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# Synthesis of nanoparticles by green chemistry process and their application in surface coatings: A review

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# ABSTRACT

Nanoparticles are in the size ranges from 10-100 nm. The appearance and usefulness of nanoparticles brings many advantages and opportunities to paint and coating industry. Addition of nanoparticles to coatings can improve many properties of coating system. These nanoparticles can be synthesized by physical, chemical and biological methods. Biological synthesis of nanoparticles provides advancement over chemical and physical methods as it is a cost effective environment friendly and no need to use high pressure, energy, temperature and toxic chemicals. Recent studies on the use of biological material in the synthesis of nanoparticles are a relatively new and exciting area of research with considerable potential for development. This paper attempts to explain ongoing research worldwide using microorganisms and plants in the biosynthesis of nanoparticles and their applications in coatings.

Keywords: Nanoparticles; Coating; Biosynthesis; microorganisms; plants.

## **INTRODUCTION**

Nanoparticles are at the leading edge of the rapidly developing field of nanotechnology. The development of reliable experimental protocols for the synthesis of nanoparticles over a range of chemical compositions, sizes, and high monodispersity is one of the challenging issues in current nanotechnology [1].

Various physical and chemical processes have been exploited in the synthesis of several nanoparticles. However, these methodologies remain expensive and involve use of toxic, hazardous chemicals which may pose potential environmental and biological risks. Therefore, there is a growing concern for the development of alternative environment friendly and sustainable methods. Increasing awareness towards green chemistry and biological processes has led to a necessity to develop simple, cost-effective and eco-friendly procedures [2]. In this regard the use of biological agents such as microorganisms and plants in the biosynthesis of nanoparticles and their applications holds immense potential.

All major paint and coating companies are investing huge amounts on their research and development sector to formulate paints and coatings which are compatible and suitable for today's aggressive environment. Though several companies have commercialized many new formulations of paints and coating products including: antibacterial, self cleaning, anti UV, anti scratch and anti corrosive coatings etc. but much potential still remains in this field as none is able to fulfill all these requirements in a single formulation. Nanotechnology in paint and coatings promises to fulfill various desire. The appearance and appliance of nanomaterials brings new opportunities to the coating industry.

Addition of nanoparticles to coatings can upgrade many properties of the conventional coatings and produces new multi-functional coatings.

#### **Properties of Nanoparticles:**

Nano-sized particles possess astonishing physical and chemical properties and have а number of fascinating potential applications in a wide range of industrial sectors such as electronics, magnetic and optoelectronics, biomedical, pharmaceutical, cosmetics, energy, environ-mental, catalytic, space technology and many others [3,4]. The unusual properties of nanoparticles such as hardness, rigidity, high yield strength, flexibility, ductility, are attributable to one of the most critical characteristics of nanoparticles which is high surface-to-volume ratio i.e. large fractions of surface atoms and thus surface properties dominate bulk properties. Another properties like the quantum size effect and macro-quantum tunneling effect that are related to their nano-size [5]. Indeed, the properties of nanoparticles may differ significantly from those observed for fine particles or bulk materials having the same chemical composition (e.g., lower melting points, higher specific surface areas, specific optical properties, mechanical strengths and specific magnetizations), properties that might prove attractive in various industrial applications. [6]. Moreover, some physicochemical properties of nanoparticles can be altered with their varying size. For instance, by decreasing the size, particles changethe color, semiconducting materials exhibit metallic pro- perties, and nonmagnetic particles become magnetic [7]. Therefore, the understanding of the sizesensitive properties of nanoparticles is essential from the scientific and technological view point. It is even more important to be able to efficiently model/predict such properties. However, how nanoparticle is viewed and is defined depends very much on the specific application.

#### Synthesis of nanoparticles:

Synthesis of nanoparticles involves the tailoring of materials at the atomic level to attain unique properties, which can be suitably manipulated for the desired applications [8].

Metal nanoparticles can be synthesized by physical, chemical and biological method. Although the physical and chemical methods produces a pure, well defined particles, these methods are not cost effective, not ecofriendly. One of the most important criteria of nanotechnology is that of the development of clean, nontoxic and eco friendly green chemistry procedures [9]. Hence, currently, there is a growing need to develop environmentally benevolent nanoparticles synthesis processes that do not use toxic chemicals in the synthesis protocol. Green chemistry procedures for synthesis of nanoparticles not only provides advancement over chemical and physical methods as it is environment friendly but also it is a cost effective and in this method there is no need to use highpressure, energy,temperature and toxic chemicals[10]. The use of environmentally benefits. During recent times several groups have achieved success in the synthesis of silver, gold, and palladium nanoparticles using extracts obtained from unicellular organisms like bacteria [11–14] and fungi[15–17] as well as extracts from plant parts, e.g., geranium leaves[18],neem leaves [19], lemon grass [20], aloevera [21] and several others[22–24]. The spectacular success in this field has opened up the prospect of developing bio-inspired methods of synthesis of metal nanoparticles with tailor-made structural properties.

