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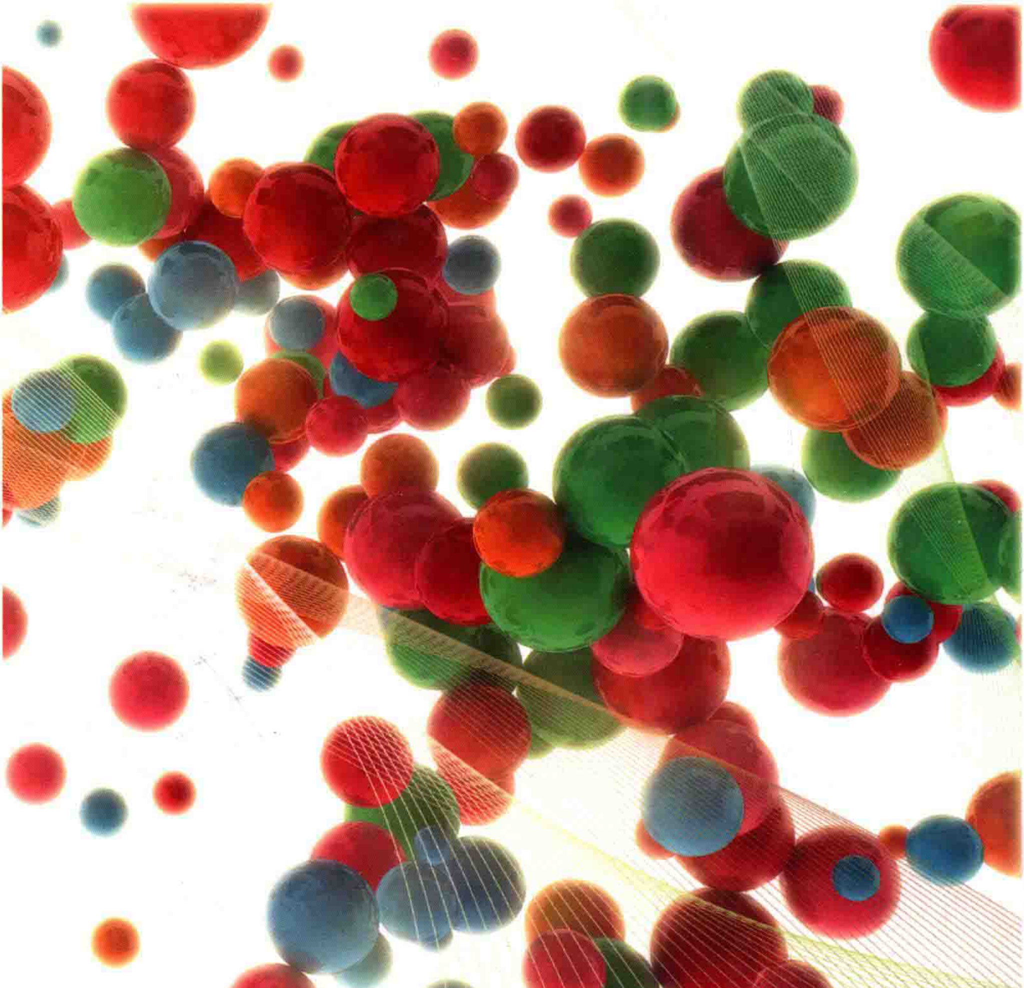
Edited by Rafael Luque and Rajender S Varma

Sustainable Preparation of Metal Nanoparticles

Methods and Applications



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RSC Green Chemistry

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Preface

Nanoscience and Nanotechnology have brought about excitement in fundamental research as well as technological advances. The word "Nano" has now become a household name. Nanomaterials can be synthesized from simple bench top methodologies all the way to advanced molecular beam epitaxy techniques. Advances made in designing new products are seen as important milestones in improving the lifestyle of developed and developing countries. Many of these products have found a niche place in the market from catalysts to consumable goods, diagnostics to drug delivery systems, and electronics to energy conversion devices. Such developments also mean that a huge production of nanoscale materials become vital to sustain the demand. An effort of this large magnitude requires changes not only in production but also in handling and transport, as well as in safety and toxicology control.

