Volume 18



Zacharie Bartul Jérôme Trenor Editors



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Contributors

Zubair Anwar Aqeela Khurshid Adeela Khursid Sadia Ahmed Zuberi Qurat E. Noor Baig Iqbal Ahmad Muhammad Ali Sheraz Sofia Ahmed Syed Abid Ali Ye Yang

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ADVANCES IN NANOTECHNOLOGY VOLUME 18

ZACHARIE BARTUL AND JÉRÔME TRENOR EDITORS



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PREFACE

Nanomaterials (NMs) or nanoparticles (NPs) are the small objects which behave as a simple single unit ranging in size from 1-100 nm. Chapter One is intended to provide detailed information on various aspects of nanomaterials including the types, characterization, methods of preparation, physicochemical properties, optical and thermal properties and various applications. Chapter Two provides comprehensive information regarding the characteristics, advantages, composition, methods of preparation, factors affecting formulation, characterization, applications, safety and toxicological considerations and future prospects for the use and preparation of nanosponges (NS). In Chapter Three, the fundamentals and applications of the mainstream top-down nanolithography techniques, which have been successfully applied in the fabrication of the graphenebased nano devices (such as the graphene nano-ribbon electronics, graphene quantum dot devices, graphene-based nano sensors and so on) are described. And in Chapter Four, the detailed method of tuning the bias voltage effect and the force effect during the AFM electric lithography is introduced and analyzed.

Chapter 1 – Nanomaterials (NMs) or nanoparticles (NPs) are the small objects which behave as a simple single unit ranging in size from 1-100 nm. The field of NPs is gaining importance day by day and in the past few decades the synthesis, characterization, handling and their use has become

an important field of scientific research. The physicochemical, optical and thermal properties of NPs have helped the researchers to design/synthesize/fabricate them according to their needs and specific use. Because of their unique and environment friendly properties they have wide applications in different fields i.e., biotechnology, pharmaceutical technology, electrochemical engineering, biomedical engineering, tissue engineering, chemical synthesis, cosmetology, etc.

The present chapter is intended to provide detailed information on various aspects of nanomaterials including the types, characterization, methods of preparation, physicochemical properties, optical and thermal properties and various applications. This information would be useful to the researchers to synthesize nanomaterials of their own interest with the desired characteristics to achieve their objectives. The applications of nanomaterials in the field of biomedical engineering, tissue engineering and targeted drug delivery system, and as diagonsite agents, chemical catalysts, and antimicrobial agents are also described. NPs have also been used for the control of impurities in chemicals. New opportunities are being created for the development of NPs in the field of targeted drug delivery system and other therapeutic applications because of their unique properties. It would be of great help to the researchers to overcome the challenges in highlighting the distinctive properties of NPs and their development for novel applications. Future perspects of NPs in the various fields are also presented.

Chapter 2 – The importance of novel drug delivery systems (NDDS) is increasing enormously because of the several advantages over conventional drug delivery systems. In the past few decades, the formulation of sponges is considered as one of the most emerging fields in the NDDS. Nanosponges (NS) entrap the drug in porous polymeric spheres ranging from 100 nm to 1 μ m. Apart from the conventional modes of drug delivery, NS possess several advantages such as they protect the drug from external environmental factors, and provides targeted drug delivery, etc. NS can be used in variety of applications such as drug delivery, analytical, biomedical and industrial applications, and agriculture, etc. This review provides comprehensive information regarding the characteristics,

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advantages, composition, methods of preparation, factors affecting formulation, characterization, applications, safety and toxicological considerations and future prospects for the use and preparation of NS.

