

Nano technology and its applications in fisheries

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Summary

Materials size below 100 nm size usually considered as nano materials and it is considered as an emerging area of science and technology last 20 years. The nano materials as powders, nanotubes or nano 2D sheets were extensively employed for different applications. Nano materials were synthesized either top to bottom or bottom-up methods. These materials were characterized by SEM, TEM, FT Raman and XRDs. Nano materials used mainly in fisheries to develop antifouling strategies, slow-release nutraceuticals, material protection from degradation and sensors.

Introduction

The term nanotechnology was coined by Prof Taniguchi, Japan in 1974 conference of the Japanese Society of Precision Engineering [1,2]. Nano technology is a domain of scientific activity oriented on synthesis, characterization, application of devices and materials and technical systems which functions at nano structures having 1 to 100 nm size [1]. Prof R. Feynman [3] American Physicist and Nobel Prize winner was the first person pointed out the importance and promising outlook for nano particles during his lecture entitled “There’s Plenty of Room at the Bottom. An Invitation to Enter a New Field of Physics,” delivered on December 29th 1959 at the California Institute of Technology. He pointed out that “... when we have some *control* of the arrangement of things on a small scale, we will get an enormously greater range of possible properties that substances can have, and of different things that we can do ... The problems of chemistry and biology can be greatly helped if our ability to see what we are doing, and to do things on an atomic level, is ultimately developed.” Later scientists realized the potential of nano particulate materials during the last decade has tremendous advancement in nano research. Governments and private sectors of the world invested huge sums to reap the benefits from novel applications of nano materials.

Nanotechnology

The principle of nano technology is that the material with known properties and functions at normal size exhibit different behaviour and functions at nano scale. By decreasing the size of the material, the surface area per unit material will increase enormously and this helps greater interactions with reactive sites. Nano technology implied that the process of fabricating and/ or controlling the material sized between 1 to 100nm.

Classification of nano materials

The 7th International Conference on Nanostructured materials recommended the following classification of nano materials

- Nano particles
- Nano porous structures
- Nano tubes and nano fibers
- Nano dispersions
- Nano structured surfaces and films
- Nano crystals and clusters.

Among the different types of nanomaterials, nanoparticles, nano tubes and nano fibres are the most economically important items and they are extensively used.

Carbon nano materials

The fullerene was discovered in 1985 by Robert Curl, Harold Kroto and Richard Smalley [3,4]. It is shaped like a football with an empty core. The number of carbon atom in fullerene was ranged from 20 to several hundreds. Simio Lijima [5-7] and it has quasi one-dimensional tube structures, which are formed by wrapping basic planes of graphite hexagonal lattice into seamless cylinders. CNT are single or multi layered and they can be opened and closed. These CNTs have an array of interesting magnetic, electronic and mechanical characteristics. It is light weight with higher strength and can conduct electricity better than copper. CNTs are extensively used in packaging material and added as additive to prepare anti-static packaging material. CNTs are considered as unique since it has stronger bonding between the carbon atoms and the tubes can have extreme aspect ratios. The characteristics of CNTs different and it depends on how graphene sheets rolled up to form the tube causing it to act either metallic or as a semiconductor. carbon nanotubes do not have free chemical bonds, therefore despite their small sizes, they do not display *surface* effects. CNTs are studied thoroughly and the countries like Japan commercially manufacturing hundreds of tons of CNTs.

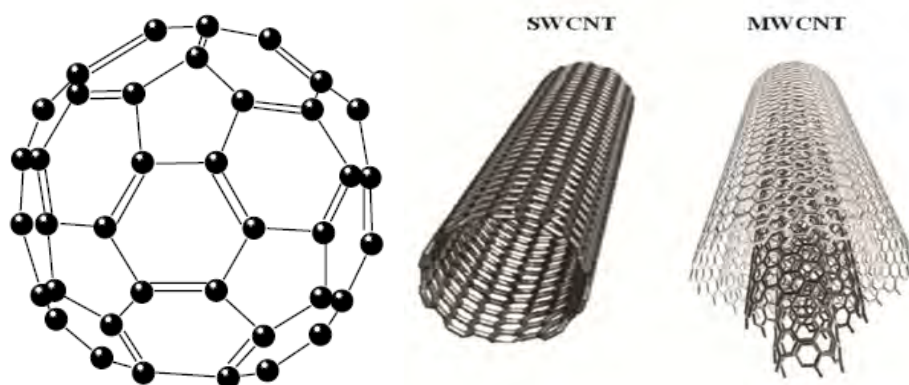


Fig 1. A) Fullerene C60 molecule B) SWCNT and C) MWCNT.

