Dheeraj Kumar Singh
Sanjay Singh
Prabhakar Singh *Editors*

Nanomaterials

Advances and Applications

Springer

Nanomaterials

Dheeraj Kumar Singh · Sanjay Singh ·
Prabhakar Singh
Editors

Nanomaterials

Advances and Applications

Springer

Editors
Dheeraj Kumar Singh
Department of Basic Sciences
Institute of Infrastructure Technology
Research And Management
Ahmedabad, Gujarat, India

Sanjay Singh
National Institute of Animal Biotechnology
Hyderabad, Telangana, India

Prabhakar Singh
Department of Physics
Indian Institute of Technology BHU
Varanasi, India

ISBN 978-981-19-7962-0 ISBN 978-981-19-7963-7 (eBook)
https://doi.org/10.1007/978-981-19-7963-7

© The Editor(s) (if applicable) and The Author(s), under exclusive license to Springer Nature Singapore Pte Ltd. 2023
This work is subject to copyright. All rights are solely and exclusively licensed by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publisher, the authors, and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Singapore Pte Ltd.
The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

Dedicated to my grandfather Late Shri Parmanand Singh

Preface

In the last two decades, nanoscience and nanotechnology have attracted tremendous research attention towards technological developments that are based on the outstanding and appealing intrinsic features of nanomaterials. A variety of nanomaterials are being synthesized that display better performances than their bulk counterparts; therefore, a wide range of applications are envisaged. Recently, significant effort has been devoted to realize applications of nanomaterials in the area of science, engineering, and medical field. Considering the technological importance of nanomaterials, this book has been designed to provide comprehensive information about the recent progress and applications shown by various nanomaterials. Editors of this book opine to provide the necessary background of nanoscience and nanotechnology to the researchers and readers to build strong fundamentals and deep knowledge about the subject. Certain emerging and well-established nanomaterials such as carbon and graphene-based nanomaterials, metal, nanometal oxides, layered chalcogenides, MXenes, ceramic nanomaterials, polymer nanocomposites, metal nanoparticles, nanofluids, etc., are discussed. For the reader, this book covers detailed information about the different nanomaterials sources of synthesis roots and their characterization techniques. Additionally, this book also provides detailed information on fundamental applications of emerging nanomaterials in a variety of fields of science and technology, including energy, electronics, medical, sensing, etc.

This book consists of 12 chapters and provides the fundamentals to advance discussion regarding the capabilities of nanomaterials and their potential applications and limitations. Chapter 1 provides a general overview of different nanomaterials. In this chapter, Dr. Dheeraj K. Singh and co-workers from IITRAM, Ahmedabad, India, have discussed the history of nanomaterials from the prehistoric era to the modern age. They also cover the properties of materials at the nanoscale, classifications of nanomaterials based on their origin, compositions, and dimensions, as well as various synthesis routes, and applications in different fields including energy, electronics, food, medical, sensing, defense, etc. Chapter 2 is based on carbon nanomaterials. In this chapter, Dr. Rajesh Kumar Singh, CUHP, Dharamshala, India, and his team have briefly discussed the various synthesis routes of carbon nanomaterials including carbon nanotubes, fullerene, and carbon dots. The discussed synthesis methods include chemical vapor deposition (CVD), arc discharge, laser ablation, etc. A separate section in this chapter is dedicated to the various applications of carbon-based nanomaterials including energy storage, biomedical, and sensing applications. In Chap. 3, Dr. Pawan Kumar Dubey from the University of Connecticut, USA, provided a detailed discussion regarding the recent development in the synthesis and applications of graphene-based nanomaterials. Chapter 4 is written by Dr. Puneet Khandelwal from JHU, Maryland, United States, that presents various synthesis approaches, characterization techniques, and applications of metal nanoparticles. In Chap. 5, Dr. Dheeraj K. Singh and his group from IITRAM, Ahmedabad, India, have summarized the synthesis routes, characterization techniques, and physiochemical properties of metal oxide-based nanoparticles (MONPs) and their applications in a variety of fields, including solar cells, batteries, biomedicines, wastewater, pollutant treatment, etc.

A summary of nanocrystalline high entropy alloys (HEAs) and high entropy oxides (HEOs) materials is provided in Chap. 6 written by the group of Dr. Rohit R. Shahi from CUSB, Bihar, India. A thorough description of the various synthesis techniques for nanocrystalline HEAs and HEOs is included along with the understanding of their remarkable properties and some of the advanced functional applications. Further, Chap. 7 provides an overview of two-dimensional (2D) transition-metal dichalcogenides (TMDCs) materials. Here, Prof. Ashish K. Mishra of IIT-BHU, India covered several synthesis techniques and briefly emphasized the characteristics of TMDs for their numerous applications in the fields of optoelectronics, energy, and biomedicine. In Chap. 8, Dr. Jeevan Jyoti, PDPU, Chandigarh, and Dr. Bhanu Pratap Singh, CSIR-NPL, New Delhi, India, provide in-depth information regarding MXene-based nanomaterials. This chapter includes a detailed discussion of the different MXene synthesis techniques, their properties, and their applications in a variety of fields. Moreover, nowadays, ceramic nanocomposite is widely used in a variety of electrochemical devices owing to their great applications in the field of energy. Therefore, in Chap. 9, Dr. Raghvendra Pandey and Prof. Prabhakar Singh describe the key concepts behind nanocomposite ceramics and explore their various types. This chapter also reveals the various fabrication techniques for the preparation and processing of nanocomposites ceramics as well as their physical properties and applications along with the benefits and flaws of nanocomposites. Polymer nanocomposites have a wide range of applications in a variety of fields because of their low toxicity and biocompatibility. Hence, Chap. 10 is devoted exclusively to polymer composite nanomaterials by Dr. Amaresh Kumar Sahoo, IIIT, Allahabad, India, where a thorough understanding of the various synthesis approaches, characterization approaches, and applications of polymer nanocomposites is developed. Chapter 11 covers the biomedical applications of advanced nanotechnologies. In this chapter, Dr. Chandraiah Godugu from NIPER, Hyderabad, India, outlines the uses and applications of several nanotechnologies and advanced nanomaterials for diagnosis and therapy. The primary focus of this chapter is on the biomedical applications of inorganic (metal and metal oxide) and organic (carbon nanotubes and liposomes) nanoparticles and their nanopattern surfaces for diagnostics, biosensing, and bioimaging applications, as well as drug delivery, theranostic systems, and bone replacing implants. In Chap. 12, Dr. Sanjay Singh from DBT-NIAB, Telangana, India, addresses the recent developments and uses of nanomaterials as nutritional supplements and therapeutic agents for animal nutrition and the treatment of various animal diseases causing microbes, parasites, and fungi as well as vaccine adjuvant made by nanotechnology. He also discusses the limitations of nanoparticles for animal health and nutrition.

It is expected that this book will make the readers enthusiastic about the recent advancement and importance of nanoscience and nanotechnology by providing a thorough understanding of the various synthesis and characterization techniques along with the fundamental applications of nanomaterials. Additionally, the outlined merits and demerits together with possible solutions will also encourage young scientists and researchers to make new discoveries in this field.