#### A. Various methods for gold nanoparticle synthesis-

#### a) Plant mediated synthesis of gold nanoparticles:

Rapid and convenient method to reductively prepare gold nanoparticles using various plant extracts has been reported in the literature. Plant extract acts as a reducing agent for the gold nanoparticles. The production of gold nanoparticles has been done by the controlled reduction of the Au3+ ion to Au0.

Green synthesis of gold nanoparticles was reported by using variety of plant materials. *Achillea wilhemsii* flowers [25], ethanolic flower extract of the plant *Nyctanthes arbortristis*[26], *Mirabilis jalapa* flowers [27], *Coleus amboinicus* L. leaf extract [28], aqueous extract of cypress leaves [29], *Barbated Skullcupherb* extract[30], aqueous extract of rose petals [31], Leaf extracts of two plants *Magnolia kobus* and *Diopyros kaki* [32], Oat (*Avena sativa*) biomass [33], flower extracts of *Ixora coccinea* (Chetty flower) [34], *Azadirachta indica* plant leaf extract [35], ethanol extract of black tea and its tannin free fraction [36], Alfalfa plants [37], Coriander leaf [38], foliar broths [39], Soybeans [40], *Dioscorea bulbifera* tuber extract [41], *Cinnamonum zeylanicum* leaf. broth[42], *mucuna pruriens* plant extract [43]. Gold nanoparticles were also synthesized using banana peel extract (BPE) and its antimicrobial activity towards most of the tested fungal and bacterial cultures was described[44]. In another study, synthesis of gold nanoparticles using *Cassia auriculata* aqueous leaf extract has been carried out and proposed that,

the stabilizing and reducing molecules of nanoparticles may promote anti-hyperglycemic activity [45]. Biologically synthesized gold nanotriangles using tamarind leaf extract and potential application in vapor sensing is reported [46]. Pear fruit extract-assisted room-temperature biosynthesis of gold nanoplates is explained [47].

#### b) Bacteria mediated synthesis of gold nanoparticles:

Bacteria are among the most extensively exploited natural resources for synthesis of metallic nanoparticles. The key reason for bacteria preference for nanoparticles synthesis is their relative ease of manipulation. Different bacterial species were successfully used to reduce gold ions to a zerovalent metal. Gold particles of nanoscale dimensions may be readily precipitated within bacterial cells by incubation of the cells with Au3+ ions. The important parameter, which controls the size and shape of gold nanoparticles, was pH value. The results demonstrated that lower pH values and initial concentrations of Au (III) were individually responsible for reductions in nano-gold particle size.

Synthesis of gold nanoparticles by Magnetospirillum gryphiswaldense MSR-1 [48], Bacillus megatherium D01 [49], mesophilic bacterium Shewanella, [50], Rhodopseudomonas capsulata [51], Pseudomonas aeruginosa [52], Stenotrophomonas maltophilia [53], Escherichia coli and Desulfovibrio desulfuricans [54], marine alga Sargassum wightii Greville [55], marine microalga Tetraselmis suecica [56], marine bacterial strain of Marinobacter pelagius [57], Aqueous Extract of the Brown Algae Laminaria Japonica [58], alkalotolerant actinomycete (Rhodococcus sp.) [59]Bacterium Actinobacter spp[60] was reported.y-proteobacterium Shewanella oneidensis can reduce tetrachloroaurate (III) ions to produce discrete extracellular spherical gold nanocrystallites. The antibacterial activity of these gold nanoparticles was assessed using Gram-negative (Escherichia coli and S. oneidensis) and Gram-positive (Bacillus subtilis) bacterial species [61]. Biosynthesis of gold nanoparticles assisted by Escherichia coli DH5α and its application on direct electrochemistry of hemoglobin are reported[62].Bioaccumulation of gold by filamentous cyanobacteria (Plectonema boryanum UTEX 485) between 25 and 200°C was investigated[63].In another study a variety of microorganisms have been screened for their ability to accumulate and reduce gold ions to form nanoparticles. In addition, the possibility to manipulate the size and shape of gold nanoparticles by altering key growth parameters was described [64]. In one of the interesting studies, plectonema terebrans, a species of filamentous, marine cyanobacteria, was found to accumulate gold from a solution of AuCl<sub>3</sub>.H<sub>2</sub>O in its sheath (glycocalyx)[65].

