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Abstract

Nanotechnology is gaining importance rapidly as a most powerful technology. Its immense potential promises the possibility of significant changes in near term future, once the most essential machines -called the Universal Assembler and the Nanocomputer are built. The present paper aims to reviews the previous work done and recent advancements in the field of nanotechnology. Today the products made using nanomaterials having general as well as special applications like treating cancer, phosgene detection, energy harvesting for self powered nanosystems, chip fabrication, batteries, aerospace materials etc.

Chitosan and its oligosaccharides, which are known to possess multiple functional properties, have attracted considerable interest due to their biological activities and potential applications in the food, pharmaceutical, agricultural and environmental industries. Many researchers have focused on chitosan as a potential source of bioactive materials in the past few decades. This review focuses on the biological activities of chitosan and chitooligosaccharides based on our and others' latest research results.

Keywords— Nanotechnology, universal assembler, biological activity, chitosan, chitooligosaccharides.

1. Introduction

Nanotechnology and research on this area are becoming more and more popular every day. The emerging field of nanoscience and nanotechnology is leading to a technological revolution in the new millennium. The application of nanotechnology has enormous potential to greatly influence the world in which we live ^[1]. From consumer goods, electronics, computers, information and biotechnology, to aerospace defence, energy, environment, and medicine, all sectors of the economy are to be profoundly impacted by nanotechnology. In the United States, Europe, Australia, and Japan, several research initiatives have been undertaken both by government and members of the private sector to intensify the research and development in nanotechnology.

The prefix 'nano' means a billionth. The size of a nanomaterial is always less than 100 nm. If it is greater than 100 nm, then it's a bulk material. The radius of a nanomaterial ranges from 1 nm to 100 nm. The radii of atoms most of the molecules are less than a nanometer. A cluster of 1 nm radius has approximately 25 atoms. The diameter of a human hair is 75000 nm. The diameter of a Hydrogen atom is 0.1 nm and it's nucleus is of 0.00001 nm.

2. History

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. Nanotechnology is a relatively recent development in scientific research. On December 29, 1959, at an American Physical Society meeting at Caltech, the American physicist Richard Feynman lectured, "There's Plenty of Room at the Bottom," which is often held to have provided inspiration for the field of nanotechnology.

In 1974 ,the Japanese scientist Norio Taniguchi of the Tokyo University of Science used the term "Nano-technology" conference to describe semiconductor processes such as thin film deposition and ion beam milling exhibiting characteristic control on the order of a nanometer ^[2]. He defined as "Nano-technology mainly consists of the processing of separation, consolidation, and deformation of materials by one atom or one molecule". However, the term was not used again until 1981 when Eric Drexler, who was unaware of Taniguchi's prior use of the term, published his first paper on nanotechnology in 1981^[3].

K. Eric Drexler developed and popularized the concept of nanotechnology and founded the field of molecular nanotechnology. He promoted the technological significance of nano-scale phenomena and devices through speeches and two influential books. In 1986, "Gerd Binnig" and "Heinrich Rohrer" won Nobel Prize in Physics for their 1981 invention of the Scanning Tunneling Microscope (STM)^[4]. Also, the term "nanotechnology" was independently applied by Drexler's book "Engines of Creation: The Coming Era of Nanotechnology" proposed the idea of a nanoscale "assembler" which would be able to build a copy of itself and of other items of arbitrary complexity. He also first published the term "grey goo" to describe what might happen if a hypothetical self-replicating machine, capable of independent operation, were constructed and released. Drexler's vision of nanotechnology is often called "Molecular Nanotechnology" (MNT) or "molecular manufacturing".

Nanotechnology and Nanoscience got a boost in the early 1980's with two major developments: the birth of cluster science and the invention of the Scanning Tunneling Microscope. These developments led to the discovery of Fullerene in 1985 and Carbon Nanotubes after some few years.

3. **Properties**

The nanoparticles show unique properties that change with their size. Classical Mechanics is able to explain properties of bulk materials but is unable to explain properties of nanoparticles. So, the Quantum mechanical principles have to be used to explain properties of the nanoparticles. Some of the properties of nanoparticles are listed below:-

3.1 **Optical properties**

The bulk materials and nanoparticle both have different colours.

e.g. Gold appears yellow in bulk while as appears bright red in colour.

3.2 Electrical properties

Consider a flat conducting plate having large length and width with small thickness. Suppose, the thickness of a plate is in nanometers. In this case, an electron will be confined along one dimension but will move freely along the remaining two dimensions. This phenomena is known as Quantum well. Consider a conducting wire having long length but the diameter of a wire is very small. In this case, an electron will freely along the length but confined in two remaining mutually perpendicular directions. This configuration is known as a Quantum wire. If all three dimensions of a conductor are in nanometer range, an electron will be confined in all three dimensions. This configuration is known as Quantum dot. The Coulomb staircase is as shown in fig.