Ahmedabad, India Dheeraj Kumar Singh
Hyderabad, India Sanjay Singh
Varanasi, India Prabhakar Singh

Acknowledgements

I would like to express my sincere gratitude to Almighty God Prabhu Shree Ram, Bajarang Balee, and Maa Saraswati to give me strength for the successful collections of quality book chapters on nanomaterials. The book entitled “Nanomaterials: Advances and Applications” consists of 12 chapters from various reputed institutions across India and abroad. The execution of the book was possible with the unconditional support and help of many individuals, scientists, and academicians. I would like to express my sincere thanks to all of them. First, I would like to show my heartfelt gratitude and thanks to all contributors for providing a quality chapter on the recent developments of nanomaterails. I extend my heartfelt gratitude to IITRAM family for their motivation and good infrastructure.

I owe my deepest gratitude towards the Springer publisher team, especially Loyola D’Silva, Sivananth S Siva Chandran, Anindya Bose, books production team, editorial team, etc., for their guidance to complete the book. I do take the opportunity to thank my seniors and collaborators Prof. Prabhakar Singh and Prof. Sanjay Singh for their enormous support and scientific discussions.

I am grateful to the Science and Engineering Research Board (SERB), DST, Government of India, for financial support to conduct research work at IITRAM which makes a basis to collaborate with the expert researchers and exchange our ideas. My heartfelt and special thanks to my Ph.D. students Hardik, Amit, Deepak, and Nirav for their valuable time to help me during editing the book. Last but not least, I would like to thank my family, my wife Dr. Shweta Singh, my daughter Drishti Singh, my father Jamuna Prasad Singh, and my mother Pramila Singh for their valuable support and sacrifices during the preparations of the book.

Dr. Dheeraj Kumar Singh
IITRAM Ahmedabad, India

Contents

Editors and Contributors

About the Editors

Dr. Dheeraj Kumar Singh (Alexander von Humboldt Fellow, Germany & JSPS Fellow, Japan), Assistant Professor of Physics IITRAM Ahmedabad, Gujarat, India—380026, Office: +91-7967775459, Mobile: +91-9415114778, Home Page: https://dsinghmscrl.wixsite.com/mysite.

He received his Ph.D. degree in Physics from Banaras Hindu University (BHU), Varanasi, India, in 2010. He was subsequently a CSIR-Nehru postdoc at NCL Pune, an NRF postdoc at Seoul, South Korea, and a prestigious Alexander von Humboldt (AvH) postdoc Fellow in Germany. He was also awarded the prestigious international award of JSPS Fellowship, Japan, Dr. DS Kothari Postdoc Fellowship, CSIR-SRF, UGC-Meritorious Fellowship (RFSMS), etc. Currently, he is working as an Assistant Professor of Physics at IITRAM Ahmedabad. His research group is mainly focused on frequency and time domain spectroscopic techniques, their development, and applications on ionic liquids, biomolecules, functionalized nanomaterials, molecular interactions, renewable energy-based materials, etc. Moreover, he has written many book chapters and has the patent granted by the USA. He has organized many workshops and conferences on functional molecules and materials. He has edited two Books in Springer Nature as a corresponding editor. He has been awarded the prestigious ECR Project grant by SERB-DST, Government of India, and DST-Inspire Project for his Ph.D. student.

He has published more than 75 research papers in an international journal of repute. e-mail: dheerajsingh@iitram.ac.in

Dr. Sanjay Singh Scientist—FDBT-National Institute of Animal Biotechnology Hyderabad—500032, Telangana, India, Phone (off): 040-23120135, Webpage: https://www.niab.res.in/peoplesanjaysingh/.

He is currently working as a Scientist—F at DBT-National Institute of Animal Biotechnology (NIAB), Hyderabad, India. He has obtained his Ph.D. degree from CSIR—National Chemical Laboratory, Pune, India. He worked as a postdoctoral research fellow at the Burnett School of Biomedical Sciences, University of Central Florida, Orlando, and at the Department of Pharmacology, College of Medicine, Pennsylvania State University, Hershey Pennsylvania, USA. Subsequently, he worked at Ahmedabad University, Ahmedabad, India, as an Assistant Professor (2012–2017) and Associate Professor (2017–2021) and worked on novel inorganic nanozymes exhibiting catalytic activities and multifunctional drug-delivering nanocarriers. He has published 95 international peer-reviewed scientific research papers, 19 book chapters, and 4 edited books in the area of Nanobiotechnology and Nanomedicines. He has been bestowed with several international awards including the prestigious Endeavour Research Fellowship, Yamagiwa-Yoshida Memorial International Grant Award, International Association of Advanced Materials Scientist Medal, and EMBO Fellowship. He has also attracted several research grants from national and international funding agencies. e-mail: sanjay@niab.org.in

Dr. Prabhakar Singh Indian Institute of Technology, Banaras Hindu University (IIT BHU) Varanasi-221005 (India).

Prabhakar Singh, Ph.D. (University of Muenster Germany), is a Professor in the Department of Physics, Indian Institute of Technology (Banaras Hindu University), Varanasi. He completed his M.Sc. in Physics and M.Tech. in Materials Science and Technology from Banaras Hindu University, Varanasi. He graduated from Udai Pratap College, Varanasi. He has served as an Assistant Professor in Udai Pratap College, Varanasi, and Indira Gandhi National Open University (IGNOU), New Delhi, for more than 8 years. He joined the Institute of Technology, Banaras Hindu University in 2007 as a Reader/Associate Professor. He became a Professor of Physics in September 2015 at IIT (BHU) Varanasi. With more than two decades of teaching and research experience, he has more than 130 peer-reviewed international publications, 7 book chapters, and 1 monograph to his credit. His research interests include physics of materials for energy applications such as solid oxide fuel cells, solar cells, and piezoelectric/dielectric. He has supervised 12 Ph.D. and 15 master's students for their Ph.D. and master's theses, respectively, and mentored several postdoctoral fellows under various national fellowship schemes. He has completed successfully six externally funded projects as principal investigator and currently two externally funded projects are running under his principal investigatorship. He has visited several countries to carry out his academic and research works and has many international collaborations. He is a member of many national and international professional societies. He has attended more than 50 national and international conferences and delivered invited talks. e-mail: psingh.app@iitbhu.ac.in

Contributors

Stuti Bhagat DBT-National Institute of Animal Biotechnology (NIAB), Gachibowli, Hyderabad, Telangana, India;
DBT-Regional Centre for Biotechnology (RCB), Faridabad, Haryana, India

Amit K. Bhojani Department of Basic Sciences, Institute of Infrastructure Technology Research And Management, Ahmedabad, Gujarat, India

Pradeep Kumar Bolla Department of Biomedical Engineering, College of Engineering, The University of Texas at El Paso, El Paso, TX, USA

Raviteja Bulusu College of Pharmacy and Pharmaceutical Sciences, Florida A&M University, Tallahassee, FL, USA