The design of semiconductor and metal nanostructures of different shapes and sizes, in particular, offers new opportunities to tailor the application of nanodevices. For example, size quantization effects in 0-D, 1-D and 3-D of semiconductors introduce unique optical and electronic properties. The use of semiconductor quantum dots in photovoltaic devices has opened up new ways to boost the efficiency of solar cells. The unique aspects such as multiple electron generation and hot electron extraction offer new opportunities to boost the efficiency of next generation of solar cells using semiconductor nanostructures. Exciton-plasmon coupling in semiconductor-metal nanostructure composites is another area of research that can aid in developing new strategies to harvest photons.

Among the large variety of nanoscale materials, metal nanoparticles are considered to be important because of the remarkable changes in their properties as compared to their bulk counterparts. Their wide range of applications is seen in diverse areas such as catalysis, biomedicine, energy conversion,

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environmental remediation, optics or telecommunications. Such metal nanostructures with unique shapes and sizes can introduce significant enhancement in surface enhanced Raman scattering (SERS) signals, thereby enabling the detection of low level contaminants. Localized surface plasmon effects as well as quantized charging effects have been shown to improve charge separation in artificial photosynthetic and photocatalytic systems.

The production of metal nanoparticles depends on the desired applications. For example, wet chemistry methods are frequently used for biomedical applications, while gas phase deposition on solid supports is commonly employed in the preparation of catalysts and electrocatalysts. The large volume of production of such nanomaterials poses a high demand on the manufacturers to develop environmentally friendly synthetic methods. It is important not only to minimize energy consumption but also use the reactants that have negligible toxic effects. In recent years, nanosafety has become a major point of concern in manufacturing nanomaterials. The toxicity effects need to be tested for size, shape and chemical structures both during manufacture and usage by the consumers.

Researchers interested in green production and environmentally safe synthesis of metal nanoparticles will find this book highly useful. The selection of topics offers a convenient way to educate important aspects of sustainable production, safe handling, toxicology, environmental remediation and energy conversion aspects of nanomaterials.

Prof. Luis M. Liz-Marzan, University of Vigo, Spain
Prof. Prashant V. Kamat, University of Notre Dame, USA

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CHAPTER 1
Introduction

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In recent years, we have experienced a "nano" revolution in which science was directly impacted with nanotechnologies forming the basis of the so-called nanoscience that are just starting nowadays to be realized as a major step forward towards future technological progress. The possibility of manipulating matter at such an ultrasmall scale (*i.e.* within the nanometer range)[1,2] has paved the way to the development of numerous nanoentities and nanosystems which currrently start to be part of our daily lives and consumer products in optics, electronic devices, sensors and even in the textile industry. The ability to directly work and control systems at the same scale as nature (*e.g.* DNA, cells) can potentially provide a very efficient approach to the production of chemicals, energy and materials (Figure 1.1).

Another important asset of nanomaterials is its inherent multidisciplinarity with a wide range of possibilities in terms of synthesis and applications that these nanoentities hold. Several subfields have been investigating nanoscale effects, properties, and applications from its infancy; every different sub-discipline is involved in modern nanoscience and technology.[2] Inputs from physicists, biologists, chemists and engineers have been a hallmark from the very early developments including the advances in nanoscience to achieve a

