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Editors
Dermot Brabazon
School of Mechanical and Manufacturing Engineering
Dublin City University
Dublin
Ireland

Eva Pellicer
Physics Department
Universitat Autònoma de Barcelona
Bellaterra
Spain

Fatima Zivic
Faculty of Engineering
University of Kragujevac
Kragujevac
Serbia

Jordi Sort
ICREA
Physics Department
Universitat Autònoma de Barcelona
Bellaterra
Spain

Maria Dolors Baró
Physics Department
Autonomous University of Barcelona
Bellaterra
Spain

Nenad Grujovic
Faculty of Engineering
University of Kragujevac
Kragujevac
Serbia

Kwang-Leong Choy
Institute for Materials Discovery
University College London
London
UK

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Preface

This book is the result of contributions from senior researchers in the various areas of nanotechnology which presents a review of the current state of development. Authors possess extensive experience in both theoretical and practical aspects in relevant subjects and have presented insights into both material development and aspects of practical end applications. Nanotechnology as one of the main drivers of products and services still lacks more focused and clear guidance on commercialization. The focus of this book is to indicate challenges and possible opportunities, fostered by discoveries in nanotechnology, towards real market products and services. Numerous novelties have emerged pertaining to both theoretical foundations to further build upon knowledge, and practical applications especially in sectors of energy, advanced manufacturing, biomedicine, environment sustainability and preservation. Along with great enthusiasm for these innovations, issues related to possible dangers of new nanomaterials and their long-term effects have started to be perceived, strongly indicating the need for a more comprehensive approach. Science has made large steps by taking advantage of the discoveries in the nanoworld, but at the same time this new field is at its infancy, facing different controversies especially regarding practical applications in real products.

Areas of nanotechnology commercialization are very diverse and it is not possible to include all of these in one book. However, some areas can be distinguished due to their prominent already proven results. The study of the multi-scale phenomena of the micro- and macroscale effects simultaneously with nanostructures and their mutual influence is a must, in aiming to develop real products. Together with all the parameters and variables important for the proper functioning, green products and environmental preservation are one of the obligatory constraints to consider, especially in nanotechnologies and nanomaterials. Possible toxicity and detrimental environmental effects therefore need to be well characterised and evaluated.

This book covers diverse areas in which nanoscience and nanotechnology have led to significant technological advances and practical applications, with special emphasis on novel types of nanomaterials and their applicability into a new generation of nano- and microdevices. Different nanomaterials are reviewed with a focus on several practical application areas and their commercial utilization. Production technologies of nanomaterials are presented as one of the challenges today—efficient commercial scale production of nanomaterials to satisfy the needs for large quantities. Both the fabrication and storage of nanoparticles impose great challenges and the costs, in general, with scarcely available technologies, which are still too costly and slow for mass production.

The energy sector has shown perhaps the most prominent recent advancements in nanotechnology commercialization, if energy production, storage and power devices are considered altogether. Ferroelectric and piezoelectric nanomaterials as well as nanomaterials for sustainable energy production and storage have already led to different practical applications, and these are reviewed along with basic theoretical foundations. The integration of nanostructured thermoelectric materials in micropower generators based on nanostructured materials is presented. Examples of several developed thin-film thermogenerators are shown, as basic elements for portable devices in microelectronics. A review of existing solutions and developing challenges is given regarding sustainable energy production, photovoltaics, solar cells, hydrogen economy and improved classes of batteries as contributions to green products and circular economy. Novel, highly promising areas in nanotechnology are also shown, such as voltage-driven nanospintronics, from theoretical and future application aspects. Recent advances in information processing nanotechnologies are also described, as well as friction characterisation at the nanolevel.

Health-related products represent another area which has taken great advantage of the nanotechnology revolution, especially in cosmetics, drug delivery systems and improved medical implants. Cosmetic products have incorporated different nanoparticles and gained highly improved effects, such as skin revitalization, and some insights into this area are collected in this book. Novel drug delivery systems have been increasingly developed and modelling of such structures is very important for proper system design and maintenance in the long run, as well as for the determination of influential properties. Methodologies in modelling of self-healing materials with nanocontainers are reviewed as one example in designing these systems that incorporate nanoparticles. Contributions and possibilities shown by nanotechnology in ophthalmology are also reviewed.

Material properties change when going from macro-bulk characteristics down to micro- and nanoscales. Nanoparticles synthesized so far have changed traditional materials in such extent that this area alone shows great further opportunities and completely justifies enormous investments into fabrication, processing, storage, transport and utilization of various classes of new nanomaterials, starting from its basic form—nanoparticles. The health sector is one of the major drivers of economies today with gigantic profits and return on investments. Moreover, the commercialization of research results form nanotechnologies is very strong in this area, with some of the largest investments ever in the history of our world. Several proven nanomaterials have been reviewed in this book pertaining to biomedicine. The use of silver nanoparticles and related nanomaterials in the cosmetic industry, and the potential for iron-based nanomaterials in biomedicine are reviewed, also with recognised challenges and possible threats of non-controlled use of nanomaterials.

Potential applications are great and commercially realised products can exhibit large benefits, but long-term effects still need to be studied and considered, especially when it comes to medical products and environmental sustainability. Innovation in practical commercial products, ranging from consumer goods, medical implants, power devices to large civil constructions and heavy loaded structures, in nanotechnologies is confronted with demand for new sustainable green products. We believe that this book will provide young researchers and professionals with valuable insights into opportunities offered by these new technologies, from aspects of different expertise: medical, engineering, physics, chemistry and material science, while emphasizing safety as an important input, to motivate them to pursue further research and practical applications in this broad and multifaceted field of science.

This work is the result of joint efforts of different companies, and academic and research institutions participating in the large international project, WIMB Tempus, 543898-TEMPUS-1-2013-1-ES-TEMPUS-JPHES, "Development of Sustainable Interrelations between Education, Research and Innovation at WBC Universities in Nanotechnologies and Advanced Materials where Innovation Means Business", co-funded by the Tempus Programme of the European Union.