Yong-Song Chen Department of Mechanical Engineering and Advanced Institute of Manufacturing With High-Tech Innovations, National Chung Cheng University, Chiayi, Taiwan

Nitika Devi Department of Mechanical Engineering and Advanced Institute of Manufacturing With High-Tech Innovations, National Chung Cheng University, Chiayi, Taiwan

Pawan Kumar Dubey Center for Clean Energy Engineering, Department of Materials Science and Engineering, University of Connecticut, Storrs, CT, USA

Chandraiah Godugu Department of Regulatory Toxicology, National Institute of Pharmaceutical Education and Research (NIPER), Balanagar, Hyderabad, Telangana, India

Amit K. Gupta Functional Materials Research Laboratory, Department of Physics, Central University of South Bihar, Gaya, Bihar, India

Jay Deep Gupta School of Materials Science and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi, India

Junsung Hong Center for Clean Energy Engineering, Department of Materials Science and Engineering, University of Connecticut, Storrs, CT, USA

Priyanka Jangra School of Materials Science and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi, India

Nirav Joshi Department of Basic Sciences, Institute of Infrastructure Technology Research And Management, Ahmedabad, Gujarat, India

Jeevan Jyoti Centre of Advanced Studies, Physics Department, Panjab University, Chandigarh, India

Hardik L. Kagdada Department of Basic Sciences, Institute of Infrastructure Technology Research And Management, Ahmedabad, Gujarat, India

Shabari Girinath Kala Department of Pharmaceutical Sciences, Jawaharlal Nehru Technological University, Ananthapuramu, Andhra Pradesh, India

Puneet Khandelwal Department of Radiology, School of Medicine, Johns Hopkins University, Baltimore, MD, USA

Nagavendra Kommineni Center for Biomedical Research, Population Council, New York, NY, USA

Rajesh Kumar Department of Mechanical Engineering, Indian Institute of Technology, Uttar Pradesh, Kanpur, India

Priyanka Kumari Functional Materials Research Laboratory, Department of Physics, Central University of South Bihar, Gaya, Bihar, India

Kevin Lee Center for Clean Energy Engineering, Department of Materials Science and Engineering, University of Connecticut, Storrs, CT, USA

Divya Mehta DBT-National Institute of Animal Biotechnology (NIAB), Gachibowli, Hyderabad, Telangana, India;
DBT-Regional Centre for Biotechnology (RCB), Faridabad, Haryana, India

Ashish Kumar Mishra School of Materials Science and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi, India

Bhavita G. Mistry Macromolecular Materials Laboratory, Applied Chemistry Department, Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda, Vadodara, India

Shashi Kant Mohapatra Functional Materials Research Laboratory, Department of Physics, Central University of South Bihar, Gaya, Bihar, India

Deepak K. Pandey Department of Basic Sciences, Institute of Infrastructure Technology Research And Management, Ahmedabad, Gujarat, India

Raghvendra Pandey Department of Physics, ARSD College, University of Delhi, New Delhi, India

Shashank Reddy Pasika Department of Biotechnology, National Institute of Pharmaceutical Education and Research – Raebareli (NIPER-R), Raebareli, India

Sivasankar Putta Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA, USA

Sneha Ranjan Department of Biotechnology, Babasaheb Bhimrao Ambedkar University, Lucknow, UP, India

Balaga Venkata Krishna Rao Department of Pharmaceutical Sciences & Technology, Birla Institute of Technology, Mesra, Ranchi, Jharkhand, India;
School of Pharmacy, Suresh Gyan Vihar University, Jagatpura, Jaipur, Rajasthan, India

Amaresh Kumar Sahoo Department of Applied Sciences, Indian Institute of Information Technology, Allahabad, Prayagraj, UP, India

Manjit Sandhu School of Mechanical Engineering Department, Indian Institute of Technology Ropar, Rupnagar, Punjab, India

Rohit R. Shahi Functional Materials Research Laboratory, Department of Physics, Central University of South Bihar, Gaya, Bihar, India

Raj Kumar Sharma Department of Radiology, School of Medicine, Johns Hopkins University, Baltimore, MD, USA

Saurabh Shivalkar Department of Applied Sciences, Indian Institute of Information Technology, Allahabad, Prayagraj, UP, India

Ankita Singh School of Materials Science and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi, India

Bhanu Pratap Singh Advanced Carbon Products and Metrology, CSIR-National Physical Laboratory, New Delhi, India

Dheeraj K. Singh Department of Basic Sciences, Institute of Infrastructure Technology Research And Management, Ahmedabad, Gujarat, India

Prabhakar Singh Center for Clean Energy Engineering, Department of Materials Science and Engineering, University of Connecticut, Storrs, CT, USA;
Department of Physics, Indian Institute of Technology (BHU), Varanasi, India

Rajesh Kumar Singh School of Physical and Material Sciences, Central University of Himachal Pradesh (CUHP), Dharamshala, HP, India

Sanjay Singh DBT-National Institute of Animal Biotechnology (NIAB), Gachibowli, Hyderabad, Telangana, India;
DBT-Regional Centre for Biotechnology (RCB), Faridabad, Haryana, India

Surya Kant Tripathi Centre of Advanced Studies, Physics Department, Panjab University, Chandigarh, India

Chapter 1
An Overview of Nanomaterials: History, Fundamentals, and Applications

Hardik L. Kagdada, Amit K. Bhojani, and Dheeraj K. Singh

Abstract Nanomaterials exhibit the tendency to alter the fundamental properties with the size in the range of nanometers. The fascinating nanomaterials exhibit excellent fundamental properties and possess numerous applications in the fields of science and technology. However, the concept of nanomaterials already existed in prehistoric times unknowingly. Therefore, the present chapter discusses the historical overview, usage, and development of nanomaterials from the prehistoric time to the modern age. The scientific milestones achieved for the development of nanomaterials and nanotechnology have also been covered. Further, the properties at the nanoscale have been discussed in terms of confinement effect and the surface-to-volume ratio. The classification of nanomaterials based on several factors such as origin, composition, and dimensionality are elaborated. This chapter also included the possible synthesis approaches along with their benefits and disadvantages. Moreover, we briefly explore the general overview of nanomaterials for a variety of applications in the fields of energy, medicine, electronics, sensing, defense, etc.

