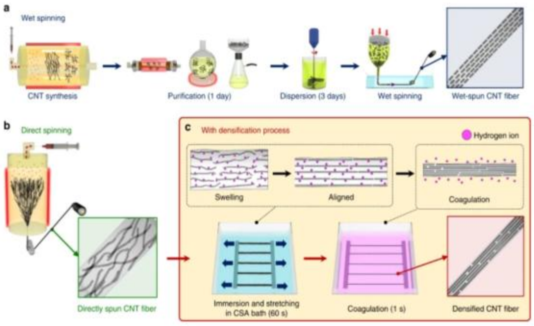

Fig 4: (a) shows wet spinning method of fabrication; (b) shows direct spinning method of fabrication.

1. Wet Spinning: the synthesized CNT is left in the reactor for an extended period to obtain vertically aligned nanotubes in an aerogel web. It is then purified and dispersed; following this, it is wet-spun. Thus, wet-spun CNT fibers are obtained.
2. Direct Spinning: the process of spinning occurs in the reactor that produces CNT. The directly spun CNT fibers are not aligned and need to be coagulated and densified.

CNT and CNT nanocomposite-containing textiles provide greater functionalities and are suitable for the rugged military conditions.

IV. NANOTECHNOLOGIES IN AUTOMOTIVE SECTOR

Nanotechnologies have already had great impact on battery and fuel cell functions of automobiles. In this report, we will focus on the application of nanomaterials for developing coatings and paints that provide self-cleaning, water-repellence, dust-resistance, corrosion resistance and potentially even scratch resistance. The corrosion resistant property of nano-coatings will particularly have advantageous impacts for ships and marine equipment.

4.1 Micro Arc Oxidation (MAO) Coatings

MAO is a method used for producing ceramic coatings on surfaces of certain metals and alloys like aluminum, magnesium, titanium, zirconium and beryllium. It is essentially a surface treatment method based on the anodizing electrochemical reactions that occur on the surface of a metallic surface.

The part to be coated, referred to as the target, is immersed in a base electrolyte. This target is electrically connected to act as an electrode. The base electrolyte consists the substances required to form the ceramic coating. The wall of the bath, or another inert material like stainless steel, acts as the other electrode. Potentials of over 200 V are applied between the 2 electrodes. It leads to the decomposition and deposition of the coating material from the electrolyte to the target.

Adding specific nanomaterials in the base electrolyte have greater impact on the properties of the coating, resulting in superior wear and corrosion resistance. The following experimental example of MAO-Al_2O_3 coating carried out by Çağatay Demirbaşa , Aysun Aydaya [2] demonstrates the impact of nano-Al_2O_3 additives in the MAO-base electrolyte.

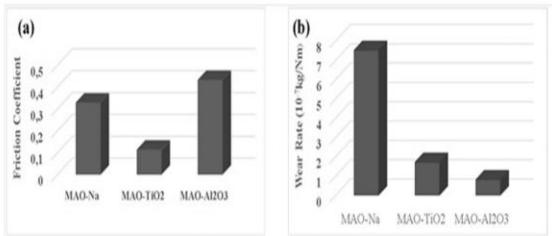

Fig 5: (a) Friction Coefficient of MAO-Na vs MAO-Al_2O_3 ; (b) Wear Rate of MAO-Na vs MAO-Al_2O_3

As is seen from the graphs, the coating with nano-Al_2O_3 had superior wear and friction properties.

Sample codes	Electrolyte components (g/l)	Nano-Al_2O_3(g/l)	Nano-TiO_2(g/l)	Electrolyte (pH)	Electrolyte conductivity (ms/cm)	Micro Hardness ($HV_{0.1}$)
Non Additive (MAO-Na)	(8,75) Na_2SiO_3/ (1,25) NaOH / (0,6) $Na_2B_4O_7$	-	-	12±0.1	11,5	520±10
MAO-TiO_2	(8,75) Na_2SiO_3/ (1,25) NaOH / (0,6) $Na_2B_4O_7$	-	(3,75)	12,3±0.1	14	580±10
MAO- Al_2O_3	(8,75) Na_2SiO_3/ (1,25) NaOH / (0,6) $Na_2B_4O_7$	(3,75)	-	12,3±0.1	14	635±10

Table 1: MAO constituents and their micro hardness value

MAO-Al_2O_3 coating shows better micro hardness than normal MAO coatings.

4.2 Fabrication of Nano-Al_2O_3

The methods of obtaining Al_2O_3 at nano scale include:

1. Grinding alumina particles of nano-dimensions (10-50 nm) by planetary ball milling with milling particles of size less than 0.1 µm.
2. Decomposing fresh chemically obtained AlOOH or $Al(OH)_3$ by rapidly achieving the

decomposition temperature of 175°C (448 K) at a pressure of about 5 bars (~500 kilo pascal) within a time period of thirty minutes to aluminium oxide. The size of nanoparticles obtained depends on the time required to attain the decomposition temperature- the faster the temperature is attained; the smaller will be the size of nanoparticles.

V. NANOTECHNOLOGIES IN COMPUTING

Computers today run on millions of electronic signals passing in multitudes of IC's, or Integrated Circuits. These IC's are basically silicon chips that consist of micro-scale transistors, which act as switches to allow or not allow an electrical signal to pass. The functioning of a computer depends upon the efficiency with which the electrical signals and voltages are regulated. While silicon has advantages of being easily available and machinable, nanomaterials such as CNTs can actually improve the efficiency of voltage regulation in computers.

As discussed above (see page 5), CNTs have superior properties:

1. CNTs have better mechanical, electrical and non-inflammable properties
2. CNTs are energy efficient

With these advantages in mind, and added benefits of cost effectiveness, CNTs are a potential replacement for silicon chips.

For fabrication of CNTs, see pages 6-7.

Furthermore, CNTs can also be seen as potential replacements for IC interconnects. The robustness and superior electrical properties of CNTs make them better than even copper wires.

VI. CONCLUSION

Nanotechnologies are advancing and developing rapidly. Efforts are on to commercialize more and more nano-products in multiple industries. While deeper research is still required to carry out risk-assessment and impact of nanomaterials on environment and health, it is certain that in the coming years, the market of nanomaterials and nanoscience will only increase.

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