Dublin, Ireland — Dermot Brabazon
Bellaterra, Spain — Eva Pellicer
Kragujevac, Serbia — Fatima Zivic
Bellaterra, Spain — Jordi Sort
Bellaterra, Spain — Maria Dolors Baró
Kragujevac, Serbia — Nenad Grujovic
London, UK — Kwang-Leong Choy
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Introduction—The Current Status and Momentum in Nanotechnology Commercialisation

Fatima Zivic, Nenad Grujovic, Inam Ul Ahad and Dermot Brabazon

Everybody is talking about nanoscience and nanotechnology. Nowadays 'nano' is very popular in science and technology, as well as in everyday news in journals, magazines and newspapers. If you ask non-scientific people "What is nano?", the majority would probably respond "something small and new"… We can use some of the definitions, starting from Feynman's famous sentence, "There's Plenty of Room at the Bottom" or some officially adopted such as "Nanotechnology is science, engineering, and technology conducted at the nanoscale, which is about 1 to 100 nm.", USA National Nanotechnology Initiative. Today, the term nano has become more than this simple definition. It is probably also becoming a kind of philosophy, as once in ancient Greece, philosophy was the science comprising mathematics, biology and other fields of natural science. Today, again, one discipline is uniting a number of scientific areas into one—nanotechnology. The distinguished feature of nanoscience is its multidisciplinarity at its core and its boosting of cooperation between different scientific fields. Nanoscience is continue to evolve only through the joint efforts from many areas—physics, chemistry, engineering, medicine, biology, mathematics, to name a few. Furthermore, if a nanometer is basic unit in nanoscience, then quantum physics and quantum theories become the foundation. There is no other scientific area that caused so many

F. Zivic (✉) · N. Grujovic
Faculty of Engineering, University of Kragujevac, Kragujevac, Serbia
e-mail: zivic@kg.ac.rs

N. Grujovic
e-mail: gruja@kg.ac.rs

I.U. Ahad · D. Brabazon
Advanced Processing Technology Research Centre, Dublin City University, Dublin 9, Ireland
e-mail: inamul.ahad@dcu.ie

D. Brabazon
e-mail: dermot.brabazon@dcu.ie

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controversies, complete acceptances and complete denials, as the appearance of quantum theories in scientific circles. Quantum mechanics is considered revolutionary because it introduced completely new approaches to the view of the world. In 1965, in one of his famous lectures, Richard Feynman said: "I think I can safely say that nobody understands quantum mechanics". Quantum mechanics is one of the foundation concepts for nanoscience. Schrödinger's cat thought experiment underlines the quantum mechanics paradox. Can we now say that we understand nanoscience? The things that in reality were considered absolutely impossible now exist in quantum world. It was a theory for many years, finally to start appearing in a real world with nanotechnologies and nanoparticles. Many unresolved and unexplained phenomena still exist in quantum and nano world, especially if scaled up to the consequences in a real macro world, but it obviously works, whether we fully understand it or not! Perhaps the best description of this new nano world is that by Feynman: "The 'paradox' is only a conflict between reality and your feeling of what reality 'ought to be'".

Material science has become one broad field of rapid discoveries. New materials have started to appear regularly in scientific literature. The pace of novelty is so fast that the experimentalists have difficulty keeping up with all the tests that common traditional practice should involve for proper introduction of the new materials as a real market product. Nanoscience has already shown results which can significantly improve the world in different ways, but at the same time it opened up so many questions and we will all see how the future will unfold.

If the object is observed as energy, then the object disappears, yet in a real world it exists strongly. Even the smallest changes at nano scale can result in dramatic changes in the macro properties. For example, the simple consequence of small changes in the crystal lattice of iron can result in iron becoming a non-magnetic material. For centuries, iron was the synonym for magnetic material. Traditional materials that were not conductive were changed to conduct electricity. Invisible materials were discovered and applied, previously existing only in fairy tales, like invisibility cloaks. Combinations between different material classes became possible, even between those traditionally incompatible to each other, and standard classification of materials to metals, polymers, ceramics, and natural materials started to dim. Combinations between non-organic and organic materials became possible. When materials are combined into new composites, such as metal—ceramic, or metal—polymer composites, or the structure is changed if compared to traditional materials, like in glassy metals or metamaterials, it produces wide possibilities for resulting products improvement or designing of completely new products. High capacity storage systems small in size, fast computers, sustainable energy production, fuel cells, new flexible aircraft parts with significantly increased load bearing and crack resistance, new lighter construction materials with highly improved resistance to earthquakes, new electronic components with superb qualities, biodegradable plastics, textiles that can withhold ultra-high temperatures, light materials that can endure high impact, food containers that enable significantly longer storage of food simultaneously providing protection from heat, light or decay and many other novelties have appeared in the recent years.

Medicine is one of the fields that can benefit greatly from nanotechnology. Micro needles controlled by magnetic field can be used for painless and blood-less surgeries. New highly improved pharmaceutical and cosmetic products are almost regularly appearing. Drug delivery systems are developed to fight against incurable diseases. Implants have been significantly improved towards human-like tissues to be fully accepted by the body and have already improved quality of life of millions of patients around the globe. New optical systems with high resolution enabled significantly improved medical diagnosis and more precise treatments with less side-effects for the patient. They also enabled further studies to understand and cure some incurable diseases, such as in neuroscience. High resolution microscopy and spectroscopy, together with very recent high resolution in situ microscopy, enabled to study the nature in a way that scientists can understand its essential foundations, thus supporting development of yet another area—biomimetics. Biomimetics has transferred structures, units and elements existing in nature onto solving the human problems, such as self-healing property. Surfaces that have extremely high hydrophobic nature are used for self-cleaning glass. The gecko effect—ultra high adhesion by designing structural properties is used for several applications.

Smart materials that can interact with their environment are studied for medical applications but also aiming for many other areas. Intelligent components that integrate different functionalities provide novel concepts in the development of structures. Changes of physical properties (shape, color, viscosity) as the response to external stimulus (temperature, stress, magnetic or electrical field) or changes in structure (crystal lattice orientation) due to external loading are only some of the examples that have been proven. Such materials can repair themself, suppress vibration, or inform the user of internal damage. Bioactive surfaces promote self-regeneration and tissue healing.

New material structures often can be applied in several other areas along with the ones that initiated research, unlike traditional materials that were designed mainly for one or several similar applications. Anti-bacterial surfaces are applied both in medicine and consumer goods, such as textile or bathroom accessories. Silver nanoparticles and ceramic nanoparticles can be used in medical implants, but also in water filtration systems, or cosmetics, or consumer goods. Self-repairing films in medical devices and self-repairing concrete in construction use similar principle. This diversity of applications further promotes collaboration between scientific disciplines.

Nanotechnology has marked our century with numerous astonishing discoveries in almost all branches of science, technologies, and products. The nanotechnology market has emerged and has initiated enormous investments, justified by highly promising scientific results. Numerous national and international, global funding programs are focused on nanotechnologies, from fundamental research aspects, to applied research and towards commercialization. Not a single scientific area has been left untouched by the nano world. Even the social sciences have begun to study the effects of nanotechnologies on the urban world. Ethics became one of the rising questions, especially important because medicine is one of the fields that is strongly effected by the nanotechnology developments in different ways.

The distinctive multidisciplinarity of nanoscience can be seen as its advantage, but sometimes it also becomes its disadvantage. Intellectual property rights were always important but in nanoscience it can be a rather difficult issue, probably due to the involvement of many actors in the discovery. The legal aspects have also emerged to deal with the specifics of commercialization that are unique to nanotechnology.