Keywords Nanomaterials · Historical overview · Classification of nanomaterials · Synthesis approaches · Applications

1.1 Historical Overview

Nanomaterials are arising as a revolutionary class of materials, unfolding a wide range of applications, by possessing the size or one or all of the dimensions in the nanometer range with unique properties. The word "Nano" is originated from the Greek phrase "nanos," which is defined as very short men. The astonishing history of nanomaterials reveals that they have existed naturally in ancient times. The history of nanomaterials is flabbergasting and long, which includes naturally occurred and man-made nanomaterials. Natural sources of nanomaterials consist the forest fire products, ocean spray, volcanic ash, etc. Moreover, from the meteorites, nanodiamonds have

---

H. L. Kagdada · A. K. Bhojani · D. K. Singh (✉)
Department of Basic Sciences, Institute of Infrastructure Technology Research And Management, Ahmedabad, Gujarat 380026, India
e-mail: dheerajsingh@iitram.ac.in; dheerajsingh84@gmail.com

D. K. Singh et al. (eds.), *Nanomaterials*,
https://doi.org/10.1007/978-981-19-7963-7_1

been obtained, also known as the most abundant presolar grain [1], which suggests that the nanomaterials may have originated from the big bang process. One example of nature's nano assembly is the Nacre, where the mollusks are formed from calcium carbonate through the nanopatterning process and provide outstanding hardening [2]. Another attraction of nature's nanomaterials is spider silk, prepared from the polymer consisting of protein and exhibits strength more than that of high-tensile steel [3].

Since, prehistoric times, humans have synthesized and utilized nanomaterials for several purposes. Specifically, artists from ancient times have strategically used nanomaterials for cave paintings. From Sulawesi, Indonesia, cave paintings consisting of hand stencils have been found dated back to 40,000 BCE, which were prepared from fat, charcoal, and plant pigments [4]. Date back to 34,000 BCE, another piece of work of the hand stencil and wild mammals have been discovered in the Chauvet Pont-d'Arc Cave, France, where graphene and other nanocomposites have been used unknowingly [5, 6]. Further, for cloth bleaching purpose Cyprus clay have been utilized since 5000 BCE [7].

In ancient times, humans are not known that soot exhibits carbon-based nanomaterials. Before 4500 years, humans utilized asbestos nanofibers having a diameter of 50–200 nm to the reinforcement of ceramic matrix materials [8]. The PbS nanoparticles (also known as galena) have been used for the hair dye material, where the PbS change the optical properties of the hair shaft with no effect on the mechanical properties of the hairs [9]. This concept provided the development of the hair dye formula 2000 years ago [9]. The azure pigment exhibits a hydrophobic nature, also known as the Maya blue used for corrosion resistance, manufactured using the indigo dye and nanoporous clay in the Mayan city of Chichen Itza [10, 11]. One of the ancient artworks from the Roman time was the Lycurgus Cup (~400 CE), which changes its color from green to red under the illumination of light (See Fig. 1.1). The material of the cup consists of the doping of silver and gold nanoparticles modifies the color according to the light [12]. In medieval times, the bright red and yellow colors of the glass windows in the churches appeared due to the presence of gold and silver nanoparticles [13]. Between 300 and 1700 AD, nanoparticles have been extensively used for manufacturing steel (also known as damascus steel) swords, where nanoparticles play a vital role in the strength, sharpness, and shatter resistance [14]. In 900 AD, the Indian civilization used cemenites nanowires and carbon nanotubes in the microstructure of wootz steel [15].

The scientific report for nanomaterials started in 1857, by Michael Faraday, synthesized the colloidal solution of gold nanoparticles, called "activated gold." Faraday discussed this work at the royal society of London with the statement, "Gold reduced in exceedingly fine particles, which becoming diffused, produce a ruby red fluid, the various preparations of gold, whether ruby, green, violet or blue consist of that substance in a metallic divided state" [16]. Figure 1.2 depicts the major milestones of the developments in the field of nanomaterials and nanotechnology. Moreover, in the 1940s, silica nanoparticles have been used as a replacement for carbon black in rubber reinforcement [17]. The concept of nanotechnology and nanoscience was boosted in 1959 through the revolutionary statement "There's plenty of room

Fig. 1.1 Lycurgus cup, left size is reflected and right side shows the transmission of light (adapted with permission from [8]). Copyright (2013) (Elsevier)

at the bottom" by physicist Richard Feynman during his talk at the American Physical Society meeting at the California Institute of Technology [18]. In the same talk, Feynman asked and discussed that "W*hy cannot we write the entire 24 volumes of the Encyclopedia Brittanica on the head of the pin.*" Moreover, Feynman suggested the possibility of modulation in materials at the atomic level, where the properties are drastically different from the large scale. Furthermore, Feynmann also depicted that smaller and smaller sizes neglect gravity, while van der Waals interactions and surface tension parameters would be more dominant. Due to his revolutionary statements and discussion, Richard Feynmann is also known as the "Father of nanotechnology," although he never mentioned explicitly the word Nanotechnology [17]. In 1974, Japanese scientist, Norio Taniguchi was the first to define the term Nanotechnology as the process of atomic-level deformation and separation of materials [19]. However, the term nanotechnology was not famous till 1986, when the American engineer Eric Drexler published a book named *Engines of creation: the Coming Era of Nanotechnology*, which brings spans the revolutionary field of nanotechnology [20]. After that, the great inventions in experimental techniques such as scanning tunneling microscopy (STM) by Heinrich Rohrer and Gerd Binnig in 1981, which allowed to see the materials at the atomic scale leads to a boost in the awareness of nanotechnology. For such an invention, Rohner and Binning were awarded the Nobel prize in physics [21]. After that, the growth in the carbon allotropes towards the nano dimensions fuels the development of nanomaterials. Started with the discovery of fullerenes by Harold W. Kroto, Richard E. Smalley, and Robert F. Curl Jr. in 1985 [22], and all three scientists were awarded the Nobel prize in 1996. Further, the IBM scientists successfully orchestrated the logo of IBM by moving the Xenon atoms on the surface using STM tips [23]. Such exceptional work moves one step closer to the Feynmann hypothesis. For carbon nanotubes, Japanese inventor and physicist Sumio Iijima is often cited as the inventor of carbon nanotubes [24]. After

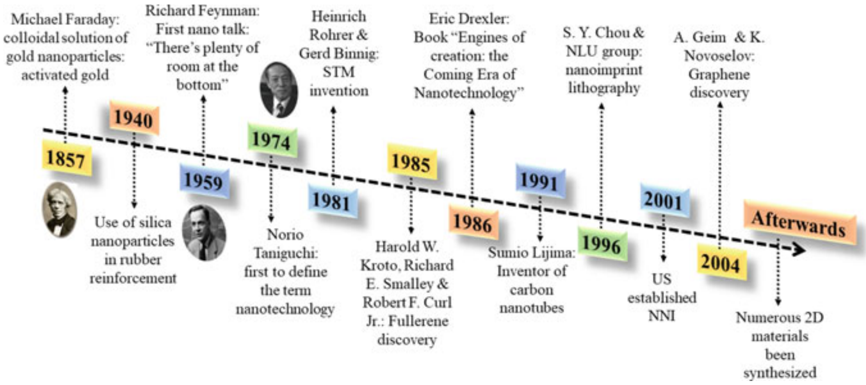

Fig. 1.2 Scientific milestones of nanomaterials and nanotechnology from the year 1857

that, the concept of nanoimprint lithography has been proposed for the first time by Chou and the group at the Nanostructure Laboratory of the University of Minnesota [25]. The transformation of integrated chips (ICs) also can be considered a part of the historical development of nanotechnology in the field of electronics. In 1947, the single transistor size was in the range of micro-objects, based on the demands of miniaturization and maintaining the pace with Moore's law, the size of transistor deduced significantly and in the year 2002, it further reduced to 90 nm [17]. Currently, the size of transistors is reduced to below 10 nm. In 2001, the United States established the national nanotechnology initiative (NNI) for the systematic and scientific development of nanomaterials and nanotechnology [26]. With novel properties and remarkable applications, the most eminent carbon-based nanomaterial, single-layer graphene has been synthesized successfully by Andre Geim and Konstantin Novoselov and awarded the Nobel prize in Physics in the year of 2010 [27]. The discovery of graphene further leads to the development of numerous two-dimensional materials. There are several specific journals devoted to nanotechnology and nanomaterials such as the International Journal of nanotechnology, Journal of nanoscience and nanotechnology, Journal of nanoparticle research, Nano letters, etc., have been started [26].