Figure 1: Coulomb Staircase

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3.3 Magnetic properties

When bulk ferromagnetic materials are subjected to alternating magnetic fields, they show hysteresis while as nanosized ferromagnetic particles does not. The B-H curve for bulk ferromagnetic material and nanosized ferromagnetic particle are as shown in fig. 2 and 3 resp.



Figure 2: B-H curve for bulk ferromagnetic material



Figure 3: B-H curve for nanosized ferromagnetic material

3.4 Structural properties

The crystal structure of small nanoparticles observed to be same as the bulk material but with different lattice parameters.

3.5 Mechanical properties

The mechanical properties like hardness, elasticity and ductility depend upon the bonds between atoms. Imperfections in the crystal structure and impurities result in changes in these properties. The Carbon Nanotubes are 20 times stronger than steel.

4. Applications

- Electronics- in FET's, LED's, hard disks etc.
- Energy- in solar cells, rechargeable batteries etc.
- Automobiles- in body frames, paintings, coatings etc.
- Space- Aerogels used in spacecrafts, light weight suits and jackets.

- Medical- for treatment of cancers and tumours. They can be injected into the body and guided towards a specific part.
- Environmental- Nanoparticle based sensors used for detection of water and air pollution.
- Cosmetics- Zinc oxide and Titanium oxide nanoparticles used in sunscreen lotions.
- Nanoparticle based dyes and colours are used in hair creams and dyes.

5. Advances in Nanotechnology

5.1 **Chip Fabrication**

Extreme ultraviolet lithography will use mirrors to direct light with a wavelength of 13nanometers to print features at 32-nanometer scale. The smaller scale will yield chips that run much faster ^{[5].}

5.2 **Aerospace Materials**

There would be significant advantages of materials that are 100 times stronger than present materials. Objects made from these materials could be up to 100 times lighter, using 100 times less of quantity of substance ^[5]. By substituting diamond composite material, this factor could be increased to about 250. As a result, ultra light cars, trucks, trains, aircraft, and spacecraft would use far less energy, especially with atomically smooth surfaces to reduce internal friction and air resistance losses. Space transportation costs could be reduced considerably with use of the products of nanotechnology.

5.3 Energy Harvesting for Self Powered Nanosystems

There are energy harvesting technologies other than the well-known solar cell and thermoelectrics that have potential for powering nanosystems. The piezoelectric nanogenerators are developed using aligned ZnO nanowire arrays. This is a potential technology for converting mechanical movement energy (such as body movement, muscle stretching, blood pressure), vibration energy (such as acoustic/ultrasonic wave), and hydraulic (such as flow of body fluid, blood flow, contraction of blood vessel, dynamic fluid in nature) into electric energy for self-powered nanosystems ^[5]. A key advantage of nanodevices and nanosystems is that they usually operate at a very low power in the range from nW to \Box W.As a result, the energy harvested from the environment may be sufficient to power the system. Biochemical power sources are mechanical energy, vibrational energy, chemical energy (glucose), and hydraulic energy. If a small fraction of such energy could be converted into electricity, the energy may be sufficient to power small devices for biomedical applications.

5.4 Nanomesh and Nanofibres

This term covers CNT's and the other polymeric nanoscale fibers. They are currently used in air and liquid filtration applications. Using a process called "electrospinning" - or e-spin- a polymer "mesh" is formed into a nanofiber membrane, hence "nanomesh", with 150 - 200 nm diameters ^[5]. Some of them have been made since 1970, but were not called "nano" until recently. One potential use is "to prevent body tissues from sticking together as they heal. They also break down in the body over time like biodegradable sutures. The diameters of Vapor grown carbon fibers can vary from 100 to 500 nm.



Figure 4: SEM of Vapor grown fibres



Figure 5: Ultra-Web(R) nanofiber produced on a SEM

5.5 Nanoguitar

It is made for fun to illustrate the technology, the world's smallest guitar is 10 micrometers long, about the size of a single cell, with six strings each about 50 nanometers or 100 atoms wide.



Figure 6: Nanoguitar

6. Chitosan

6.1 Introduction

Chitosan is a nanoparticle that has been used extensively in the medical field as an adhesive and antibacterial agent. Chitosan has been investigated extensively as a potential drug carrier, due to it's biocompatible properties. Some studies have suggested using chitosan to coat nanoparticles made of other materials, in order to reduce their impact on the body and increase their bioavailability. The degree of deacetylation and the molecular weight of chitosan can be modified in order to obtain different physical and mechanical properties.