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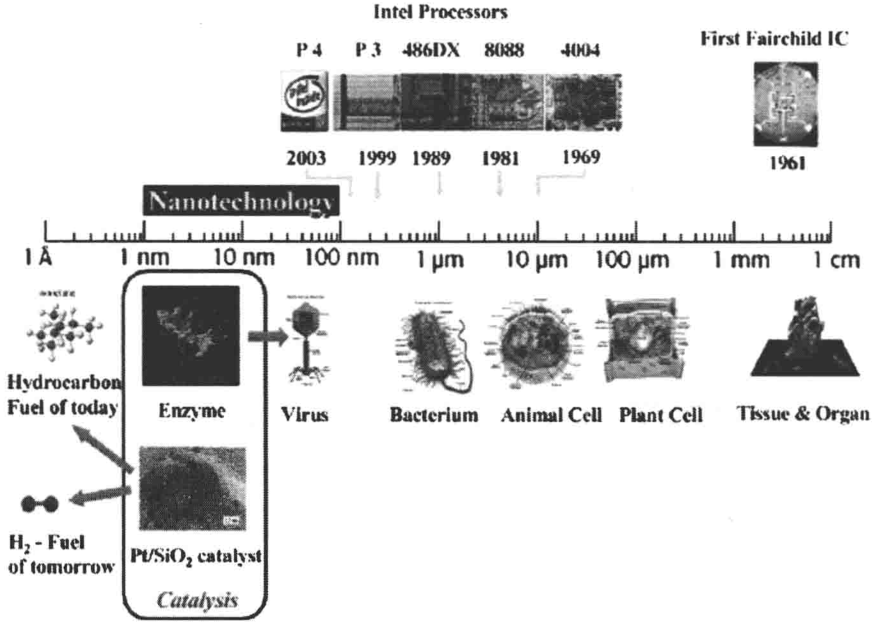

Figure 1.1 Catalysts and the nanometer regime.[2b]
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better understanding of the preparation, application and impact of these new nanotechnologies.

A *nanoparticle* can be generally defined as a particle that has a structure in which at least one of its phases has one or more dimensions in the nanometer size range (1 to 100 nm, Figure 1.1). Nanoparticles (NPs) have remarkably different properties as compared to their bulk equivalents that mainly include a degenerated density of energy states (as compared to bulk metals) and a large surface to volume ratio together with the sizes in the nanometer scale.[1–3] These nanoparticles have associated remarkable properties including a relatively high chemical activity and specificity of interaction as compared to bulk metals (*e.g.* Au). With all the aforementioned advantages and outstanding features of NPs, it is not surprising that the interest in NPs has experienced a staggering exponential increase over past years, with over 10 000 publications referring to NPs in 2010. The amplitude of research efforts is expected to continue increasing as beneficial application of the chemical properties achieved at the nanolevel become increasingly apparent.

One of the key driving forces for the rapidly developing field of nanoparticle synthesis is the contrasting physicochemical properties of nanoparticles compared to their bulk counterparts. Nanoparticles typically provide highly active centers but they are very small and not thermodynamically stable. Structures in this size regime are generally unstable due to their high surface energies and large surfaces.[1,3] To achieve stable NPs, the particle growth reaction has to be carefully controlled and minimized. This has been rendered feasible by a number of methods including the addition of organic ligands, inorganic capping materials or metal salts, colloids or soluble polymers creating core shell type particle morphologies.[4,5] These materials can be grouped in the so-called "unsupported" MNPs.

In parallel, a significant volume of research has been devoted to protocols to achieve homogeneous size dispersed nanoparticles on different supports including porous materials.[6–8] These nanoentities can consequently be grouped in the so-called "supported" nanoparticles (SNPs).

Recent advances in the design and preparation of nanomaterials have shown that a wide variety of them can be synthesized through different preparation routes and tailored to a desired size and distribution, overcoming the limitations of traditional synthetic methodologies.

In conjuction with the nanorevolution, environmental issues, growing demand for energy, political concerns and medium-term depletion of petroleum-derived products have created the need to develop sustainable technologies and low environmental impact processes not only for the production of chemicals, fuels and materials but also for the generation of nanomaterials, nanoparticles and related nanoentities. The state-of-the-art preparation techniques of many NPs attempt to follow more efficient and sustainable routes, taking special considerations to the safety and toxicity of the prepared nanoparticles. These routes include the use of alternative energy input methodologies, such as ultrasound-, microwave irradiation, and ball milling, the use of natural products and biomass (*e.g.* vitamins, fruits, agricultural residues, *etc.*) for NP preparation, and the controllable deposition and stabilization of NP using a related technology, that of nanoporous materials.