1.2 What Happened at the Nanoscale?

The nanometer is the distance, which is equal to the 1 billionth part of the one-meter distance (1 nm = 10^{-9} m). The properties of nanomaterials show a drastic change when one of the dimensions or sizes belongs to the nanometer range. Now, the question is: why the properties of materials are so different at the nanometer scale compared to their bulk structure? The classical mechanics or thermodynamics failed to reveal the proper explanation of the properties of nanomaterials. While quantum mechanics unveil the fundamental aspects of the materials at the nanoscale region, where the motion of the electron is confined. The size or dimension of materials is analogous to the de Broglie wavelengths of electrons, phonons, or excitons, the confinement effect originated, which leads to the dramatic variations in the properties of the materials. Based on the amount of confinement, the materials can be distinguished into (i) quantum dots or zero-dimensional materials (0D), (ii) quantum wires or one-dimensional (1D) materials, and (iii) two-dimensional (2D) materials or thin films. The detailed classification of nanomaterials is discussed in the next section. Due to the confinement effects, the density of states (DOS) plays an important role in the fundamental understanding of the transport, spectroscopic and optical properties of materials at the nanoscale region [28]. The density of states is defined as the number of energy states for the range of unit energy. For each dimensionality of the particles, the density of states related to the energy is presented in Fig. 1.3. It is clear that the DOS for 0D materials has discrete energy levels and is represented by the Dirac delta function. In the case of 1D materials or nanowires, the energy states are inversely proportional to the square root of the energy. However, for 2D materials or thin films, the density of states becomes constant as a function of energy, while the same is proportional to the square root of the energy for the case of 3D materials, where no quantum confinement is probed [28]. Moreover, reducing the particle size increases the portion of atoms at the surface of the nanomaterials. Therefore, the nanomaterials exhibit a larger surface area to volume ratio, compared to the bulk materials, which results in anomalous changes in the fundamental properties. Furthermore, at the surface region, the atoms may possess unsatisfied dangling bonds, which exhibit lower stability than that of the bulk materials. The interaction of materials occurred at the surface, and therefore, due to unsatisfied bonds and large surface-to-volume ratio, the nanomaterials reveal a higher chemical activity compared to the 3D materials. The fascinating impact of the quantum confinement on the physical properties is the variation in the band gap with the size of the nanomaterials [29, 30]. Here, the confinement leads to an increase in the band gap of nanomaterials. Figure 1.4 shows the schematic diagram of the particle size-dependent band gap variation. For the weak confinement region, the coulomb energy is stronger than the confinement energy, which results in the electron–hole as a pair product, while, for the strong confinement regime, the energy of confinement overcomes the Coulomb energy and the electron and hole exhibit separate confinement in the spherical potential [31–33]. The optical absorption spectrum of the nanomaterials responds according to the size confinement of the nanoparticles, which provides the tunning of the light-absorbing properties at the nanoscale. For example, the photoluminescence peak of the CdSe quantum dots reduces with increasing size and exhibits the shifting of the peak toward blue light [34]. The optoelectronic properties of the graphene have been significantly tunned by preparing graphene nanosheet using the bottom-up approach, where hydrocarbons covered the graphene to maintain the sp^2 configuration [35].

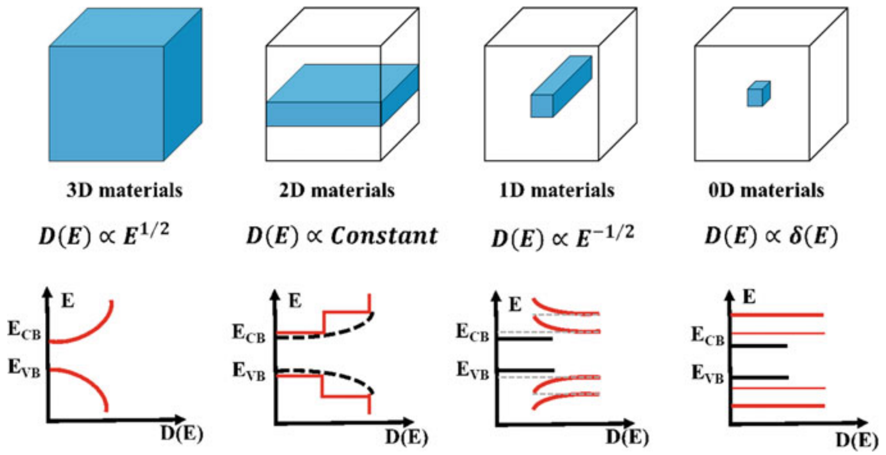

Fig. 1.3 Upper panel represents the schematic presentation of confinement effect. While lower panel depicts the nature of density of states with increasing the confinement in each dimension

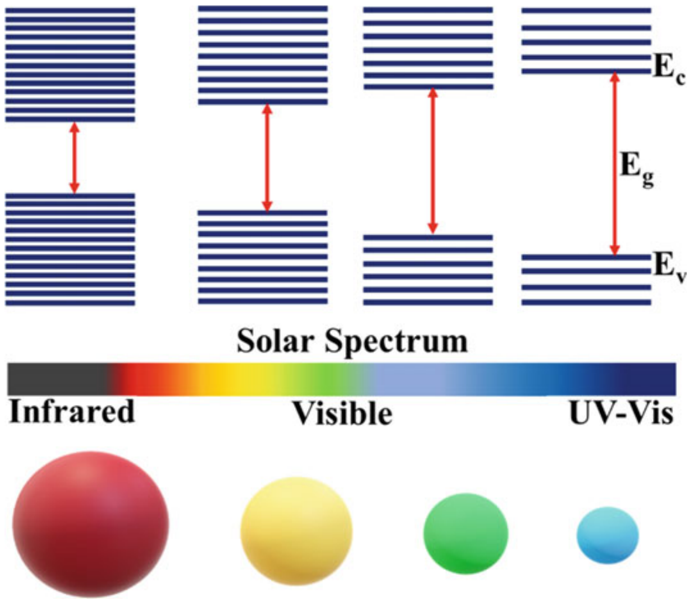

Fig. 1.4 Schematic presentation of the electronic properties of the nanoparticles with various sizes

1.3 Classification of Nanomaterials

The most studied materials of the current century, nanomaterials, gave birth to the new field of science and technology, often called nanotechnology. This class of materials is manufactured or fabricated at the nanometer scale and the properties of nanomaterials are drastically changed compared to that of bulk materials. The classification of nanomaterials depends on several factors such as the origin, size, shape, chemical composition, characteristics, and applications. Based on the origin, there are two types of nanomaterials, naturally originated which are produced non-intentionally and belong to the environment, while another class consisting the nanomaterials made up of defined purpose through the systematic synthesis or fabrication process such as top-down and bottom-up approaches.