## c) Fungus mediated synthesis of gold nanoparticles:

The metabolic activity of microorganisms can lead to precipitation of nanoparticles in external environment of a cell, the fungi being extremely good candidates for such processes. The extracellular synthesis of gold nanoparticles by the different species of fungus has been reported. A two-step mechanism was generally suggested. The first step involves trapping of Au+ ions at the surface of the fungal cells. In the second step, enzymes present in the cell reduce gold ions.

Synthesis of gold nanoparticles using the cell-free filtrate of fungus, *Sclerotium rolfsii* [66] extremophilic *Thermomonospora* sp. Biomass [67], fungus *Verticillium* sp.,[68], tropical marine yeast *Yarrowia lipolytica* NCIM 3589 [69], fungus *Trichoderma harzianum* [70] was reported in literature. Extracellular biosynthesis of gold nanoparticles using *Aspergillus niger*[71], extremophilic actinomycete, *Thermomonospora* [72] was described. Intracellular synthesis of gold nanoparticles by a novel alkalotolerant *actinomycetes, Rhodococcus* species [73], *Aureobasidium pullulans* (*A. pullulans*), *Fusarium* sp. and *Fusarium oxysporum* (*F. oxysporum*) [74] was also described. Absar and coworkers (2005) reported extra- and intracellular biosynthesis of GNPs by fungus *Trichothecium* sp. [75].Important advancement in the use of fungal proteins of *Coriolus versicolor* for the extracellular synthesis of functional gold nanoparticles was reported by [76].*Candida albicans*mediated biological synthesis of gold nanaoparticles and its potential in detection of liver cancer was investigated by [77].

Gold nanoparticles synthesized from the supernatant broth (SB) and live cell filtrate (LCF) of the industrially important fungus *Penicillium rugulosum* their conjugation with genomic DNA isolated from *Escherichia coli* and *Staphylococcus aureus* is described [78]. Microbial synthesis of gold nanoparticles using the fungus *Penicillium brevicompactum* and cytotoxic nature of prepared nanoparticles has been analyzed using mouse mayo blast cancer C(2)C(12) cells [79]. One of the studies represents an important advancement in the use of fungal enzymes for the biosynthesis of highly stable gold nanoparticles by using fungus *Phanerochaete Chrysosporium* [80].

#### **B.** Various methods for silver nanoparticle synthesisa) Plant mediated synthesis of silver nanoparticle:

Synthesis of nanoparticles through biochemical routes, using plant extracts as reducing and capping agents, has received special attention. synthesis of plant-mediated silver nanoparticlesby *Solanum torvum* [81], papaya fruit extract [82], *Withania somnifera* [83], leaves of *Euphorbia hirta* [84], *Nicotiana tobaccum* leaf extract [85], *Elettaria cardamomom*[86], *Opuntia ficus-indica*[87], onion (*Allium cepa*) [88]and their promising antimicrobial activity is reported. In another study, synthesis of silver nanoparticles using *Acalypha indica* leaf extracts and its antibacterial activity against water borne pathogens was examined by [89]. Green synthesis of small silver nanoparticles using Geraniol and its cytotoxicity against Fibrosarcoma-Wehi 164 were evaluated by [90].Synthesis of silver nanoparticles using *Dioscorea bulbifera* tuber extract and evaluation of its synergistic potential in combination with antimicrobial agents was studied by [91]. Green synthesis, antimicrobial and cytotoxic effects of silver nanoparticles using *Eucalyptus Chapmaniana* leaves extract was described by [92]. Biosynthesis of Silver nanoparticles using *Coriandrum Sativum* leaf extract and their application in nonlinear optics is reported [93].

Green synthesis of silver nanoparticles using aqueous leaves extracts of *Catharanthus roseus* (*C. roseus*) [94], *Euphorbia hirta* (*E. hirta*) plant leaf extract [95], *Eclipta prostrata*[96] *Nelumbo nucifera* leaf extract[97], *Mimosa pudica* Gaertn (Mimosaceae)[98] which has been proven active against malaria parasite. Acaricidal and larvicidal of synthesized silver nanoparticles (AgNPs) utilizing aqueous leaf extract from *Musa paradisiaca* L. (Musaceae) is reported [99].