Chapter 3 – In virtue of the extraordinary mechanical, electrical, optical and thermal properties of the graphene materials, graphene-based nanodevices have attracted the worldwide interest for its potential applications in the energy storage, electric circuits, novel sensors and so on. The nanoscale fabrication techniques are the indispensable basis to reliably achieve the specific nanoscale graphene structure and device fabrication. In this review, the fundamentals and applications of the mainstream top-down nanolithography techniques, which have been successfully applied in the fabrication of the graphene-based nanodevices (such as the graphene nanoribbon electronics, graphene quantum dot devices, graphene-based nanosensors and so on) are described. These top-down nanolithography techniques include the electron beam lithography (EBL), focused ion beam lithography (FIBL), femtosecond laser lithography, nanoimprint lithography (NIL) and scanning probe lithography (SPL). In this chapter, the characteristics and suitable applications of each technique are focused on and the comparison of their fabrication accuracy, reliability and scalability is also provided.

Chapter 4 – As one of the top-down nanofabrication techniques, the AFM electric nanolithography has nowadays attracted growing attention due to its incomparable advantages in the capability of fabricating the sub-100 nm scale patterns in the ambient environment directly, in-situ imaging of the fabrication results and so on. During the AFM electric lithography processes conducted in the contact mode, both the bias voltage effect and the force effect play the decisive roles in the fabrication results. In this work, by tuning the bias voltage effect and the force effect during the AFM electric lithography on the metallic copper film surface, the nanoscale structures of different shapes and sizes were realized. The permitted tunability of the fabricated patterns in the geometric size and the surface roughness is of great significance to the improvement of the controllability of the AFM electric nanolithography.

In this chapter, the detailed method of tuning the bias voltage effect and the force effect during the AFM electric lithography has been introduced and analyzed. Firstly, the fabrication results carried out under the bias voltage dominated scheme and the force dominated scheme respectively were compared quantitatively. Secondly, the material removal mechanisms under the two different schemes were analyzed based on the experimental observations, including the mechanical scratching and the localized material phase transition. Moreover, both the 2D and semi-3D nanostructures were fabricated to verify the machining capability of the tunable AFM electric lithography method.

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Chapter 1

NANOPARTICLES: PHYSICOCHEMICAL PROPERTIES, CHARACTERIZATION, METHODS OF PREPARATION AND APPLICATIONS

Zubair Anwar^{1,*}, Aqeela Khurshid², Adeela Khursid², Sadia Ahmed Zuberi¹, Qurat E. Noor Baig¹ and Iqbal Ahmad¹

¹Baqai Institute of Pharmaceutical Sciences, Baqai Medical University, Karachi, Pakistan ²Faculty of Pharmacy, Jinnah University for Women, Karachi, Pakistan

ABSTRACT

Nanomaterials (NMs) or nanoparticles (NPs) are the small objects which behave as a simple single unit ranging in size from 1-100 nm. The field of NPs is gaining importance day by day and in the past few decades the synthesis, characterization, handling and their use has become an

^{*}Corresponding Author E-mail: zubair_ana@hotmail.com

important field of scientific research. The physicochemical, optical and thermal properties of NPs have helped the researchers to design/synthesize/fabricate them according to their needs and specific use. Because of their unique and environment friendly properties they have wide applications in different fields i.e., biotechnology, pharmaceutical technology, electrochemical engineering, biomedical engineering, tissue engineering, chemical synthesis, cosmetology, etc.

The present chapter is intended to provide detailed information on various aspects of nanomaterials including the types, characterization, methods of preparation, physicochemical properties, optical and thermal properties and various applications. This information would be useful to the researchers to synthesize nanomaterials of their own interest with the desired characteristics to achieve their objectives. The applications of nanomaterials in the field of biomedical engineering, tissue engineering and targeted drug delivery system, and as diagnostic agents, chemical catalysts, and antimicrobial agents are also described. NPs have also been used for the control of impurities in chemicals. New opportunities are being created for the development of NPs in the field of targeted drug delivery system and other therapeutic applications because of their unique properties. It would be of great help to the researchers to overcome the challenges in highlighting the distinctive properties of NPs and their development for novel applications. Future prospects of NPs in the various fields are also presented.