On the other hand, based on composition, the nanomaterials are classified into majorly four categories, carbonaceous, organic, inorganic, and composite-based nanomaterials. The carbonaceous nanomaterials exhibit the sp^2 hybridization in their orbital configuration. Graphene, nanodiamond, carbon nanotubes, fibers, nanowires, and nanographite are examples of carbonaceous nanomaterials. Chapter 2 consisting a detailed discussion of carbon-based nanomaterials. The organic category includes bioinspired nanomaterials such as micelles, dendrimers, ferritin, liposomes, etc., and exhibits a size ranging from 10 to 1000 nm [36]. On the other hand, the inorganic nanomaterials consisting of non-carbon elements such as metal and metal oxides (Chaps. 4 and 5), metallic nanoclusters, magnetic nanomaterials (Chap. 6), nanoclay, zeolite, groups IV–VII-based nanomaterials (specifically the chalcogenides, Chap. 7), MXenes (Chap. 8), etc. The majority of the inorganic nanomaterials exhibit a crystalline nature and different sizes and shapes (spheres, cubes, stars, ellipsoids, cylinders, etc.) in their structure, resulting in a wide range of desired properties for various fields of science and technology. The fourth category in this section includes the composite-based nanomaterials (Chaps. 9 and 10), which exhibit the matrix-based structure, where the metal, polymer, hydrogel, or ceramic are considered as the matrix in the nanostructure. The hydrogels depict biocompatible activities in precise surroundings and have been utilized for drug delivery applications [37].

Based on the dimensionality the nanomaterials have been classified into three types; zero-dimensional (0D), one-dimensional (1D), and two-dimensional (2D) nanomaterials. The size and morphology change according to the dimensionality of the nanomaterials, which provides a significant tunning of the properties.

0D nanomaterials: All three dimensions are confined to the nanometer scale, consisting of a few tens to thousands of atoms in the range of 2–100 nm. The 0D materials include fullerenes, quantum dots, nanoclusters, nanoparticles (magnetic and metallic), etc. Fullerenes having 60 carbon atoms, named buckminsterfullerene (C_{60}), honor the American architect Buckminster Fuller who is known to bring geodesic structures into the field of architecture [22]. The cage-like structure has the shape of a soccer and a diameter of ~1 nm, fullerenes consisting of the bonds of each carbon atom to the other three carbon atoms similar to graphite. Despite having a sphere-like structure all carbon atoms in the structure exhibit the sp^2 hybridization and possess a higher surface-to-volume ratio for broad applications in the field of science and technology. Other 0D nanomaterials are the quantum dots (QDs), which exhibit a semiconducting nature having a size in the range of 2–10 nm and consisting the 10–50 atoms. The optical properties of the quantum dots are quite different than that of the bulk materials as QD emits various colors of light with the size and surface morphology. Due to its very small size, the optical properties are highly sensitive to the number of atoms. For example, the carbon quantum dots having a size <1.2 nm possess the emission of ultraviolet (UV) light, while the same has emitted visible light with a size between 1.5 and 3 nm, which further provides the infrared light for the size of ~3.8 nm [38, 39]. On the other hand, metal and metal oxide nanoparticles exhibit a similar nature of size-dependent optical properties, which is also known as surface plasmon resonance (SPR) [40, 41]. The silver and gold nanoparticles were studied most for the SPR phenomena, where the electric field inside the particle will be significantly enhanced through the coupling of plasmon with the external incident light and provides the scattering and absorption of light [42–51]. Both gold and silver nanoparticles exhibit potential applications in medical science, diagnostics, sensors, and solar cells. Specifically, silver nanoparticles possess promising usability as antibacterial and anti-microorganisms [52, 53]. Similarly, metal oxide nanoparticles such as ZnO, TiO_2, Fe_2O_3, etc., possess excellent size and shape-dependent physicochemical properties and broad applications in renewable energy and medical sectors [54–56].

1D nanomaterials: This class of nanomaterials exhibits the two dimensions in the nanoscale range. Examples are nanotubes, nanofibers, and nanowires, which are heavily attractive for usage in thin film-based devices [57–59]. One of the most studied 1D nanomaterials is the carbon nanotubes (CNTs), which are the elongation of the fullerenes in one of the dimensions with a cylindrical shape, consisting of the micron to the millimeter of length and nanometer range of diameter. CNTs are of two types, one is single-walled CNTs (SWCNTs), while another is multi-walled CNTs (MWCNTs), which exhibit an interlayer distance similar to that of graphite [60]. Based on the chirality and diameter of the nanotubes the desired range of physical properties can be achieved. For example, the bandgap of the CNTs is highly sensitive to the diameter, where the larger the bandgap results from the smaller diameter and vice versa [61]. CNTs possess exceptional mechanical properties among all carbon materials, whereas Young's modulus of CNTs is approximately five times higher than that of steel [62, 63]. Apart from carbon-based 1D nanomaterials, metal chalcogenides and boron nitride-based 1D nanomaterials are also reported significantly for their physical properties and variety of applications with the size and length of the nanoribbon and nanotubes [64].

2D nanomaterials: With the plane-like structure in two dimensions, 2D nanomaterials have one dimension in the nanometer range, where electrons are confined to move. This class of materials includes graphene and graphene oxides (Chap. 3), transition metal dichalcogenides and oxides, boron nitride and pnictides, group-IV chalcogenides, group-IV-based elemental 2D nanomaterials, and MXenes. The 2D materials revealed the prospective applications in the electronic, optoelectronic and sensing devices, energy and environmental sector as well as in biomedicine, attributed to their exceptional physical properties such as high mechanical strength, electronic and optical tunability and flexibility in the structure [65–67].

1.4 Synthesis of Nanomaterials

Over the decades, nanostructured materials have captivated a significant research interest due to their size and shape depending on physical, chemical, electronic, and magnetic properties. The performance of nanomaterials depends on their properties, which mainly depend on the structure, composition, defects, and interfaces, and are directed by synthesis root. Therefore, several synthesis techniques have been developed to construct different types of nanomaterials with controlled size, shape, structure, and dimension. Such available synthesis techniques are used to fabricate the various form of nanomaterials like nanocolloids, powders, clusters, roads, tubes, and so on. The synthesis methods of nanomaterials (nanoparticles) are categorized into two parts: (i) top-down, and (ii) bottom-up approaches. The first approach is a breakdown method in which a solid material is converted into nano-sized particles in the presence of external force. In the second approach, the nanoparticles build by assembling atoms and molecules from atomic to the nanoscale, also called as build-up method. Figure 1.5 classified the top-down and bottom-up techniques.