Many plants such as Geranium leaf [100], Alfalfa sprouts [101], *Capsicum annuum* L. extract [102], *Boswellia ovalifoliolata* stem bark [103], *Gliricidia sepium* (Jacq.) [104], latex of *Jatropha curcas* [105], Cycas leaf [106], Switchgrass (*Panicum virgatum*) Extract [107], calli cells of *Citrullus colocynthis* (L.) Schrad [108], *Desmodium latifolium*[109], *Clerodendrum inerme*[110], dried leaves of *Pongamia pinnata* (L) Pierre [111], leaf extracts of *Euphorbia hirta* and *Nerium indicum*[112], and many weeds [113], [114], [115] have shown the potential of reducing silver nitrate to give formation ofsilver nanoparticles.

#### b) Bacteria mediated synthesis of silver nanoparticles:

In 1999, Klaus et al. [116] initiated the biosynthesis of silver nanoparticles by bacteria (*Pseudomonas stutzeri* AG259). Later on many other groups reported bacterial synthesis of silver nanoparticles. The extracellular production of Ag nanoparticles has been described by using psychrophilic bacteria [117], cell filtrate of *Streptomyces* sp. ERI-3[118], culture supernatant of *Bacillus licheniformis* [119], *Morganella* sp. [120].

Report on the synthesis of metallic nanoparticles of silver using culture supernatants of *Klebsiella pneumonia* and evaluation for their part in increasing the antimicrobial activities of various antibiotics against *Staphylococcus aureus* and *Escherichia coli*was evaluated[121]. Synthesis by using different species of bacteria such as, Enterobacteriaceae [122], *Lactobacillus* spp. [123], *Rhodococcus*sp. [124] was described earlier.Extracellular synthesis of silver nanoparticles (Ag NPs), by using *Pseudomonas aeruginosa* (MTCC 424), and their significant antimycotic activity against the common plant pathogenic fungi *Fusarium moniliforme* (MTCC 1848) and *Phoma glomerata* (MTCC 2710) was reported [125].Possible involvement of proteins in synthesizing Ag NPs was observed in filamentous *cyanobacterium*, *Plectonema boryanum UTEX* 485 [126],synthesis of silver using culture supernatants of *Staphylococcus aureus* and evaluation of its antimicrobial activity against MRSA and MRSE has been reported [127]. Onestudy reports the optimal conditions for maximum synthesis ofsilver nanoparticles(AgNPs) through reduction of Ag<sup>+</sup> ions by the culture supernatant of *Escherichia coli*[128].Extracellular biosynthesis of silver nanoparticles using *Bacillus subtillus* IA751 and antimicrobial properties of silver nanoparticles using *Escherichia coli*, *Staphylococcus epidermidis*, *Staphylococcus coagualase positive*, *Serratia spp.* and *Salmonella typhi*were investigated by [129].

# c) Fungus mediated synthesis of silver nanoparticles:

Shift from bacteria to fungus was leaded by Sastry and o-workers. They have opened the field to the synthesis of silver nanoparticle by eukaryotic organism like Verticillium sp. [130]. Among fungi *Aspergillus* sp. are the cost effective source of biomaterial for biosynthesis of silver nanoparticle. Extra cellular production of silver nanoparticles by *Aspergillus niger* and evaluation of its wound healing activity in experimental rat model is described [131]. Use of filamentous fungus *Phoma* sp.3.2883 [132], white rot fungus, *Phanerochaete chrysosporium* [133] in the synthesis of silver nanoparticle was reported. *Penicillium fellutanum* isolated from coastal mangrove sediment [134], aqueous extract from the compactin producing fungal strain*Penicillium brevicompactum* WA