This monograph is intended to be a contribution towards the aforementioned selected methodologies for the environmentally friendly preparation of nanoparticles and their applications in various fields including energy storage, environmental remediation, biomedical applications, production of fine chemicals, and biofuels from biomass, with two additional contributions on the toxicology of designer nanoparticles and an introduction to nanosafety. Due to the rapidly expanding nature of this field, this book is hoped to provide a useful introduction to readers to this exciting research area.

Subsequent to this introductory chapter, the first part of the book commences with a chapter by Varma *et al.* that includes a description of sustainable, novel and innovative methodologies for the development of biosynthetic methods for NP preparation including the use of fungi, bacteria, algae, plants, carbohydrates and vitamins. A range of nanoparticles with different nanoparticles sizes and shapes can be achieved using these interesting methods. Chapter 3 by Özkar *et al.* then continues along the lines of sustainable ways to synthesize nanoparticles stabilized in the framework of porous materials (supported metal nanoparticles, SMNPs). This chapter reviews protocols and preparation routes of SMNPs, including physico-chemical methods, the aforementioned alternative methodologies, and detailed case studies on the utilization of various supports such as zeolites, clays, porous silica's, carbonaceous materials, MOFs and some others. This chapter also delineates some interesting catalytic applications of these materials in an array of catalytic processes including coupling and redox chemistries.

After these introductory chapters pertaining to the nanoparticle preparation and associated applications in catalysis, the second part of the book focuses on applications of nanoparticles in various research areas. Chapter 4 from Wang *et al.* deals with an interesting topic of energy conversion and storage through nanoparticles where the authors discuss the possibilities of quantum confinements in nanoparticles, preparation of quantum dots and applications in solar cells and lithium ion batteries. Following this chapter, Dionysiou *et al.* disclose the greener preparation of an assortment of nanomaterials including metal and metal oxide NPs using various methodologies for their utilization in photocatalytic applications for environmental remediation in Chapter five. The chapter includes interesting sections on the immobilization of nanoparticles and the subsequent applications to sustainable environmental systems.

Chapter 6 from Katti *et al.* deals with the uses of nanoparticles (particularly gold NPs synthesized from natural sources) for biomedical applications and treatment of tumors.

The last chapter of the applications section by Obare *et al.* comprises an overview of selected nanomaterials and nanosystems for the production of high-value added chemicals and biofuels from biomass valorization practises. This encompasses some synthetic protocols for the preparation of metallic and biometallic nanoparticles all the way to various applications in chemical processes including conversion of sugars, production of hydrocarbons, synthesis of biodiesel and the design of fuel cells, with some future perspectives in the field.

The final part of the book consists of two chapters devoted to the toxicology of designer/engineered nanoparticles by Ming *et al.* (Chapter 8) and a brief introduction to nanosafety in the lab (Chapter 9) by Balas. The later provides a novel and unique approach to issues associated to the use of nanoparticles, often missing in most nanoparticle-related books to date. Chapter 8 contains some critical information of biophysicochemical interactions at the nano/bio interface, with some important aspects on nanotoxicity. Chapter 9 wraps up the book with some fresh concepts on nanosafety, a relatively novel concept and approach. This Chapter aims to provide some discussion on the introductory issues of risks in handling nanoparticles and strategies for risk reduction together with some general guidelines on safety and prevention in a nanotechnology laboratory from control banding to techniques related to the assessment of nanoparticle emissions.

With the 21st century heralding the dawn of a new age in materials science (where scientists no longer observe the behavior of matter but with the advent of nanoparticles, materials and technology but is able to predict and manipulate matter for specific applications, with sensitivity and efficiency far surpassing previous systems), we hope this book can provide a starting point to readers in the fascinating nanoworld as well as some useful points in terms of nanosafety and nanotoxicity/environmental impact associated with nanoparticles.

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