In general, the basic units of nanoscience are nanoparticles. Nanomaterials can be classified into 2D—nanolayers, 1D—nanopillars, nanowires and nanotubes and 0D—nanoparticles. The history of nanoparticles started with discovery of the C60—fullerene. A carbon molecule can be in a form of hollow sphere, tube, ellipsoid or other shape. Buckminsterfullerenes or 'buckyballs' are the spherical fullerenes discovered in 1985. After the discovery of the first nanoparticles of carbon, a range of other nanoparticles have been synthesized and fabricated and this is still an area of cutting-edge research. Graphene is a carbon nanomaterial with astonishing properties, including the strength of 130 GPa, and a conductivity capability almost as good as superconductors. Perhaps the most utilized carbon nanoparticles are carbon nanotubes (CNTs) because these are the longest studied so far and their addition to the traditional materials showed different improvements in properties, dominantly increase of strength with rather small amounts of CNTs within the structure. Different nanoparticles are studied theoretically and experimentally, but in general the cost of production is high and mass production is still unavailable. The future will show which types of other nanoparticles will be fabricated and the effects they can provide. There is still lack of fully established procedures in production, storage and transportation for many nanoparticles and many nanoparticles are experimentally still out of reach. For example, pure ceramic nanoparticles have been successfully produced only in recent months. In theory, nanomaterials can be based on any existing chemical element, but in reality, only a limited range of nanomaterials have been experimentally fabricated and investigated.

There is a very large collection of literature pertaining to different nanoparticles and related research, as well as various effects that can be obtained by their use. Very good overview of already commercialized nanomaterials is given in nanomaterial consumer products inventory by Vance et al. (2015) with dedicated website: http://www.nanotechproject.org/cpi/browse/nanomaterials/. Some nanoparticles that have been produced and used in commercial products are shown in Table 1, but this list is not exhaustive, as new products are being discovered on regular bases. Furthermore, each nanoparticle can be combined with other nanoparticles to form different hybrid materials. Carbon based nanomaterials represent the largest group of investigated nanomaterials so far, but silver nanoparticles can be noted as already heavily applied in numerous real world applications, including anti-bacterial effects.

There are numerous news reports about the effects promised by nanoparticles utilization, appearing almost every day. For example, seamlessly integrated wearable technology that can inform the user about their health condition, or deliver drugs, such as high tech bra that fights breast cancer, or shoes that can inform about the risk of injury, http://www.dailymail.co.uk/health/article-2987245/The-hi-tech-bra-helps-beat-breast-cancer-clothes-treat-prevent-illness.html.

Table 1 Commercially used nanoparticles (http://www.nanotechproject.org)

Nanoparticles	Applications
Aluminum oxide	Alumina powders used in medical implants, cosmetics, electronics, sport and fitness devices—bicycles, automotive accessories—polishing creams
Calcium	Added in health supplements, food and beverages, cosmetics, dental mouthwash; Research aimed at materials for medical implants
Carbon based (including carbon nanotubes, fullerenes, graphene, graphite)	Numerous different applications: added to improve mechanical properties (e.g. sporting goods: bicycles—tyres, frames; handlebars in fitness devices or tennis and badminton racquets; golf clubs and balls; bowling balls; baseball bats); food and beverage containers; textile and clothing—underwear; sports shoes; cleaning agents; consumer goods (e.g. toothbrushes, safety masks and vests); water filtration systems; air conditioners; aircraft elements; display thin coatings; electronics and computers (RAM memory)
Ceramics	Consumer goods (hairdryers, hair straightener, cooking pans); coatings (cutting tools, durable heavy loaded surfaces); water filters and purifiers; automotive paint finishes; automotive accessories—batteries; coatings in construction elements—flooring; added in civil engineering materials in general aiming to obtain wear resistant, nice looking surfaces; home furnishings; photo paper; cleaning agents
Clay	Beer bottle plastics; cosmetics; outdoor paints; food and beverage containers
Cobalt	Electronics—Metal Nano Dot (MND) memory; food supplements
Copper	Water filtration systems; food supplements; cosmetics; Electronics—Intel® Core™ Duo Processor
Gold	Cosmetics; food supplements; automotive engine oil; consumer goods (toothpaste); clothing; filtration; cleaning agents; air conditioners
Iron	Food supplements; kitchen appliances; food and beverage storage; sporting goods—Sandvik Nanoflex® Alloy
Lead	Cosmetics—Sunscreen
Magnesium	Food supplements; sporting goods (tennis and badminton racquets); cosmetics
Nanocellulose	Food supplements; clothing
Platinum	Cosmetics; food supplements

(continued)

Table 1 (continued)

Nanoparticles	Applications
Polymer	Textiles and clothing; Hybrid Membrane Technology (HMT); ecology coatings; coatings in construction materials—water repellents
Quantum dots	Sensors; Research aimed at solar cells, computing and quantum calculations—quantum computers; optical applications such as high resolution cell imaging or light emitting diodes
Silicon (including Silicon dioxide)	Electronics and computers—Flash memory; 45 nm processors; AMD® Athlon™ 64 Processors; IBM Hard Disk Drive (High Capacity—GMR head); IBM® PowerPC® 970FX/970MP Processors; Intel® Processors; Intel® StrataFlash® Cellular Memory; Sanyo® Organic Electroluminscent (OEL) Displays; Air filtration systems; cosmetics; Siemens® Hearing Instruments; food supplements; sporting goods—wet suits; auto sealants; anti fog products; cleaning agents; protective paints—anti-graffiti paint; flooring Treatment (absorbent surfaces); nano-coatings for: glass, ceramic, microporous surfaces, sand-blasted surfaces, stones, textiles
Silver	Added to numerous different materials to obtain anti-bacterial effects: textiles (wound dressings, cotton sheets, socks, towels), refrigerators, door handles, water taps, food containers, cosmetic products, consumer goods—toothpaste, toothbrushes, hair brushes; filtration systems—air purifiers, vacuum cleaners; food supplements; and many more products
Titanium (including Titanium dioxide)	Sporting goods: tennis and badminton racquets, surf boards, fishing rods; hairdryers; cleaning agents; paints; glues and sealants; filtration systems—air purifiers; cosmetics—protection sunscreens, lip balms, Dove deodorant; Head and Shoulders 2 in 1 Shampoo, Pantene shampoo and conditioner; kitchen appliances—refrigerators; cleaning agents; Self-cleaning glass; Photocatalyst Environment Cleaner
Tungsten disulfide	Lubricants in automotive industry
Zeolite	Food and beverage supplements
Zinc oxide	Protection sunscreens; cosmetics; health supplements; paints; self-cleaning coatings
Zirconia	Research aimed at materials for medical implants

This technology is based on micro-encapsulation of drugs into the fabrics and is developed by Master students.