2315[135] and Aspergillus flavus [136] for silver nanoparticles production was reported earlier. Possibility of using marine yeasts to achieve a faster rate of silver nanoparticle synthesis supported[137]. Use of common fungus, Alternaria alternate for extracellular biosynthesis of silver nanoparticles and evaluation of these nanoparticles for their part in increasing the antifungal activity of fluconazole against Phoma glomerata, Phoma herbarum, Fusarium semitectum, Trichoderma sp., and Candida albicans reported [138]. A simple and effective approach to aqueous based biosynthesis of silver nanoparticlewas demonstrated and the effect of temperature on controlling size of silver nanoparticlewas studied [139].Controlled and up-scalable biosynthetic route to nanocrystalline silver particles with well-defined morphology using cell-free aqueous filtrate of a non-pathogenic and commercially viable biocontrol agent Trichoderma asperellum is being reported for the first time[140]. Mycosynthesis of silver nanoparticles using the fungus Fusarium acuminatum and its activity against some human pathogenic bacteria examined[141]. Extracellular biosynthesis of silver nanoparticles employing the fungus Penicillium [142], Cladosporium cladosporioides [143], Fusarium oxysporum [144], Aspergillus fumigates [145], Trichoderma reesei [146], Fusarium semitectum [147], silver-tolerant yeast strain MKY3 [148], has been reported. In another study the use of the fungus Trichoderma viride for the extracellular biosynthesis of silver nanoparticles, their synergistic effect with antibiotics and study against gram-positive and gram-negative bacteria was investigated [149]. In another investigationextracellular biosynthesis of silver nanoparticles using fungi Penicillium diversum and their antimicrobial activity against Escherichia coli, Salmonella typhi, Vibrio cholerae and the clinical isolate of Paratyphia was investigated [150].

#### C. Various methods for titanium dioxide nanoparticle synthesisa) Plant mediated synthesis of titanium dioxide nanoparticle:

Biosynthesis of titanium dioxide nanoparticles by Nyctanthes leaves extract [151], Eclipta prostrata leaf extract [152], *Annona squamosa* peel extract [153], aqueous extract of *J. curcas* latex [154] was reported. Assessments of the antiparasitic activities of synthesized titanium dioxide nanoparticles utilizing aqueous leaf extract of *Catharanthus roseus* against theadults of hematophagous fly, *Hippobosca maculata* Leach (Diptera: Hippoboscidae), and sheep-biting louse, *Bovicola ovis* Schrank (Phthiraptera: Trichodectidae) was reported [155]. Use of rice husk as non-metallic precursor to synthesize titanium dioxide and enhanced photocatalytic properties for dye degradation was evaluated [156].

## b) Bacteria mediated synthesis of titanium dioxide nanoparticles:

Titanium dioxide nanoparticle synthesis by using *Lactobacillus sp.* and *Sachharomyces cerevisae* [157], *Bacillus subtilis* [158] was reported. The nanotitanium dioxidewas synthesized biologically employing *Bacillus subtilis* (FJ460362). The results reveal that biogenic titanium dioxide nanomaterial acts as good photocatalyst [159]. *Actinobacter* spp. mediated bacterial synthesis of photocatalytically active and biocompatible titanium dioxide and zinc oxidenanoparticles was investigated [160].

## c) Fungus mediated synthesis of titanium dioxide nanoparticles:

Titanium nanoparticles produced by using fungus *Fusarium oxysporum* [161]. In another study, biosynthesis of titanium nanoparticles was achieved by using *Aspergillus flavus* as a reducing and capping agent and assessed the antimicrobial activity of fungus-mediated synthesizednanoparticles, which was proved to be a good novel antibacterial material [162].

## D. Various methods for zinc oxide nanoparticle synthesis-

## a) Plant mediated synthesis of zinc oxide nanoparticle:

Nanoparticle biosynthesis is an eco-friendly approach for recovering metals. Zinc oxide nanoparticles have beensynthesized using orange juice [163], aloe vera extract [164], *Citrus aurantifolia* extracts [165], and milky latex of *Calotropis procera* [166]. One of the studies reported the synthesis of zinc oxidenanoparticles from the plant rhizome of *Alpinia purpurata* and their antimicrobial activity was assessed [167].

The mixed copper and zinc oxide(Cu/ZnO) nanoparticles have been synthesized using *Brassica juncea* L. plants [168]. The synthetic method of synthesizing zinc oxidenanoparticles from Zn hyper accumulator plants (Physalis alkekengi L.) constitutes a new insight into the recycling of metals in plant sources, was described [169].

#### b) Bacteria mediated synthesis zinc oxide nanoparticles:

Extracellular production of metal oxide nanoparticles by *Streptomyces* sp. isolated from a site Pichavaram mangrove in Indiawas carried out. These nanoparticle showed promise when applied as a coating to the surface of protective cloth by reducing the risk of transmission of infectious agents [170].

