



Green Biosynthesis of Nanoparticles

Mechanisms and Applications

Edited by
Mahendra Rai and Clemens Posten

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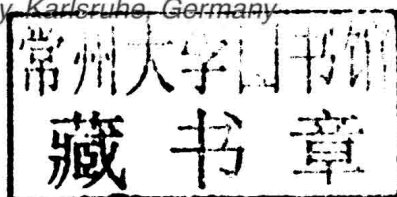
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Mechanisms and Applications

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Preface

There are physical and chemical methods for the synthesis of nanomaterials. But, due to the damage these methods cause to the environment, there is a pressing need for a green nanotechnology that is clean and eco-friendly for the development of nanomaterials. More precisely, green nanotechnology can be developed to minimize the potential environmental and human health risks associated with the fabrication and use of nano-based materials and products.

Recently, biological synthesis has attracted the focus of scientists. The importance of biological synthesis is being emphasized globally, because chemical methods are capital-intensive, use toxic chemicals and have low productivity. Thus, the need for clean, eco-friendly, cost-effective and biocompatible synthesis of metal nanoparticles has encouraged researchers to exploit biological sources as nanofactories. Biological synthesis of nanoparticles is quite novel, leading to a truly green approach that provides advancement over chemical and physical methods, as it is cheaper, environment friendly and easily scaled up for large-scale synthesis. In these methods there is no need to use high pressure, energy, temperature and toxic chemicals.

Different biological systems are exploited for the rapid synthesis of nanoparticles, including bacteria, fungi and plant extracts. Microbes are the 'nanofactories' for the synthesis of nanoparticles.

This book includes the green synthesis of nanoparticles by algae, diatoms, bacteria and plants. Moreover, the mechanisms behind the synthesis of nanoparticles have been discussed.

The book should be immensely useful for students, researchers and teachers of biology, chemistry, chemical technology, nanotechnology, microbial technology and those who are interested in green nanotechnology.

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Mahendra Rai
Clemens Posten
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1 Green Technology for Nanoparticles in Biomedical Applications

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Introduction

A growing number of scientists and engineers are exploring and tweaking material properties at the atomic scale to create designer materials that ultimately might increase the efficiency of current energy sources or make new energy sources practical on a commercial scale. At the nanoscale, fundamental mechanical, electrical, optical and other properties can differ significantly from their bulk material counterparts, and materials can self-assemble spontaneously into ordered structures. Nanostructured materials also have enormous surface areas per unit weight or volume, so that vastly more surface area is available for interactions with the other materials around them. That is useful, because many important chemical and electrical reactions occur only at surfaces and are sensitive to the shape and texture of a surface as well as its chemical composition (Van Hove, 2006; Ashby *et al.*, 2009).

Green technologies have been around since the first public health projects were set up in cities to provide people with clean drinking water. Since then, many other green techniques such as scrubbers for smokestacks, catalytic converters for cars, recycling

plants, solar panels and energy-efficient appliances have been introduced. To date, a new generation of green technologies is imminent, as pressures on resources grow and investors see a healthy profit in a wide range of innovative products.

With the development of science and technology, a growing number of researchers are merging green chemistry and green engineering with nanotechnology, and these researchers see a bright future for a new field known as 'green nano'. Some want to help green up industries that use emerging nanotechnologies. Others who are working on green technologies such as solar cells, remediation techniques and water filters are turning to nanotechnology in order to achieve their goals of creating better devices to help the environment. These researchers assert that a strong marriage between nanotechnology and green chemistry/engineering holds the key to building an environmentally sustainable society in the 21st century.

Nanoparticles

Unlike bulk materials, nanoparticles have characteristic physical, chemical, electronic,

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electrical, mechanical, magnetic, thermal, dielectric, optical and biological properties (Chuang and Chen, 2011). Decreasing the dimension of nanoparticles has a pronounced effect on the physical properties, which differ significantly from the bulk materials. These physical properties are caused by their large surface atom, large surface energy, spatial confinement and reduced imperfections. Nanoparticles have advantages over bulk materials due to their surface plasmon resonance (SPR), enhanced Rayleigh scattering and surface-enhanced Raman scattering (SERS) in metal nanoparticles and their quantum-size effect in semiconductors and supermagnetism in magnetic materials. Therefore, nanoparticles are considered as building blocks of the next generation of optoelectronics, electronics and various chemical and biochemical sensors, etc. (Hahn *et al.*, 2011; Kameya and Hanamura, 2011).

By now, an astonishing multitude of materials ranging from inorganic to polymeric nanoparticles, biological building blocks and nanostructured thin films with many different electronic, magnetic, optical and bio properties have been synthesized and characterized in great detail. The pivotal point is the directed assembly or self-assembly of these systems into hierarchically ordered and/or arbitrarily defined structures. The production and use of nanostructured and nanoscaled materials has become a key technology in many more fields, for example pharmacy (Kathiravan *et al.*, 2011; Tran *et al.*, 2011), regenerative medicine (Harrison and Sirivisoot, 2011), diagnostics (Zhang and Kataoka, 2009), cosmetics (Kokura *et al.*, 2010) and food technology (Dudo *et al.*, 2011).