Keywords: nanoparticles, types, physicochemical properties, methods of preparation, pharmaceutical applications, biomedical applications

1. Introduction

The word nano is derived from a Greek word dwarf and nanometer is the one-billionth of a meter (10⁻⁹ m). The word nanotechnology (NT) was first used by Norio Taniguchi in Japan in 1974 (Royal Society, 2004). Eric Drexler (1986, 1992), who is known to be a God Father of NT and defined NT as a molecular nanotechnology/process which deals with the transfer of molecules and atoms to the nanoscale products. NT is a vast term and it deals with more than one disciplines based on the scientific and technological principles for the design, preparation and characterization of nanomaterials (NMs) (Farokhzad and Langer, 2009; Ferrari, 2005; Fox,

2000; Jiang et al., 2007; Brannon-Peppas and Blanchette, 2004; Sinha et al., 2006; Uchegbu, 2006). It is also defined as the activity which is aimed to understand the natural laws on the level of nanoscale (Balzani, 2005). NT is referred as science, technology and engineering for the preparation of NMs on the scale of 1-100 nm (Alexis et al., 2010). In NT, NMs are defined as any small material or object which itself behaves as a simple single unit for transportation and exhibiting its properties. These NMs cover the range of 100-2500 nm. Ultrafine particles are in the size range of 1–100 nm and their physical and chemical properties depend on the nature of material through which they are prepared. NPs are the engineered structures with a diameter of less than 100 nm and are prepared by the physical and chemical process with many definite properties (Gwinn and Vallyathan, 2006). Different organizations have defined NPs which is given in Table 1. There are certain limitations which were applied to NT as the utilization of materials with structural orientation between the atom and at molecular scale but at least the dimensions must be in the nanoscale range (Rao and Cheetham, 2001; Rao et al., 2002; Jortner and Rao, 2002). NPs are gaining importance in the modern science and technology which is due to the ability of a scientist to manipulate the properties of NPs according to the requirements.

2. HISTORICAL DEVELOPMENT

In the era of 1950s and 1960s there has been tremendous advancement that leads to the development of sustained release and controlled release drug formulations. Professor Speiser in Zurich was pioneer in this field and along with his research group investigated polyacrylic beads for oral administration (Khanna and Speiser, 1969; Khanna et al., 1970; Speiser and Khanna, 1970). Later, Merkle and Speiser (1973) focussed on microcapsules and developed first nanoparticles (NPs) for the drug delivery and vaccine purposes. The major focus was to prepare nanocapsules for the sustained drug release that helps to circulate the drug in blood for a longer duration of time. In order to examine the applicability

of sustained release formulations using such NPs, Speiser first attempted to develop the NPs for vaccination purposes. Since tetanus, diphtheria and other infections require more than one injection for the booster dose to achieve the antibody levels for an appropriate protection, the major aim was to achieve the sustained release NPs for a constant immune stimulation and that the only single dose would result in the achievement of an antibody response (Kreuter, 2007).

Table 1. Definition of nanoparticles (NPs) and nanomaterials (NMs) according to different Organizations (Horikoshi and Serpone, 2013)

Organization	NPs	NMs
International Organization	1–100 nm	_
for Standardization (ISO)		
American Society of	Ultrafine particle whose	-
Testing and Materials	length in 2 or 3 places is	
(ASTM)	1–100 nm	
National Institute of	Particle diameter in the	-
Occupational Safety and	range of 1–100 nm or fiber	
Health (NIOSH)	spanning range in 1–100 nm	
Scientific Committee on	At least one dimension in	Internal structure
Consumer Products	nanoscale	or one side in
(SCCP)		nanoscale range
British Standards	All the dimensions are in	Internal structure
Institution (BSI)	the nanoscale range	or one side in
		nanoscale range
Bundesanstalt für	All the dimensions are in	Material
Arbeitsschutz und	the nanoscale range	consisting of a
Arbeitsmedizin (BAuA)		nanostructure or a
		nanosubstance

In 1969, Gerd Birrenbach who was working in the research group of Speiser was intrested to prepare a micelle by the process of polymerization which they called micelle polymerization (Birrenbach, 1973; Birrenbach and Speiser, 1976). During this process they prepared a mixture of tetanus