Another example is the enhancement of the touch sensing by nanomembranes, https://www.newscientist.com/article/dn22162-fingertip-tingle-enhances-a-surgeons-sense-of-touch.

The liquid solution made from ultra-fine conductive nanoparticles that can change the gloves to touchscreen friendly is another good example, https://www.thegrommet.com/nanotips.

There are also numerous new ideas, conceived in promised nano-products, such as idea of a kitchen that can dynamically flex itself as per wishes of the user—appearing and disappearing kitchen fixtures by using nanobots, http://dornob.com/living-kitchen-wall-uses-multi-touch-nanotechnology/.

Another interesting application of nanotechnology in biomedical engineering is highly promising recently commercialized biodegradable generators that can produce energy to power implantable medical devices for some time and then degrade and vanish from the body, http://www.hexapolis.com/2016/03/09/biodegradable-nanogenerators-could-soon-power-medical-implants/.

Some nanomaterials really shows astonishing properties, such as newly developed TiO_2 based nanomaterial that can produce energy, generate hydrogen and purify water, http://inhabitat.com/scientists-develop-wonder-nanomaterial-that-can-produce-energy-clean-water-and-hydrogen/#ixzz2aeIG00dr&i.

This list of news can go on and on, and it clearly shows that commercialization of nanomaterials and in nanoscience, is progressing at fast pace and we shall see what the future will bring. The renowned sources that provide lectures, instructional materials, activities and labs and reference material are listed in Annex 1. However this list is indeed not exhaustive.

One aspect of nanoscience that must not be overlooked is the toxicity that can be induced by nanoparticles. Nano today has also raised very serious questions on the health risks and environmental sustainability. Along with increasing waste and environment pollution in the world, the appearance of nanoparticles with proven toxic effects adds up to environment sustainability concerns. There are many literature sources with investigations pertaining to the toxic aspects of nanoparticles. Based on numerous analyses, particles with nano sizes can be toxic with different pathways of exposure, depending on the organism in question. The majority of studies are related to the consequences of nanoparticle on human health, though there are also significant studies on potential risks to plants and animals, such as cell mutations, soil and water contamination. However, this research area is still in infancy and further research is needed. In general, there is a lack of numerous standards related to nanoparticles in the food sector, medical devices (particularly implantable devices), novel drugs and drug delivery systems which use some form of nano/micro structures, and filtration systems and waste management of nanoparticles released into the soil and water and their further behaviour. It is obvious that detailed studies related to nanotoxicology are necessary but the extent of this is also conditioned by the level of development in the field of nanoparticles fabrication, storage, transport and use.

Annex 1

Useful links with information about nanoscience and nanotechnology

A. Lectures and Instructional Material

1. Trynano-Nanomaterials
   Explore nanomaterials
   http://www.trynano.org/
2. Trynano-Nanotechnology Applications
   Nanotechnology Applications
   http://www.trynano.org/
3. Micro/Nano Processing Technology
   A course to introduce the theory and technology of micro/nano fabrication.
   http://ocw.mit.edu/
4. Multi-Scale System Design
   Multi-scale systems (MuSS) consist of components from two or more length scales (nano, micro, meso, or macro-scales)
   http://ocw.mit.edu/
5. Introduction to Nanoelectronics
   This course covers the "bottom up" approach to electronic devices
   http://ocw.mit.edu/
6. Nano-tribology and Macro-tribology
   This course considers the relationship between nano-tribology and macro-tribology
   http://ocw.mit.edu/
7. Design and Fabrication of Microelectromechanical Devices
   An introduction to microsystem design
   http://ocw.mit.edu/
8. Integrated Microelectronic Devices
   This course examines the physics of microelectronic semiconductor devices for silicon integrated circuit applications
   http://ocw.mit.edu/
9. Nanomechanics of Materials and Biomaterials
   Latest scientific developments and discoveries in the field of nanomechanics
   http://ocw.mit.edu/
10. The Power of Graphene
    Lesson focuses on graphene and its electrical properties and applications.
    http://tryengineering.org/
11. Try Your Hand at Nano
    Lesson focuses on two simple activities younger students can do to gain an appreciation of nanotechnology
    http://tryengineering.org/
12. Be A Scanning Probe Microscope

Lesson focuses on how engineers have developed and use special tools that can observe the landscape of materials when they are working at the nano scale.
http://tryengineering.org/

13. Fizzy Nano Challenge
Students learn about nanotechnology and how engineers can harness the differences in how materials behave when small to solutions for challenges in many industries.
http://tryengineering.org/
14. Sugar Crystal Challenge
Students explore surface area, nanostructures, and work in teams and participate in hands-on activities.
http://tryengineering.org/
15. What is a Nanometer?
Lesson focuses on how to measure at the nano scale and provides students with an understanding of how small a nanometer really is.
http://tryengineering.org/
16. Nano Waterproofing
Lesson focuses on how nanotechnology has impacted the design and engineering of many everyday items, from paint to fabrics.
http://tryengineering.org/
17. Exploring at the Nanoscale
Lesson focuses on how nanotechnology has impacted our society and how engineers have learned to explore the world at the nanoscale.
http://tryengineering.org/
18. NanoSense Size Matters: Introduction to Nanoscience
Lecture notes promote the learning of science concepts that account for nanoscale phenomena
http://nanosense.sri.com/
19. NanoSense Clear Sunscreen: How Light Interacts with Matter
Lecture notes promote the learning of science concepts that account for nanoscale phenomena
http://nanosense.sri.com/
20. NanoSense—Clean Energy: Converting Light to Energy
Lecture notes promote the learning of science concepts that account for nanoscale phenomena
http://nanosense.sri.com/
21. NanoSense—Fine Filters: Filtering Solutions for Clean Water
Lecture notes promote the learning of science concepts that account for nanoscale phenomena
http://nanosense.sri.com/
22. NanoDays
The NanoDays digital kit contains hands-on activities and programs to engage a public audience in nanoscale science, technology, and engineering.
http://nisenet.org

23. NISENet
    Nisenet nanotechnology educational video
    http://nisenet.org
24. NISENET—Programs and Activities
    Nisenet nanotechnology educational activities
    http://nisenet.org
25. NISENET—Media
    Nisenet nanotechnology educational activities
    http://nisenet.org
26. What is Nano
    Nanotechnology educational video
    http://whatisnano.org/
27. Scale of the Universe
    Video lessons attempt to comprehend the scale of the universe
    http://www.khanacademy.org
28. Nanotechnology
    Uses of nanotechnology, and descriptions of nanomaterials and lesson plans for teachers and students
    http://www.understandingnano.com/