6.2 **Composition**

Chitosan is a linear polysaccharide composed of randomly distributed β -(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit)^[6]. It is made by treating shrimp and other crustacean shells with the alkali sodium hydroxide. The elemental composition of the chitosan polymer is carbon (44.11%), hydrogen (6.84%) and nitrogen (7.97%). Chitosan is soluble in acidic conditions - in solution the free amino groups on its polymeric chains can protonate, giving it a positive charge.



Figure 7: Chemical structure (a) of chitin poly (b) of chitosan (c) Structure of partially acetylated chitosan

6.3 **Properties**

activity The of chitosan depends its on weight, concentration, molecular degree of substitution, and the type of functional groups added to the chitosan, as well as the type of fungus. The derivatives of the chitosan can be created to target specific pathogens, chitosan shows natural antifungal activity without the need for chemical modification. Due to its poor solubility at pH more than 6.5, a number of chemically modified chitosan derivatives with improved water solubility can be used as well In addition, when fat and chitosan are eaten together, the viscous chitosan will entrap the fat droplets in the stomach. When the complex arrives at the small intestine, chitosan precipitates together with the entrapped fat at neutral pH to prevent the digestion of fat.



Figure 8: The IR spectrum of Chitosan and Chitosa fat compound. The absorption peak at 2924.69 m and 2854.81 cm were resulted from saturated

hydrocarbon radical. Absorption peak at 1744.38 cm⁻¹ indicated the existence of carboxyl ^[7]

6.4 **Solubility of chitosan**

A highly deacetylated polymer has been used to explore methods of characterization. The solution properties of a chitosan depend not only on its average DA but also on the distribution of the acetyl groups along the main chain in addition of the molecular weight. The deacetylation, usually done in the solid state, gives an irregular structure due the semicrystalline character of the initial polymer ^[8]. Examination of the role of the protonation of chitosan in the presence of acetic acid and hydrochloric acid on solubility showed that the degree of ionization depends on the pH and the pK of the acid. Solubilization of chitosan with a low DA occurs for an average degree of ionization a of chitosan around 0.5; in HCl, a 1/4 0:5 corresponds to a pH of 4.5–5. Solubility also depends on the ionic concentration, and a salting-out effect was observed in excess of HCl (1M HCl), making it possible to prepare the chlorhydrate form of chitosan. When the chlorhydrate and acetate forms of chitosan are isolated, they are directly soluble in water giving an acidic solution with pK0 1/4 670.1, in agreement with previous data and corresponding to the extrapolation of pK for a degree of protonation a 1/4 0. Thus, chitosan is soluble at pH below 6. The solubility of chitosan is usually tested in acetic acid by dissolving it in 1% or 0.1M acetic acid.

Study shows that the amount of acid needed depends on the quantity of chitosan to be dissolved. The concentration of protons needed is at least equal to the concentration of _NH2 units involved. In fact, the solubility is a very difficult parameter to control: it is related to the DA, the ionic concentration, the pH, the nature of the acid used for protonation, and the distribution of acetyl groups along the chain, as well as the conditions of isolation and drying of the polysaccharide. It is important also to consider the intra-chain H bonds involving the hydroxyl groups as shown below. The role of the microstructure of the polymer is clearly shown when a fully deacetylated chitin is reacetylated in solution; the critical value of chitosan DA to achieve insolubility

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in acidic media is then greater than 60%. In addition, solubility at neutral pH has also been claimed for chitosan with DA around 50%. Recently, a water-soluble form of chitosan at neutral pH was obtained in the presence of glycerol 2 phosphate. Stable solutions were obtained at pH 7 7.1 and room temperature, but a gel formed on heating to about 40 1C. The sol-gel transition was partially reversible and the gelation temperature depended slightly upon experimental conditions (Figs. 9 and 10).



Figure 9: Dynamic rheology giving the moduli G0 and G00 at 1Hz frequency as a function of temperature for a chitosan-glycerol-phosphate solution ^[8]



Figure 10: Dynamic rheological moduli for chitosan-glycerol 2-phosphate at pH ¹/₄ 7.19 at two different temperatures ^[8]

6.5 Applications

Applications of chitosan and chitosan derivative Table 1 summarizes the main properties of chitosan and potential biomedical and other applications that they imply. The great current interest in medical applications of chitosan and some of its derivatives is readily understood. The cationic character of chitosan is unique: it is the only pseudo-natural cationic polymer. Its film forming properties and biological activity invite new applications. Table 2 recalls the main applications of chitosan. The most important fields where the specificity of chitosan must be recognized are cosmetics (especially for hair care in relation to electrostatic interactions) (Table 3) and the pharmaceutical and biomedical applications on which we focus, which probably offer the greatest promise. Drug delivery applications include oral, nasal, parenteral and transdermal administration, implants and gene delivery.