Progress in nanotechnology is aiming not only at miniaturization but also at systems with increased complexity. This is not only just a matter of geometrical structurization but also a matter of specific functionalities that are positioned at discrete locations and in defined distances. Nature and its highly precise mechanisms of life, mainly based on two classes of biomacromolecules, proteins or polypeptides and polynucleic acids, set the benchmark for functional structures down to atomic scales. Thus, the use of biomolecules is considered as an obvious step in the synthesis and construction of next-generation nanomaterials and devices.

A whole new branch termed 'bionanotechnology' seeks for scientific as well as economic breakthroughs in the development of bioinorganic nanomaterials with novel properties for computation and nanotechnology, new methods in diagnosis and analytics or new drugs and drug delivery systems (Mahmoud *et al.*, 2011).

In medicine, nanoparticles can be used in bioanalysis and as biosensors. Bioanalysis can have a variety of applications. For example, nanoparticles can be used to induce signal transduction, as quantitation identifiers, in bioassays, and finally they can be used for specific functions in biological systems (Penn *et al.*, 2003). Maxwell *et al.* (2002) showed that colloidal gold could be used to create biosensors to identify specific DNA sequences and base mutations. It has also been shown that copper-gold bimetallic nanoparticles can be used as oligonucleotide labels for the electrochemical stripping detection of DNA hybridization (Cai *et al.*, 2003).

Related to health and environmental issues, it has been shown that nanoparticles can be used in the remediation of organic pollutants in the environment (Obare and Meyer, 2004). Iron nanoparticles have been proven to be effective in the dechlorination of polychlorinated biphenyls. It has also been shown in the literature that bimetallic nanoparticles can be used for groundwater treatment (Elliott and Zhang, 2001). Results show the destruction of trichlorethylene (TCE) and other chlorinated hydrocarbons using bimetallic nanoparticles. The results of this study showed that 96% of the TCE was eliminated within 4 weeks of injecting the nanoparticles.

Over the past few decades, nanoscale particles have elicited much interest due to their distinct chemical, physical and biological properties. A variety of nanoparticles (NPs) with various shapes such as spheres, nanotubes, nanohorns and nanocages, made of different materials, from organic dendrimers, liposomes, gold, carbon, semiconductors, silicon to iron oxide, have already been fabricated and explored in many scientific fields, including chemistry, materials sciences, physics, medicine and electronics.

The novel properties of NPs, attributed primarily to the quantum size effect, are

confronted by their conventional ecologically hazardous synthesis protocols (Jackson and Halas, 2001). Endeavours are under way to develop greener avenues in the domain of nanotechnology. It is pertinent to mention that carbohydrate-templated silver NPs (Babu *et al.*, 2010) have carved a unique niche in the domain of nanobiotechnology with an immense spectrum of applications, particularly as antimicrobial biopolymer nanocomposite. Macromolecules such as starch, when used for encapsulation or entrapment of inorganic particles, can impart novel properties to the latter (Ziolo *et al.*, 1992). Enhanced compatibility, reduced leaching and protection of surfaces from damage, with concomitant improvement in dispersibility and stability of the NPs, are a few of the desired facets of polymer-templated nanomaterial over uncoated counterparts (Bourgeat-Lami and Lang, 1998).

Green Nanoparticles

Silver nanoparticles

Nanotechnology is emerging as a cutting-edge technology interdisciplinary with biology, chemistry and material science. Silver nanoparticles (Ag-NPs) are important materials that have been studied extensively. Such nanoscale materials possess unique electrical, optical, as well as biological properties and are thus applied in catalysis, biosensing, imaging, drug delivery, nanodevice fabrication and medicine (Smith *et al.*, 2010). Due to strong antimicrobial activity, Ag-NPs are also used in clothing, the food industry, sunscreens and cosmetics (Kokura *et al.*, 2010). Additionally, Ag-NPs have been shown to undergo size-dependent interactions with HIV-1 and inhibit binding to the host cell *in vitro* (du Toit *et al.*, 2010; Shegokar *et al.*, 2011).

Although different techniques such as ultraviolet irradiation, aerosol technologies, lithography, laser ablation, ultrasonic fields and photochemical reduction have been used successfully to produce metal NPs, they remain expensive and sometimes involve the

use of hazardous chemicals (Butkus *et al.*, 2003; Ashby *et al.*, 2009). Consequently, green synthesis of NPs has received increasing attention due to the growing need to develop an environmentally benign technology in nanoparticle synthesis. Several biological systems including bacteria, fungi, yeast and plants have been used in this regard (Nabikhan *et al.*, 2010; Shivaji *et al.*, 2011; Zaki *et al.*, 2011). Although the green synthesis of Ag-NPs by various plants has been reported, the potential of plants as biological materials for the synthesis of NPs is yet to be explored fully. In addition, information on the biological response of human cells to green synthesized Ag-NPs is also very limited.