B. Activities and Labs

1. Nanohub
   Online hub for nanotechnology resources and activities
   http://www.nanohub.org
2. Nanohub Courses
   Nanotechnology resources and courses
   http://www.nanohub.org
3. Bone Regrowth
   Scientists using nanotechnology to help regenerate nerves and bones
   http://pbskids.org/dragonflytv
4. Hockey Sticks
   Do nanotubes really make a better hockey stick? http://pbskids.org/dragonflytv
5. What's Nano
   Science fair project idea for your elementary or middle school science fair
   http://pbskids.org/dragonflytv
6. Where's Nano
   Science fair project idea for your elementary or middle school science fair
   http://pbskids.org/dragonflytv
7. Nanotechnology—101
   What is nanotechnology and how it works
   http://www.nano.gov/
8. Nanotechnology and You
   Nanotechnology benefits and applications
   http://www.nano.gov/

9. Macro Concerns in a Nano World
   QUEST looks further into nanotechnology, as this rapidly expanding field begins to play a larger part in our lives.
   http://kqed.org
10. Nanotechnology Takes Off
    Discover the nanotech boom where researchers are working to unlock the potential of nanoscience to battle global warming, and disease.
    http://kqed.org
11. Science on the SPOT: Color By Nano
    How Kate uses the phenomenon known as "structural color" to transform nanotechnology into creativity.
    http://kqed.org
12. Solar City: The Future of Nanosolar
    Nanosolar is creating paper-thin solar panels harnessing nanotechnology, a product that could revolutionize solar power.
    http://kqed.org
13. The World's Most Powerful Microscope
    Electron microscope ability to make images to a resolution half the width of a hydrogen atom made it the most powerful microscope in the world.
    http://kqed.org
14. Atomic Force Microscopy
    Videos explaining basic techniques of microscopy
    http://umassk12.net
15. Nanofilm: Oleic Acid Langmuir Film
    Videos explaining basic techniques of nano fabrication
    http://umassk12.net
16. Spin Coating
    Videos explaining basic techniques of nano fabrication
    http://umassk12.net
17. Photolithography
    Videos explaining basic techniques of nano fabrication
    http://umassk12.net
18. Electrochemical Deposition
    Videos explaining basic techniques of nano fabrication
    http://umassk12.net
19. Magnetism
    Videos explaining basic techniques of a section on concepts of magnetism
    http://umassk12.net
20. What's so BIG About Nano-technology?
    Nano related activities
    http://www.sciencebuzz.org
21. NNIN Education and Training
    NNIN's education programs address the explosive growth of nanotechnology and its growing need for a skilled workforce and informed public by offering education and training to individuals (school-aged students to Higher educations).

http://www.nnin.org

22. Nanotechnology Poster
A series of posters with accompanying educator and learner guides for Public engagement with Nanotechnology
http://www.jivemedia.co.za
23. Nanozone
Nano related activities
http://www.nanozone.org
24. A Hands-On Introduction to Nanoscience and Technology
A lab-based hands-on introduction to nanoscience and nanotechnology for early undergraduates
http://www.virlab.virginia.edu/

C. Reference Material

1. Secret Worlds: The Universe Within
Video Milky Way to Nano scale illustration
http://micro.magnet.fsu.edu/primer/java/electronmicroscopy/magnify1/index.
2. Tejal Desai
Tejal Desai is a biomedical engineer who designs tiny, nano-sized capsules to transport medicine in the body to the exact spot it is needed
http://pbskids.org/dragonflytv
3. UVA Virtual Lab
The UVA Virtual Lab is based at the University of Virginia. It employs emerging software visualization tools to explain technologies affecting our daily lives
http://www.virlab.virginia.edu/
4. Graphene the 2D Material That Could Change Everything
Graphene the 2D material that could change everything infograph
http://www.visualcapitalist.com/
5. Nano-to-Macro Transport Processes
Video overview of the course and the research in the field of nanoscience and technology
http://ocw.mit.edu/
6. Submicrometer and Nanometer Technology
A course that surveys techniques to fabricate and analyze submicron and nanometer structures, with applications
http://ocw.mit.edu/
7. Nanotechnologies: Principles, Applications, Implications and Hands-On Activities. A compendium for educators
A publication by the European Commission outlines nanoscience and nanotechnology. Educational material that will help inform, motivate and inspire young people about nanotechnologies and their applications
http://ec.europa.eu/research/industrial_technologies/e-library.cfm

8. Nanotechnology: The Invisible Giant Tackling Europe's Future Challenges
   A publication by the European Commission outlines nanoscience and nanotechnology
   http://ec.europa.eu/research/industrial_technologies/e-library.cfm
9. Nanometrics—A Technometric and Socio-Economic Analysis System to Support the Development of the European Nanotechnology Strategy Options
   A publication by the European Commission outlines nanoscience and nanotechnology
   http://ec.europa.eu/research/industrial_technologies/e-library.cfm
10. Nanometrics—A Technometric and Socio-Economic Analysis System to Support the Development of the European Nanotechnology Strategy Options—Case Study
    A publication by the European Commission outlines nanoscience and nanotechnology
    http://ec.europa.eu/research/industrial_technologies/e-library.cfm
11. Reaching Out to the Future
    A publication by the European Commission outlines nanoscience and nanotechnology
    http://ec.europa.eu/research/industrial_technologies/e-library.cfm
12. Photovoltaics and Nanotechnology: From Innovation to Industry
    A publication by the European Commission outlines nanoscience and nanotechnology
    http://ec.europa.eu/research/industrial_technologies/e-library.cfm
13. Successful European Nanotechnology Research
    A publication by the European Commission outlines nanoscience and nanotechnology
    http://ec.europa.eu/research/industrial_technologies/e-library.cfm
14. Communicating Nanotechnology
    A publication by the European Commission outlines nanoscience and nanotechnology
    http://ec.europa.eu/research/industrial_technologies/e-library.cfm
15. Knowledge, Attitudes and Opinions on Nanotechnology Across European Youth
    A publication by the European Commission outlines nanoscience and nanotechnology
    http://ec.europa.eu/research/industrial_technologies/e-library.cfm
16. Report on Legal, Ethical Issues Related to Nanotechnologies
    A publication by the European Commission outlines nanoscience and nanotechnology
    http://ec.europa.eu/research/industrial_technologies/e-library.cfm
17. Nanomedicine the Future of Medicine
    How Nanomedicine Works and applications
    http://www.associates-degree-in-nursing.org/

18. Fabricating a Tiny High-Tech Future
    How advanced manufacturing drives the tiny, high-tech future
    http://www.jabil.com/blog/fabricating-a-tiny-high-tech-future-infographic.
19. Big Things from a Tiny World
    Brochure that explains nanotechnology and its potential in a format that appeals to general audiences
    http://www.nano.gov/
20. Nano and Energy: Powerful Things from a Tiny World
    Brochure provides an overview of nanotechnology's potential applications in the energy sector, including information on batteries, catalysts, solar cells, and green fuels
    http://www.nano.gov/
21. An Introduction to Nanotechnology
    An Introduction to Nanotechnology and its applications
    http://www.understandingnano.com/
22. Nanotechnology Applications
    Nanotechnology applications
    http://www.understandingnano.com/
23. Nanoreisen
    Nano-journeys to micro- and nano-cosmos
    http://www.nanoreisen.de/
24. Nanokids
    NanoKids(TM) is an education and outreach program for intermediate-level (middle-school) students intended to increase their knowledge of nanotechnology and emerging research and technology in this field,
    http://www.nanokids.rice.edu/
25. NanoTech: Insights into a Nano-Sized World
    Students learn about nanotechnology, its extreme smallness, and its vast and growing applications
    http://www.worldteachengineering.org.