The manganese and zinc nanoparticles successfully synthesized by using *Streptomyces* sp. HBUM171191 [171], *Lactobacillus sporogens* [172]. *Aeromonas hydrophila* mediated zinc oxidenanoparticleswere synthesized and proved to be a good novel antimicrobial material [173]. In one of the studies, use of bacterium, *Bacillus cereus* as a biotemplating agent for the formation of zinc oxide nanoparticles with raspberry- and plate-like structures was studied [174]. *Actinobacter* spp. mediated bacterial synthesis of photocatalytically active and biocompatibletitanium dioxide and zinc oxidenanoparticles were investigated [175]. Synthesis of metal oxide nanoparticles by a *Streptomyces* sp. and investigation on its antibacterial activity as a key factor in making it suitable for long life application in food packaging was reported [176].

#### c) Fungus mediated synthesis of zinc oxide nanoparticles:

19 fungal cultures were isolated from the rhizospheric soils of plants naturally growing at a zinc mine area in India. *Aspergillus aeneus* isolate NJP12 has been shown to have a high zinc metal tolerance ability and a potential for extracellular synthesis of zinc oxide nanoparticles under ambient conditions [177].

## E. Various methods for copper oxide nanoparticle synthesis-

# a) Plant mediated synthesis of copperoxidenanoparticle:

Copper nanoparticles were biologically synthesized using plant leaf extract of Magnoliaas a reducing agent and assessed its antibacterial activity [178]. Many other plants have also been used in synthesis of copper oxide nanoparticles. *Aloe barbadensis* Miller [179], latex of *Calotropis procera* L. [180],soybeans [181], *Manihot esculenta* leaf extract [182], common wetlands plants *Phragmites australis* and *Iris pseudoacorus* [183]. One of the studies investigated the antibacterial activity of copper oxide nanoparticles on E.coli synthesized from *Tridax procumbens* leaf extract [184].

## b) Bacteria mediated synthesis of copper oxide nanoparticles:

Biological method for extracellular synthesis of copper oxide nanoparticles using*Escherichia coli* (E. coli) [185],gram-negative bacterium belonging to the genus *Serratia* [186], and non-pathogenic bacterial strain *Pseudomonas stutzeri* isolated from soil[187] was reported. Aqueous phase biosynthesis of phase-pure metallic copper nanoparticles using a silver resistant bacterium *Morganella morganii* was investigated [188].Green synthesis of copper oxide by *Streptomyces* Sp. for development of antimicrobial textiles which can be useful in hospitals to prevent or to minimize infection with pathogenic bacteria was studied [189]. Facile biosynthesis of copper oxide nano particles by hydrolysis of copper precursor using bacteria *Phormidium cyanobacterium* was reported [190].

## c) Fungus mediated synthesis of copper oxidenanoparticles:

Extracellular production of copper oxide nanoparticles by using *Penicillium aurantiogriseum, Penicillium citrinum* and *Penicillium waksmanii* isolated from soil was reported [191].

## Application of nanoparticles in coating:

Nanotechnology applications in coatings have shown remarkable growth in recent years. This is a result of two main factors: 1) increased availability of nanoscale materials such as various types of nanoparticles, and 2) advancement in processes that can control coating structure at the nano-scale. Another important reason for this growth is the potential of nanotechnology to address many performance challenges presented by the vast range of products and structure that coatings are an integral part of. At a much smaller scale, coatings are used in numerous electronics products (both consumer and industrial electronics) and biomedical products. Coating layer thickness can vary from hundreds of micrometres (e.g., anti-skid coating on the deck of an aircraft carrier) to less than 100 nm (e.g., insulating coatings in microchips). Coating play one or more of three key roles in these applications: 1) improve products aesthetic appeal. 2) Protect the substrate from a wide range of abuses (e.g., damages due to scratches or impact, corrosion, long term weathering, and bio-fouling), and 3) provide specialized functionality to the product (e.g., conductivity, insulation, water repellency, and heat reflection). It is in the latter two roles where nanotechnology has opened up exciting possibilities to improve performance attributes of costings and the associated products.

Nanoparticulate materials candidates for coating property improvement

#### Main Advantage of Nano-coating

Some of the main advantages of nano-coating are:

- Better surface appearance.
- Good chemical resistance.
- Decrease in permeability to corrosive environment and hence better corrosion properties.
- Optical clarity.
- Increase in modulus and thermal stability.
- Easy to clean surface.
- Anti-skid, anti-fogging, anti-fouling and anti-graffiti properties.
- Better thermal and electrical conductivity.
- Better retention of gloss and other mechanical properties like scratch resistance.
- Anti-reflective in nature
- Chromate and lead free
- Good adherence on different type of materials