Furthermore, it should be noted that lack of access to potable water is a leading cause of death worldwide. Dehydration, diarrhoeal diseases, contaminated water sources, water-borne pathogens, water needed for food production (starvation) and water for sanitation are just some of the factors that impact health. The water-health nexus is crucial for the survival of humanity. Meanwhile, people all over the world face profound threats to the availability of sufficient safe and clean water, affecting their health and economic well-being. The problems with providing clean water economically are growing so quickly that incremental improvements in the current methods of water purification could leave much of the world with inadequate supplies of clean water in mere decades. Recent advances strongly suggest that many of the current problems involving water quality can be addressed and potentially resolved using nanosorbents, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes and nanoparticle-enhanced filtration, among other products and processes resulting from the development of nanotechnology (Zäch *et al.*, 2006; Ashby *et al.*, 2009; Van Hove, 2009). Moreover, nanotechnology solutions are essential because the abiotic and biotic impurities most difficult to separate in water are in the nanoscale range. At the same time, nanotechnology has enabled the development of a new class of atomic-scale materials capable of fighting waterborne disease-causing microbes. The explosive growth in nanotechnology research has opened the doors to new strategies

using nanometallic particles for oligodynamic disinfection (Anshup, 2009; Diallo *et al.*, 2009). The excellent microbicidal properties of the oligodynamic NPs qualify their use as viable alternatives for water disinfection. Oligodynamic metallic NPs such as silver, copper, zinc, titanium, nickel and cobalt are among the most promising nanomaterials with bactericidal and viricidal properties owing to their charge capacity, high surface-to-volume ratios, crystallographic structure and adaptability to various substrates for increased contact efficiency. This new class of nanometallic particles produces antimicrobial action referred to as oligodynamic disinfection for their ability to inactivate microorganisms at low concentrations. When oligodynamic metals with microbicidal, bactericidal and viricidal properties are reduced to nanosize scale, they show tremendous advantages in disinfection capacity due to the greater surface area, contact efficiency and often better elution properties. These qualities enable materials such as silver (Ag), copper (Cu), zinc (Zn), titanium (Ti) and cobalt (Co) to be considered as viable alternative disinfectants. New combinatorial oligodynamic materials consisting of these nanometallic particles have been deployed among a number of substrates for their use in water disinfection (Kim *et al.*, 2006). Materials such as Ag deposited on titanium oxide and Ag-coated iron oxide have displayed faster kinetics and greater efficiency in eliminating bacteria.

To date, Ag is the most widely studied oligodynamic material due to its wide range in microbicidal effectiveness, low toxicity and ease of incorporation on various substrates in a host of dynamic disinfection applications. Furthermore, the systems supported with nanometallic Ag particles are effective in reducing the presence of target microorganisms in a wide variety of water disinfection applications. The main known negative health effect from Ag is argyria, which is an irreversible darkening of the skin and mucous membrane resulting from over-exposure to ionic silver (Ag(I), Ag⁺) (Butkus *et al.*, 2005).

Typically, Ag-NPs are derived from silver salts (silver nitrate (AgNO₃), silver chloride (AgCl), silver bromide (AgBr) and silver

iodide (AgI)), and a variety of the substrates that Ag is deployed on, such as activated carbon, activated carbon fibres (ACFs), polyurethane, zeolites and ceramics in point of entry (POE) and point of use (POU) applications, display the effective inactivation of pathogens in water (Byeon and Kim, 2010).

Wang *et al.* (1998) prepared viscose-based activated carbon fibre supporting silver (ACF(Ag)) by pretreatment, carbonization, activation, vacuum impregnation and decomposition processes. The ACFs were then subjected successively to a vacuum impregnation treatment in unsaturated silver nitrate (analytical grade) aqueous (AgNO₃) solutions (NH₄H₂PO₄ 3.3 g l⁻¹, (NH₄)₂SO₄ 6.7 g l⁻¹) with varying concentrations for different times and were finally heated to different temperatures for decomposition, thus producing ACF(Ag). Moreover, ACF(Ag) containing as little as 0.065 wt% of Ag exhibits strong antibacterial property against *Escherichia coli* and *Staphylococcus aureus*.

Garlic (*Allium sativum*) has long been considered a herbal remedy to prevent and treat various metabolic diseases such as thrombosis, hypertension, diabetes, dementia and atherosclerosis. Garlic is a very good source of vitamin C and vitamin B6, along with beta-carotene, thiamine, riboflavin, niacin and folate, which function as antioxidants. Recently, Ahamed *et al.* (2011) studied a simple, cost-effective and environmentally benign synthesis of Ag-NPs at ambient conditions using garlic clove extract as a reducing and stabilizing agent in order to apply the biological response of Ag-NPs in human lung epithelial (A549) cells.

Furthermore, Guidelli *et al.* (2011) investigated a totally green synthesis of colloidal Ag-NPs using the natural rubber latex (NRL) extracted from *Hevea brasiliensis*. The synthesis was fast and occurred at a relatively low temperature (water boiling temperature). Moreover, it was very simple, inexpensive and environmentally benign, devoid of photochemical, electrochemical or irradiation processes. The colloidal particles could be used and stored in their liquid form, or even as a film obtained by drying the starting solution. Combining the angiogenic properties of the NRL and Ag-NPs, the nanostructured material