There are different types of carbon nanotubes viz single walled (SWCNTs) and multiwalled carbon nano tubes (MWCNTs). SWCNT has one layer whereas MWCNTs are having a collection of nested tubes of continuously increasing diameters. There may two or higher number of tubes or walls. Each wall is separated at a certain distance between the inner and outer tubes through interatomic forces. Carbon nanotubes are extensively applied for strengthening the rebar to concrete.

Synthesis of nano materials

There are two approaches used for the synthesis of nanomaterials, viz., top-down principle and bottom-up approach [5,6]. The bottom-up technology is based the development of nanomaterials of desired structure directly from “lowest level” elements (atoms, molecules, structure blocks etc). Here we have to identify the desired material in advance. The carbon nanotubes are synthesised by passing simple carbohydrates (eg acetylene) through a volume containing catalysts at a temperature of 600 – 800°C. CNTs are formed on the catalysts [7]. Development of nanomaterials from larger size particles to lower sizes is termed as top-down approach. Eg. Synthesis of nano cerium oxide from cerium chloride. Dilute solutions of cerium nitrate were oxidized using ammonia under controlled environment and then calcined at 400 oC will give nano cerium oxide.

Equipments for testing nanomaterials

The instruments used for characterization of nanomaterials are

Transmission Electron Microscopes

Scanning Electron Microscopes and its variants like Scanning Tunneling Microscope,

Near field Scanning Optical Microscope etc.

X – Ray Diffraction,

Atomic Force Microscopes

FT Raman spectroscope,

UV- Vis Spectrophotometers

Particle size analyser with zeta potential etc.

Characterisation of nano materials

Nanostructures have interesting features and physico-chemical characteristics and successful use of nanotechnology is possible only after a careful study of their properties. Some of the properties to be studied generally are mechanical, thermo physical, electrical, magnetic, optical and chemical properties. The details are available in different text books of nanotechnology.

Applications of nano technology

Material science: the major application in material science is the development of new materials. CIFT is doing research on development of new aluminium metal matrix composites by incorporating nano cerium oxide, nano samarium oxide, nano titanium oxide etc.

Antifouling strategies:

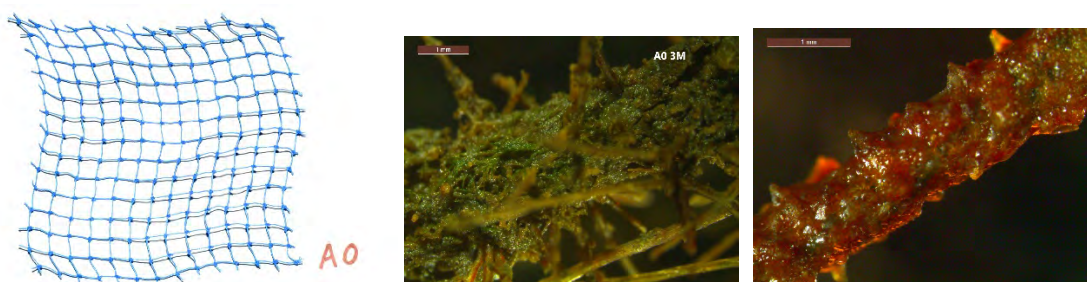


Fig 1. A) PE cage net b) PE cagenet after 3 months c) PE cagenet treated with PANI+nano CuO after three months exposure in the estuary.

Biofouling is a major problem in the aquaculture cage nettings and its management measures are very expensive. CIFT carried out research on nano material coated aquaculture cage nets and tests revealed that the coatings were efficient in preventing the biofouling in cage nets. Polyethylene cage nettings surface was modified with polyaniline and the nano copper oxide coating prevented the attachment of foulers.

Medicine and bio nanotechnology: Nano materials can be used for precise drug delivery, to the the targeted organs or body parts or tissues.