#### **Antimicrobial coatings:**

Due to fact that nano particles effectively inhibit growth of many microorganisms, many researchers are interested to develop many applications such as nanoparticle based resist-germ paint, nanoparticle-coated face mask etc. However, silver nanoparticles are most widely used among other nanoparticles in antimicrobial coatings and paints. Silver and silver-based compounds are highly antimicrobial by virtue of their antiseptic properties to several kinds of bacterium, including *Escherichia coli* and *Staphylococcus aureus* [192-194]. Silver based antimicrobial agents receive much attention, because of the low toxicity of the active Ag ion to human cells [195, 196], as well as it being a long-lasting biocide with high thermal stability and low volatility. Silver nanoparticles are known to exhibit antibacterial properties and various research groups have investigated the mechanism of silver nanoparticles mediated antibacterial activity [197, 198]. As the size of the silver particles decreases down to the nanoscale regime, their antibacterial efficacy increases because of their larger total surface area per unit volume [199, 200].

Along with silver, nano-sized particles of zinc oxide have more pronounced antimicrobial activities than large size particles, since the small size (less than 100 nm) and high surface-to-volume ratio of nanoparticles allow for better interaction with bacteria. Recent studies have shown that these nanoparticles have selective toxicity to bacteria but exhibit minimal effects on human cells [201]. *Zinc* oxide nanoparticles were shown to have a wide range of antibacterial activities on both Gram-positive and Gram-negative bacteria, including major foodborne pathogens like *E. coli* O157:H7, *Salmonella, Listeria monocytogenes*, and *Staphylococcusaureus* [202, 203].

#### Self-Cleaning coatings:

The technology of self cleaning coatings has developed rapidly in recent years. The use of self cleaning coatings is attractive as these are labour saving and effectively improve the appearance. In 1997, Barthelott and coworkers showed that the self-cleaning property of lotus leaves was due to their specialized surface morphology and hydrophobicity [204]. This specialized morphology prevents dirt from forming an intimate contact with the surface, while the high hydrophobicity makes the leaf water-repellent. Consequently, water droplets pick up small particles of dirt as they roll, making a surface clean. Since the initial discovery by Barthelott, many groups have made an efforts to mimic this activity to develop self-cleaning or lotus-effect coatings [205].

During the past few years, self-cleaning coatings using photo catalytic titanium dioxide (Tio<sub>2</sub>; especially the antase crystalline form) have attracted considerable attention. When photo catalytic TiO2 particles are illuminated with an ultraviolet light source (e.g., sunlight), electrons are seen to be promoted from the valence band (VB) to the conduction band (CB) of the particle [206, 207]. This creates a region of positive charge (h+), holes, in the VB and a free electron in the CB. These charge carriers can either recombine or migrate to the surface, while the holes can react with the hydroxyl or adsorbed water molecules on the surface and produce different radicals such as hydroxyl radicals (OH·) and hydroperoxy radicals (HO2·). By contrast, the electrons combine with the oxygen and produce super oxide radicals. These photo-produced radicals are powerful oxidizing species and can cause the deterioration of organic contaminants or microbials pieces on the particle surface. The other beneficial effect of TiO2 is its super

hydrophilic behavior, commonly known as the "water sheathing effect" [208]. This allows contaminants to be easily washed away with water or rainfall if the coatings are applied to external surfaces.

Both photo-catalysis and hydrophilicity occur simultaneously, despite their underlying mechanisms being of an entirely different nature. The addition of silicon oxide to TiO2 has also been shown to enhance the overall self cleaning properties [209]. Photo-catalytic TiO2 particles cannot be incorporated or deposited on the organic coating, as they oxidize the polymer. Recent developments have revealed the use ofTiO2 particles in combination with organic resins [210]. One very recent report noted that lotus leaves may be either hydrophilic or hydrophobic, depending on the contact of water molecules at the leaf surface [211].

#### **UV Resistant coatings:**

Exterior coatings are designed to provide protection from the harsh environment of outdoor weathering, especially the deterioration caused by UV radiation. Photochemical degradation caused by UV rays is common mode of failures of most of the coating systems. One of the main influences on the coatings performance is the amount and type of UV absorbers used in the coatings. UV blockers are of organic and inorganic types. However, conventional organic UV absorbers are prone to degradation and do not provide the long-term protection an inorganic UV absorber, such as zinc oxide and titanium dioxide nanoparticles provides. The inorganic types are more suitable for their non toxicity and chemical stability to high temperature as well as UV radiation [212]. Inorganic UV blockers include titanium dioxide, zinc oxide, silicon dioxide and aluminium oxide, which are semiconductors. Among these titanium dioxide and zinc oxide are commonly used [213]. Nano size titanium dioxide and zinc oxide particles have been found to be more efficient at absorbing and scattering UV radiation effectively and thus have been able to more effectively block the UV radiation [214]. This could be attributed to nano particles having larger surface area per unit mass and volume in comparison with the conventional ones, which makes them more effective in blocking UV radiation.