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Review of Production Routes of Nanomaterials

Shei Sia Su and Isaac Chang

Abstract Manufacturing and commercialization of nanomaterials are often hampered due to lack of appropriate large scale production of these nanomaterials. In this review article, we discuss different types of commercial scale production, including vapour, liquid and solid phase synthesis. The choice of production methods will influence the nanomaterials' properties and functionalities, scalability and production costs. This review emphasized on the fundamental process of each production method, including merits and drawbacks.

1 Introduction

Nanomaterials can be classified as materials with the size less than ~100 nm diameter and exhibit unique properties due to their nanoscale dimensions. With the development of new techniques and tools to synthesis and manipulate the size, shape and structure of nanomaterials, nanomaterials have been utilised in numerous technological applications, including catalytic systems, hydrogen storage, chemical sensors, biomedical applications, electronic, etc.

Although there is an extraordinary growth of using nanomaterials in the consumer end-products, many unprecedented materials innovations are still remain on the laboratory bench. One of the main challenges faced in commercialising the application of these nanomaterials is lack of appropriate large scale production of these nanoparticles. This chapter will discuss different types of commercial scale

S.S. Su
School of Metallurgy and Materials, College of Engineering and Physical Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK
e-mail: sheisiasu@gmail.com

I. Chang (✉)
Brunel Centre for Advanced Solidification Technology (BCAST), Institute of Materials and Manufacturing, Brunel University London, Kingston Lane, Uxbridge UB8 3PH, UK
e-mail: Isaac.Chang@brunel.ac.uk

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production, with the focus on the inorganic nanoparticles and carbon-related nanoparticles.

There are two main approaches to fabricate nanomaterials, namely top down and bottom up approaches. Figure 1 showed the schematic illustration of top down and bottom up approaches. The top down approach involved decreasing the size of the large uniform piece of material in order to create the required nanostructures from it. This method is very much used in the electronic industry, whereby lithography and etching techniques are applied to create the unique electronic circuitry. Mechanical milling is another common top down approach to generate nanoparticles. However, it poses some difficulties to generate uniform nanoparticles and is more likely to introduce internal stress, structural defects and contaminations. The bottom up approach, on the other hand, arranges the basic building blocks such as atoms or molecules into large nanostructures using chemical or physical forces.

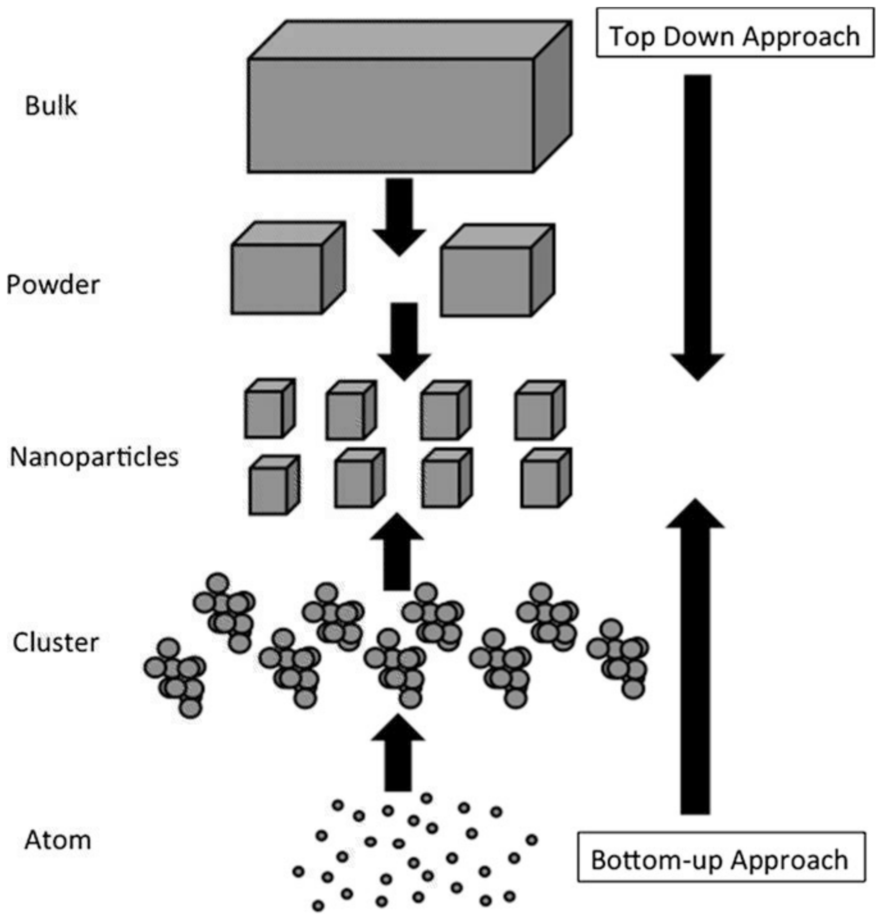

Fig. 1 Top down and bottom up approaches of nanoparticles production

The growth and self-assembly of the building blocks allows designing and controlling nanoparticles with more precise structures, shape, size and chemical composition.

This chapter will discuss the pros and cons of different production methods of creating nanomaterials. Scientists and engineers have to weigh between the needs for quantity or quality of the nanoparticles before they make their decision on choosing the right production methods to produce the nanoparticle with the desired properties.

2 Vapour Phase Synthesis

The works on vapour phase synthesis have evolved considerably since the early 1960s. Since then, there has been numerous of reports and references detailing the works on direct gas to particles conversion synthesis methods. Formation of nanoparticles through the vapour phase synthesis generally undergoes three main processes. It first started with nucleation of clusters from the supersaturated vapours, either homogenously or heterogeneously. Homogeneous nucleation occurs when the vapour molecules condense to form nuclei without the presence of foreign particles or ions. Heterogeneous nucleation, on the other hand, occurs on the foreign nuclei, ions or surfaces. The nanocrystal nuclei condense from the constituent vapour later on undergoes growth due to collision and coalescence. Finally, the primary particles coagulate and form aggregates as the temperature decreases.