Nano sensors: Design of nano sensors and nano devices of autonomous or as administered inside the human body. This will help the recognition of molecules of specific types like cancer and its treatment [13-16]. Nano materials like gold and other organo polymeric composites were successfully employed for the development of thermochromic sensors, colourimetric sensors and electrochemical sensors for detection of contaminant in the human body or food products or adulterants. Nano engineered biodegradable material incorporated with insulin used for slow-release insulin to control blood glucose concentrations [18]. Applications of nano materials in medicine are like mucosal lining treatment [19,20] and inflammatory bowel treatment using nano pharmaceuticals [21].

Food science

Nano materials were potential to apply as food supplements for example, antioxidant nutrients may be included in nanocomposites, nanoemulsions, nanofibers, nanolaminates and nanofilms, or nanotubes etc.

Research in CIFT

Nano application in aquaculture cage nets

Nano copper oxide coated HDPE cage nets

Polyethylene fibres are extensively used to prepare the aquaculture cage nets. Polyethylene is non polar polymeric molecule and difficult to introduce the biocide over the molecule. Generally, biocide coatings were made over the cage nets using adhesives. The major disadvantages of biocides like copper oxide coating over the cage net is leaching to the aquatic environment and disposal of nets after use. The major advantage of nano materials as biocide very less quantity used, increased surface area of exposure and exhibit higher efficiency. Since polyethylene is non polar, we have undertaken different methodology to make the polyethylene surface polar. The surface was coated with in situ synthesised polyaniline, a conducting polymer. Over this surface nano copper coated and their characteristics were studied. Uniform coating of polyaniline and copper was showed by Scanning electron micrograph and Atomic force micrographs. The formation of the biocide was verified by analysing FTIR spectra [24]. Polyaniline coated polyethylene showed IR absorption was shifted from 1362 to 1396 cm^{-1} indicating the attachment of polyaniline over PE. Quinonoid peak of $\text{NH}_4^+/\text{NH}_2^+$ in polyaniline was exhibited at 1047/1161 cm^{-1} and the same was shifted further to 1070 / 1179 cm^{-1} due to nano copper coating over polyaniline.

To study the biofouling resistance of the treated net can be evaluated by different methods. The field evaluation of the cage net showed the excellent biofouling resistance after 90 days exposure in the estuarine environment. The experiment was repeated by constructing a cage with treated and control panels and exposed in the Vizhinjam coast for 7 months (fig 1). The fishes grown in the cages and controlled environments were compared and exhibited significant difference in growth was shown.



Fig 1. Control and treated net after 7 months exposure in the marine environments.

Different tests to verify the biofouling resistance are mentioned in detail by Ekbalad et al 2008. Deterrence of biofouling organisms to the treated surface was tested by cyprid assays. The treated surfaces were exposed to the testing organisms in natural or artificial seawater at controlled environments. Callow et al 1997 described assays using microorganisms like *Ulva* zoospore over the treated surface. The exposed surface in controlled environment were evaluated based on the attachment of spores. Callow et al and Schultz et al [25, 26] described about the determination of adhesive strength using a calibrated flow channel. Diatom assays were generally carried out using *Navicula perminuta* [27] by suspending the treated surface in artificial seawater containing chlorophyll a 0.30 $\mu\text{g ml}^{-1}$. After 2 h exposure the surface was evaluated for the adherence and deterrence of organisms. Antibacterial property of the biocide treated surfaces were evaluated using two marine bacteria viz. *Cobetia marina* and *Marinobacter hydrocarbonoclasticus* [28, 29]. The former bacteria are considered first settled microbes over marine exposed surfaces. The measurement was carried as per the protocols described by Akesso et al [28].

Societal Issues

As with any emerging technology, the full consequences of pervasive incorporation into society are currently unknown. For example, what are the outcomes if the byproducts of nanoshells or nanoparticles, or the nanoparticles themselves, used in cancer treatment enter circulation and healthy tissues and cells? Other issues like free radical formation during sun exposure [22], health environment and safety issued [23]. The ethical and legal ramifications of nanotechnology are primed for public consideration. The greater the awareness and understanding of nanotechnology among the society is essential for safe application and reaping the benefits. The society must be more informed about advantages and disadvantages of nanotechnology through public deliberations, discussions and suitable decisions by the public and government for brighter tomorrow.

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