#### **Anti-fouling coatings:**

Fouling is the accumulation of unwanted material on solid surfaces to the detriment of function. The fouling material can consist of either living organisms (biofouling) or a non-living substance (inorganic or organic). Fouling is usually distinguished from other surface-growth phenomena in that it occurs on a surface of a component, system or plant performing a defined and useful function, and that the fouling process impedes or interferes with this function.

Anti-fouling is the ability of specifically designed coatings to remove or prevent biofouling by any number of organisms on wetted surfaces. A variety of anti-fouling methods have historically been implemented in order to combat biofouling [215]. Nanomaterials are finding applications in marine antifouling.Due to inherently small size of nanoparticles they remain in the lattice of the antifoul coating. Although they do not readily leach out, they slowly release ions to provide long term antifouling performance. The long used tributyltin (TBT) antifouling compounds are now widely banned by the International Maritime Organization due to its serious toxic effects on marine life and replacements are required. The longevity of organic biocides and copper oxide is not up to the required level but nanoparticles are offering a new alternative. In one of the recent study scientists have discovered that vanadium pentoxide nanowires have the potential to be an alternative approach to conventional anti-biofouling agents [216].

#### Scratch resistant coatings:

Coatings are susceptible to damage caused by scratch and/or abrasion. An added problem is that scratches may also cause damage to the underlying substrate. Scratch resistance of coating can be improved by adding large no. of cross links in the coating's binder but unfortunately highly cross linked (hard) films have poor impact resistance due to less flexibility. However, less-cross linked (softer) film will show better performance with regard to other properties such as antifingerprint and impact resistance but will have less scratch and abrasion resistance. Thus, in order to obtain optimal scratch resistance, the correct combination of hardness and flexibility is required. Recent advances in nanotechnology plays an important role in the development of scratch-resistant coatings [217]. For many years, large micron size aluminum oxide has been added to coating sto improve scratch and abrasion resistance in hard surfaces like vinyl and hardwood flooring, decorative laminates, and furniture. In this way the scratch resistance is enhanced due to an enrichment of the nanoparticles near the coating surface [218]. Coatings with good abrasion and scratch resistant properties have also been reported by others [219]. Use of nanoparticles such as zirconium dioxide, aluminium oxide hydroxide and silicon dioxide have been shown to improve scratch resistance. Homogeneous

distribution of nano particles in polymers is another important factor which leads to significant improvement of the scratch resistance of coatings [220].

#### Anticorrosive coatings:

Corrosion is a tremendous problem and cost to society. Anticorrosive properties of coating with optimum level of nanoparticles show far better results than conventional coating. Corrosion resistance of a coating depends upon several parameters. Pigment-binder ratio is one important factor by which anticorrosive performance of the coating get influenced, which also plays important role in determining properties of coating and is related to transportation of harmful corrosive species in electrolyte through the coating system.

Nano particles possess greater surface activity hence they can absorb more resins than conventional pigments and thus reduces the free space present between the pigment and the resin. Consequently, addition of nanoparticles increase the density of coating and decreases the transport path of corrosive species which further improve the protective performance. [220].

In one of the studies it was observed that, curing behavior of the epoxy coating was influenced in presence of nanoparticles. This study also revealed that, corrosion resistance of the epoxy coating was increased using zinc oxide nanoparticles and coating resistance against hydrolytic degradation was improved using nano zinc oxide [221].

## CONCLUSION

In this review we overviewed different types of functional coatings and uses of biosynthetic methods (i.e. use of plant, bacteria and fungus) to synthesize nanoparticles. Application of nanotechnology in the field of coating recently gained momentum as nanoparticles have unique physical, chemical and physicochemical properties, which may improve the properties of conventional paints and coatings. Green chemistry approach for synthesis of nanoparticles have been suggested as a valuable alternative to physical and chemical methods with cost effective and environment friendly technique.

The field of nano biotechnology is still in its infancy and more research needs to be focused on the mechanism of formation of nanoparticle and understanding of the biochemical and molecular mechanisms of the reaction for obtaining better chemical composition, shape, size, and monodispersity which will ultimately leading to the synthesis of nanoparticles with a strict control over the size and shape parameters.

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