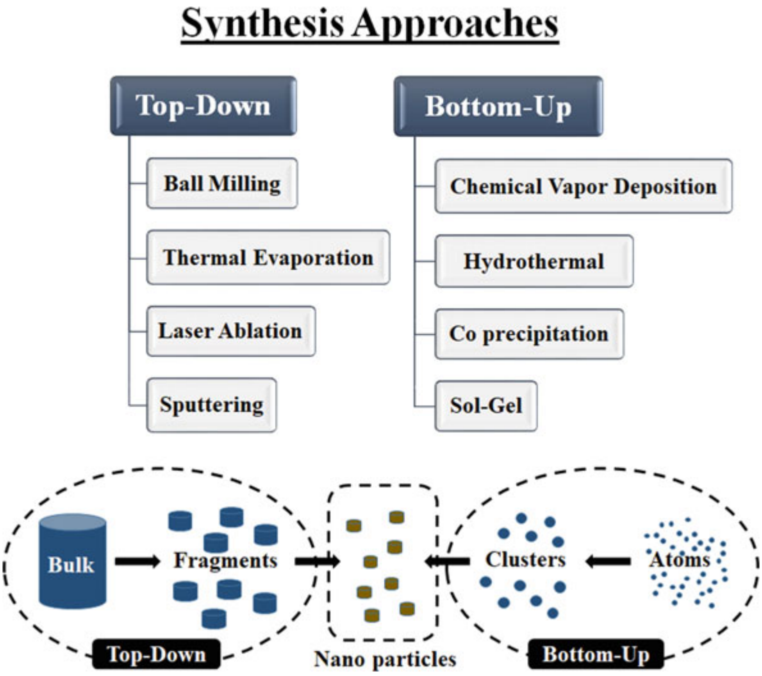

Fig. 1.5 Nanomaterials synthesis techniques: top-down and bottom-up approaches

1.4.1 Top-Down Approach

The top-down approach is easy to use for the transformation of bulk materials into nano-sized structures/particles via wet and dry grinding techniques. Presently, at the industry level, the top-down approach is dominant for the fabrication of man-made nanomaterials. For example, in the semiconductor industry, the photolithography procedure has been used to imprint the metal oxide semiconductor field–effect transistor (MOSFET) onto a silica wafer [68, 69]. In this approach, several operations have been performed on large-scale materials to convert them into nanoscale particles. However, these approaches required a large installation area for setup which makes them quite expensive. Further, the slow growth rate makes them impropriate for the production of large-scale amounts. Top-down approaches are also not suitable methods for soft materials because the mechanical parts used in these devices to grind the materials are rigid and hard. The major downside of these techniques is the irregularity in the shape and particle size of constructed nanomaterials, e.g., the fabricated nanowires using the lithography technique contain lots of structural defects and impurities. Some of the well-known top-down approaches are ball milling, thermal evaporation, laser ablation, and sputtering techniques.

Ball milling. Ball milling is a well-known top-down grinding approach for the fabrication of nanoparticles in powder form. It is one of the easiest and most productive mechanical processes used to create a variety of nanoparticles and metal alloys by transferring the kinetic energy of the grinding medium into the sample material. Ball milling works on the principle of impact and attrition (i.e., friction). As demonstrated in Fig. 1.6, the ball mill consists of a hollow cylindrical shell rotating around its axis horizontally or at a small angle with a horizontal line. Based on the rotation of the ball mill, the ball milling process is divided into various types: planetary, attrition, horizontal, rotatory, and vibratory mill. The grinding medium partially filled inside the ball mill is the hard sphere balls made from steel (chrome and stainless), rubber, flint pebbles, or ceramic materials. The sample material is also placed inside the ball mill along with the grinding medium. As the ball mill rotates, the grinding balls lift near the top of the mill and then drop down to the ground, resulting in the reduction in the size of the target materials by impact. The impact between the grinding balls, mill wall, and target materials creates a fine powder of sample material. The ball milling process is also used for several purposes such as mixing two or more materials, compression of particle size, change in particle structure, agglomeration, modifying the material characteristics, and so on [70]. Some examples of synthesized nanomaterials using different ball milling processes are ZnO nanoparticles (10–30 nm) using high-energy ball milling [71], GR oxide nanoparticles (40 nm) [72], CuO nanoparticles (13.8 nm) [73], and graphite oxide nanoparticles using planetary ball milling process [74].

The ball milling technique possesses several advantages and benefits. Such as, it is a low expensive process, suitable for continuous operation, nanoparticles with the size of 2–20 nm can be produced, simple in serving, reliable and safe, long lifetime, helpful for thickness reduction of various materials, and high capacity, for open and

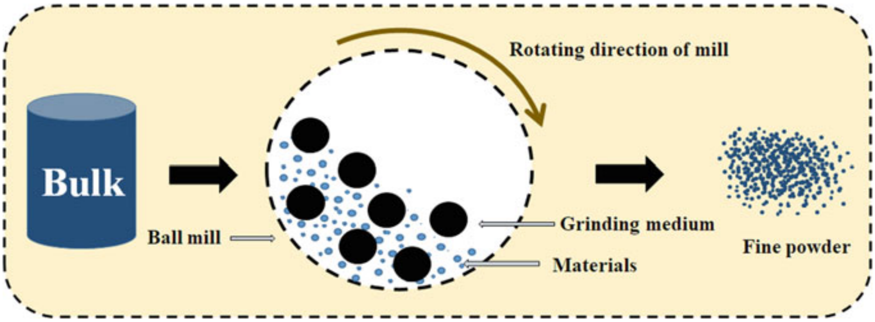

Fig. 1.6 Schematic diagram of ball milling top-down approach

close circuit grinding, to synthesize few milligrams to kilogram nanoparticles within a short time interval of few minutes to few hours [28, 76–78]. The ball milling technique also possesses several drawbacks like low surface, irregular shape nanoparticles, formation of disordered crystal structure, and grinding needs a bunch of energy, noise, and heavyweight [28, 75, 76].

Thermal evaporation. Around the 1850s, Faraday [16] construct an endothermic process known as thermal evaporation in which heat is used for the chemical breakdown of a molecule [79]. Thermal evaporation is also a popular top-down approach for the production of various nanomaterials such as inorganic nanoparticles [80], thin films [81], etc. Figure 1.7 demonstrates the schematic representation of the thermal evaporation technique. As shown in Fig. 1.7, the metal crucible containing the target material is placed inside a high vacuum chamber having pressure below 10^{-4} Torr. In this process, the atoms/clusters/molecules are gets ejected from the target material in vapor form by heating or passing the electrical current from the metal crucible. The generated vapor flux condensed on the surface of the substrate. In electron beam evaporation, when an electron beam is bombarded on the target material it generates the vapor flux. While in the case of thermal evaporation, the joule effect with a suitable temperature has been used to heat the target material. By contacting the target materials with hot surface evaporation can be achieved, known as resistive heating, and used for materials that get vaporized below 1500 °C temperature. Carbon, tungsten, boron nitride and TiB_2 composite ceramics, and molybdenum are well-known resistive heating elements [82]. Some examples of synthesized nanomaterials by thermal evaporation technique are MoS_2 nanowafers (0.7 nm thick) [83], Zn_2GeO_4 nanocrystals (10 nm thick) [84], thin films of SnS (720 nm thick) [85], Ga_2O_3 (350 nm thick) [86].