Table 1: Principal properties of chitosan in relationto its use in biomedical applications

Potential biomedical applications	Principal characteristics
Surgical Sutures	Biocompatible
Dental Implants	Biodegradable
Artificial Skin	Renewable
Rebuilding of Bone	Film Forming
Corneal Contact Lenses	Hydrating Agent
Time Release drugs for Animals and Humans	Nontoxic, Biological Tolerance
Encapsulating Material	Hydrolyzed by Izosyme Wound Healing Properties, Efficient Against Bacteria, Viruses, Fungi

Table 2: Principal applications for chitosan

Agriculure	Defensive Mechanism in Plant
	Simulation in Plant Growth,
	Seed Coating, Frost Protection,
	Time Release of Fertilizers and
	Nutrients into the Soil

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Water and	Flocculant to Clarify Water
Waste	(Drinking Water, Pools),
Treatment	Removal of Metal Ions,
	Ecological Polymers
	(Eliminating Synthetic
	Polymers), Reduce Odors
Food and	Not Digestible by Human
Beverages	(Dietary Fiber), Bind Lipids
	(Reduce Cholesterol),
	Preservative, Thickener and
	Stabilizer for Sauces,
	Protective, Fungistatic,
	Antibacterial Coating for Fruit
Cosmetics and	Maintain Skin Moisture, Treat
Toiletries	Acne, Improve Suppleness of
	Hair, Reduce Static Electricity
	in Hair, Tone Skin, Oral Care
	(Toothpaste, Chewing Gum)
Biopharmaceuti	Immunologic, Antitumoral,
-cs	Hemostatic and Anticoagulant,
	Healing, Bacteriostatic

They can be used as antibacterial agents, gene delivery vectors and carriers for protein release and drugs. Chitosan nanoparticles used as a potential adjuvant for vaccines such as hepatitis B and piglet vaccine. They can be used as a novel nasal delivery system for vaccines. These can also be used as an additive in antimicrobial textiles for producing clothes for healthcare and other professionals. Chitosan is also used to prevent infection in wounds and quicken the wound-healing process by enhancing the growth of skin cells.

7. Conclusion

Nanotechnology is often referred to as a general purpose technology. The use of Nanotechnology is continuously transforming daily use products, making consumer goods plentiful, inexpensive and highly durable. Space travel and colonization will become safe an affordable with the advances that nanotechnology is bringing in aerospace materials. The nanotechnology will have a drastic impact on the human behavior and society.

Chitosan has the desired properties for safe use as a pharmaceutical excipient. This has prompted accelerated research activities worldwide on chitosan micro and nanoparticles as drug delivery vehicles. Chemical modifications of chitosan are important to get the desired physicochemical properties such as solubility, hydrophilicity, etc. The published literature indicates that in the near future, chitosanbased particulate systems will have more commercial status in the market than in the past.

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References

- 1. Kurapati Srinivas, Need of nanotechnology in education, Science Journal of Education.
- 2. Toumey, Chris (2008). "Reading Feynman into Nanotechnology: A Text for a New Science".
- Bassett, Deborah R. (2010). "Taniguchi, Norio". In Guston, David H. *Encyclopedia of nanoscience and society*. London: SAGE. p. 747. ISBN 9781452266176. Retrieved 3 August 2014.
- Drexler, K. Eric (1992). Nanosystems: Molecular Machinery, Manufacturing, and Computation. Wiley. ISBN 0-471-57518-6. Retrieved 14 May 2011.
- 5. Kuldeep Purohit, Pooja Khitoliya and Rajesh Purohit, Recent Advances in Nanotechnology,International Journal of

Scientific & Engineering Research, Volume 3, Issue 11, November-2012.

- Sunil A. Agnihotri, Nadagouda N. Mallikarjuna, Tejraj M. Aminabhavi Recent advances in Chitosan-based-micro and Nanoparticles in drug delivery. Division, Center of Excellence in Polymer Science, Karnatak University, Dharwad 580 003, India.
- Wenshui Xia, Ping Liu, Jiali Zhang, Jie Chen, Biological activities of chitosan and chitooligosaccharides, State key laboratory of food science and technology, Jiangnan University, Lihu Road 1800, Wuxi 214122, Jiangsu, PR China.
- 8. Marguerite Rinaudo- Chitin and chitosan: Properties and applications, CERMAV-CNRS, affiliated with Joseph Fourier University, BP53, 38041 Grenoble Cedex 9, France.

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