A number of different vapour phase methods of synthesis have been developed to increase the production of nanoparticles. This section will discuss the vapour synthesis methods including flame synthesis, chemical vapour condensation, arc discharge and laser ablation in more details.

2.1 Flame Synthesis

Flame synthesis is an inexpensive and widely used method for commercial production of nanoparticles. The most common examples of nanoparticles produced using the flame synthesis are titania, fumed silica and carbon blacks (Swihart 2003; Stamatakis et al. 1991), with the annual production rate reaching several million metrics tons. These nanoparticles are used extensively as pigments, catalysts, flowing aids and in telecommunication.

In flame synthesis, synthesis of particles is carried out within the flame, produced by the combustion reactions. Flame heat is employed to initiate the chemical reactions and to form flames of dust clouds comprising the corresponding metals. The volatile precursors are oxidized within the flame to form metal-oxide monomers, which later nucleate and coalescence to form aggregated nanoparticles. Unlike the wet chemistry synthesis route, the desired crystal phases are formed directly without the need for a calcination step due to the high temperature of the flame. Figure 2 shows a typical flame synthesis unit, which consists of a precursor unit, a burner incorporated with the gas delivery systems, and a filter unit for particle collection.

The main fuels used in flame synthesis are methane, hydrogen or ethylene and air or oxygen as oxidants. These gases sometimes are diluted with inert gases such as argon, helium or nitrogen. An example of the flame synthesis is synthesis of iron oxide nanoparticles from iron pentacarbonyl precursor using $CH_4/O_2/Ar$ flame, as reported by Buyukhatipoglu and Morss Clyne (2010). It was found that change of flame configuration from diffusion flame configuration to inverse diffusion flame configuration reduces the size range of the nanoparticles from 50–60 to 6–12 nm.

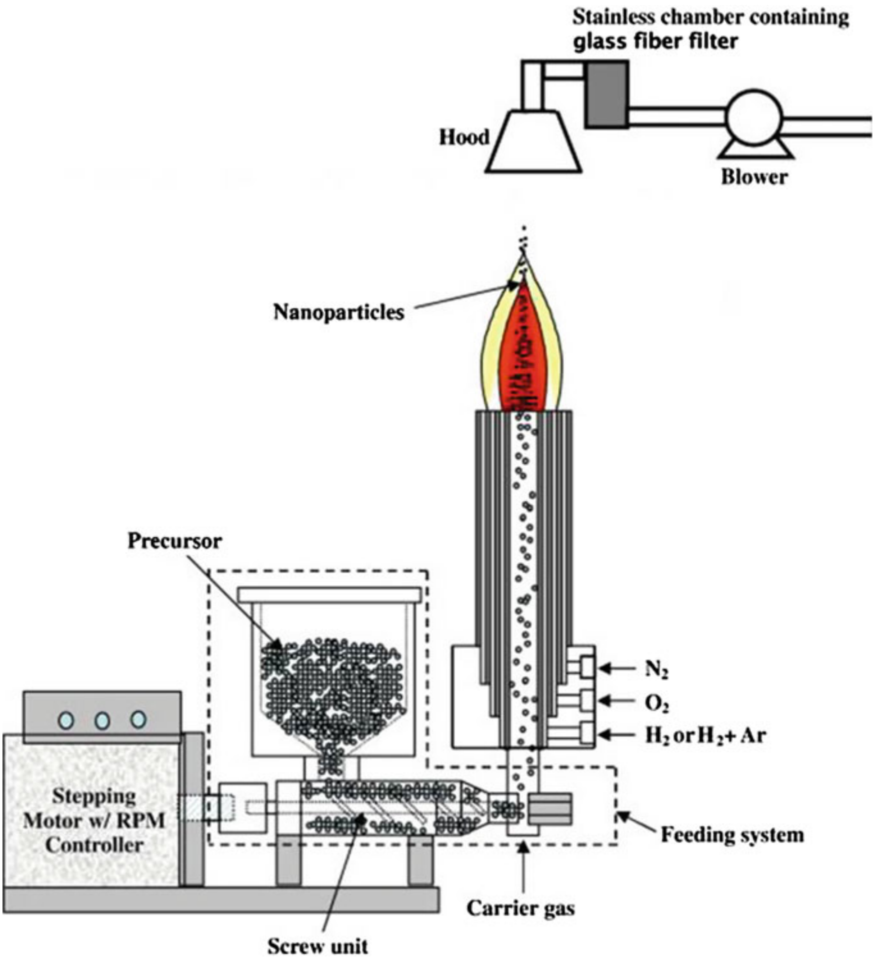

Fig. 2 Typical set up for flame synthesis (Yang et al. 2010). Reprinted from Powder Technology, 2010. 197(3), Yang, S. et al., A flame metal combustion method for production of nanoparticles, pp. 170–176. Copyright 2010, with permission from Elsevier

The addition of N_2 gas cooling further lowers the flame temperature and leads to the formation of magnetite Fe_3O_4 instead of hematite α-Fe_2O_3 (Buyukhatipoglu and Morss Clyne 2010). The main parameters influencing the flame synthesis of iron oxide are the flame temperature and particle residence time. The characteristics of the flame-made nanoparticles are also controlled by the composition of the precursors, burner configuration, turbulence, precursor injection and particle collection location, supplementary laser irradiation and external electric fields (Buyukhatipoglu and Morss Clyne 2010; Yang et al. 2010).

Apart from the simplicity of experimental set up, flame synthesis involves only a 'one-step' process. A wide array of precursors can be employed using the flame synthesis. Thus, a broad range of the nanosized powders can be synthesized using this method. Johannessen et al. also reported other complex products including composite metal oxide (e.g. $ZnAl_2O_4$, $MgAl_2O_4$ spinel) and supported noble catalysts are synthesized using the flame synthesis (Johannessen et al. 2004). The synthesized products require no subsequent post-processing and less process waste is obtained as flame synthesis is a solvent free process. In spite of simplicity and efficiency of flame synthesis of nanoparticles, agglomeration of nanoparticles remains a significant challenge for this synthesis method.

2.2 *Laser Ablation Method*

Since the discovery of laser decades ago, laser has been used extensively in various applications including nanomaterials synthesis, surface cleaning and surface nanopatterning (Zhong et al. 2012). Synthesis of nanoparticles using laser ablation involves vaporization of source materials or precursor through laser irradiation. A wide variety of materials including high melting point elements or compounds can be produced at low temperature, including metals such as silver (Tsuji et al. 2008), silicon (Khang and Lee 2010), ceramics, oxide composites and nitrides (Kononenko et al. 1997). Figure 3 displays an illustration of laser ablation systems connected with particles analyser.