In comparison with other techniques, the thermal evaporation process acquires numerous advantages. Some of the major advantages are high deposition rate, low-cost apparatus/cost-effective, no need for solvent, suitable for low melting point materials, monitoring and controlling of deposition rate, vapors, and thickness of the film are easy, ultrathin layer materials can be deposited [87, 88]. The thermal evaporation technique also exhibits a few disadvantages. It is incompatible with

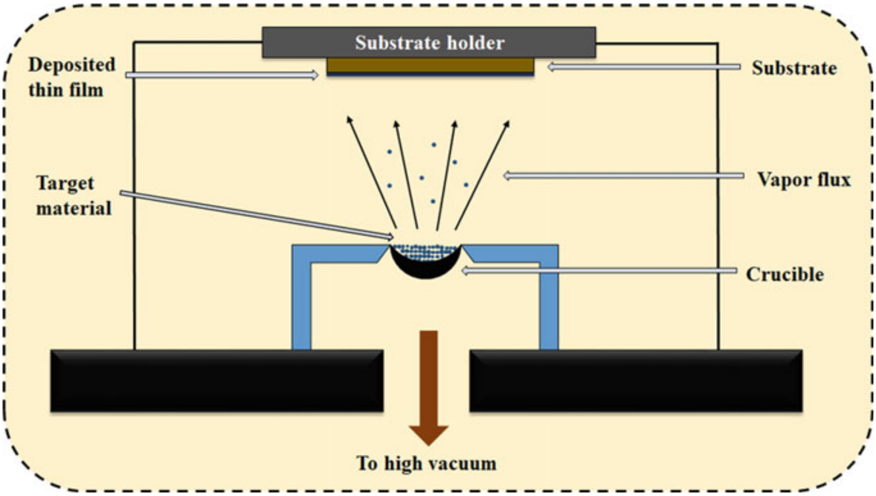

Fig. 1.7 Schematic diagram of thermal evaporation top-down approach

multicomponent thin film production, limited processing variables to control film properties, poor source material, and deposition of various alloys together is also difficult.

Laser ablation (vaporization). Laser ablation is a top-down vaporization method used to fabricate multi-component nanocrystals using high-intensity laser pulses. Laser means high power beam of electromagnetic radiation amplified by stimulated emission which has various applications in the field of medicine, industry, printing, and military [89]. Laser ablation is one of the easiest techniques presented for the synthesis of nanoparticles from multiple solvents by controlling the evaporation process in a short period of time [79]. In this process, a pulsed laser beam has been focused and bombarded on the target interest to vaporize the atoms and molecules from the surface of the target material and fabricates nanostructures as illustrated in Fig. 1.8. When a focused laser beam is targeted on the surface material, it produces vapor/plasma/liquefied metal, which interacts with the liquid medium and generates specific nanoparticles [90] The structure and properties of produced nanoparticles can be tuned by laser and liquid medium (water, ethanol, etc.) [91]. The ablation process only takes place when a target material starts evaporating or melting through absorbing a sufficient amount of energy. It means ablation is a process associated with both evaporation and melting [92].

Usually, the synthesis rate of nanoparticles depends on the energy of the laser pulse. Laser is classified into two types (Infrared and UV/excimer laser) according to their wavelengths, in which excimer is a pulsed gas laser used to generate UV light with power efficiency in the range of 0.2–2% [92]. Laser ablation has applications in numerous fields of ceramics, polymer, and glass industries as well as in cutting,

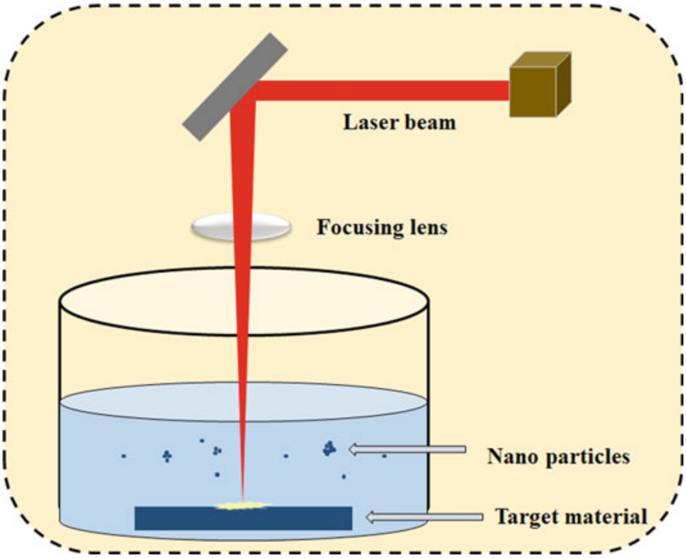

Fig. 1.8 Schematic diagram of laser ablation top-down approach

drilling, and milling through a laser beam. Some examples of synthesized nanoparticles by laser ablation process are carbon nanomaterials [93], ZnO [89, 90]-, SnO [91]-, TiO_2 [90, 94]-, CdO [95]-, and Ag [96]-based nanoparticles.

Some advantages of the laser ablation technique are the ability to produce novel and multicomponent nanoparticles, and energy loss is low during the generation of nanoparticles. There are a few disadvantages of the laser ablation process such as, it needs a large amount of energy to obtain high ablation efficiency, and the increase in the ablation time reduces the effectiveness of the process [97].

Sputtering. Sputtering is a non-thermal vaporization technique, widely used for surface coating, etching, and deposition of thin layers [98, 99]. Sputtering works under low pressure (<0.67 Pa) [100], is controlled by using a vacuum pump, and contains various components like an isolated chamber, sputtering gas source, etc. The high-energy inert gas ions are used to deposit the nanomaterials on the surface of the substrate ejected from the target material as depicted in Fig. 1.9. The interaction mechanism between the ions and target material mainly depends on the ratio of ions–target atomic mass and the energy of incident ions. When the ions get to interact with the surface of the target material, various phenomenon takes place such as generating photons, sputtering out the atoms and molecules from the surface of the target material, secondary electrons, and the creation of vacancy and defects in the target material. Therefore, it is a very effective method for spintronic applications to deposit multilayer films [28]. Depending on their source materials, the sputtering technique is divided into the following types: (i) direct current (DC) sputtering, (ii) reactive sputtering, (iii) radio frequency (RF) sputtering, and (iv) magnetron sputtering. The efficiency of the sputtering technique can be improved by increasing