The most common source laser source for ablation is neodymium-doped yttrium aluminium garnet (Nd:YAG). During laser ablation, the laser beam is irradiated onto the surface of the target materials at specific incident angle, either 90 or 45 degree. The energy of the laser beam can be transferred to the target materials through different pathways depending on the laser power, wavelength and pulse duration. Photothermal ablation will take place if low laser power (100–500 MW/cm^2) and longer pulse length (>10 ns) are used (Wang et al. 2002). During the photothermal ablation, the free or bound electrons on the target materials will absorb the energy. The excited electrons transfer the energy through the collision interaction with other electrons and lattice phonons, resulting in heat transfer and increase of the temperature of the material, which melts the target material (Zhong et al. 2012). The melted material continues to absorb the energy from the laser beam and subsequently forms the plasma plumes on the surface. The atoms on

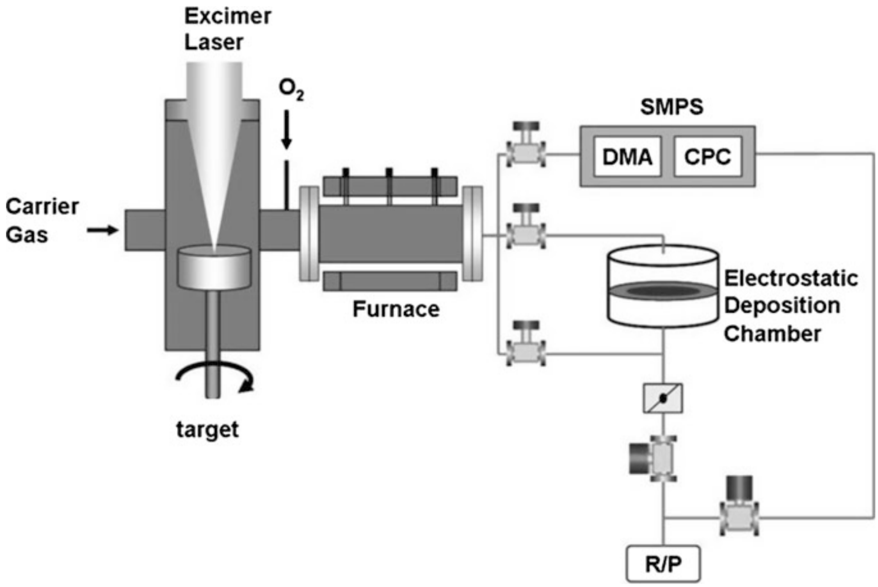

Fig. 3 Schematic illustration of laser ablation systems connected with particles analyser (Khang and Lee 2010). Reprinted from Journal of Nanoparticle Research, 2010. 12(4), Khang, Y. and Lee, J., Synthesis of Si nanoparticles with narrow size distribution by pulsed laser ablation, pp. 1349–1354. Copyright 2009, with permission from Springer

the heated surface are finally ejected and vaporized due to the rapid volume expansion.

Plasma assisted ablation is the second pathway, in which temporary plasma is produced above the target material when high peak power in the laser pulse is used. Generally, high laser power (>500 MW/cm^2) is applied to provide high-energy ions, which bombard the surface of the target materials. The atoms of the target materials are then heated and ejected from the surface. Due to the high energy of the laser ablation, both photothermal and plasma assisted ablation will leave crates on the surface of the target material. At the same time, the liquid droplets of the melted materials solidified and create a rim. Photochemical or photolytic ablation, on the other hand, occurs when laser photon energy similar to the bonding energy of the molecules is absorbed and lead to dissociation of the bond. This later causes the ejection of the material. Unlike photothermal and plasma assisted ablation, only the target material irradiated by the laser beam is ablated and the remaining area remains unaffected for the photochemical ablation Wang et al. (2002).

Laser ablation technique is applicable to synthesis a wide range of materials with the complex chemical structure and stoichiometry composition similar to the target. The properties of nanoparticles synthesized using this method can be easily controlled by altering the laser pulse energy, pulse fluence, repetition rate, pulse duration and laser spot size. Due to the monochromatic characteristics of laser, selective excitation of molecules will occur by applying the appropriate laser wavelength. Apart from having the ablation carries out in vacuum and gas, there are also numerous studies reported to have laser ablation in the liquid medium (Tsuji et al. 2008; Neddersen et al. 1993).

In the last decade, Pulsed Laser Ablation in Liquid (PLAL) has emerged as an alternative synthesis technique to generate, excite, fragment, and conjugate a large variety of ultrapure nanostructures for large scale production (Intartaglia et al. 2014). This technique has overcome most of the shortcomings of traditional wet chemical synthesis, presenting a simple, straightforward and versatile technique to produce ligand-free nanoparticles which are a prerequisite for specific biological or electrical applications (Barcikowski and Compagnini 2013). In addition, the liquid phase can be tailored in order to produce viscosities suitable for ink jet printing or other conventional controlled fluid surface coating techniques (Bagga et al. 2015) Ablation in liquid medium offers a number of advantages including higher cooling rate which tends to form smaller size nanoparticles, allows surface modification, and increase stability of nanoparticles. While the liquid can be as benign as deionised water, other solvent species used could affect the chemical composition of the nanoaprticles synthesized in a positive or negative manner depending on application.

2.3 Arc Discharge Method

Fabrication of nanoparticles using arc discharge method has gained much interests due to its simplicity in apparatus set up and ability to scale up the production rate of nanoparticles (Ashkarran et al. 2009). Different types of nanoparticles have been reported to synthesize using this method, ranging from metal to refractory metals. One of the most widely reported nanoparticles synthesized using this method is carbon nanotubes (CNTs) using the direct current (DC) arc discharge. For the production of single walled carbon nanotubes (SWNTs), catalyst metals for instance Ni, Y, Fe, Co or Mo are required, whereas it is not required for the multi-walled carbon nanotubes (MWNTs).

Arc discharge involves very simple setups with two electrodes acting as cathode and anode respectively. These electrodes are subjected to a potential and subsequently cause an electrical breakdown. Arc discharge generally requires low voltage (few to several tens of V) and high current density (10^5–10^{11} A/m^2) (Xu 2007). Synthesis of nanoparticles using arc discharge method can be either in pulsed (Su et al. 2014) or continuous mode. To produce MWNTs and SWNTs, high purity graphite are used as electrodes and arc discharge can be carried out in helium (Waldorff et al. 2004) or hydrogen gas (Zhao et al. 1997). Figure 4 showed a schematic illustration of the experimental set up for the arc discharge.

During the arc discharge, electrons are emitted either through heating or field emission due to large electric field generated. Plasma is thus formed due to the ionization and this exerts large amount of heat, which subsequently evaporate the