Carbon Nanostructures

J. Tharini
Sabu Thomas *Editors*

Carbon Nanomaterials and their Composites as Adsorbents

Springer

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Carbon is intimately connected to almost everything we deal with in a daily basis. Due to its outstanding properties, such as high stability at environmental conditions, different hybridizations, strong covalent bond formation and easy of compounds formation, carbon has been a topic of scientific interest in several areas. Indeed, starting in the 19th century, chemists have devoted a whole field to study carbon-based compounds, which is, nowadays, known as Organic Chemistry. Remarkably, the last 30 years have been witnessing an exponential advance in the science involving carbon and carbon structures. Since the discovery of Fullerenes in 1985, which was awarded the Nobel Prize in Chemistry in 1996, carbon nanostructures have been attracting a great deal of attention from the research community. This public interest dramatically increased after the publications by the Iijima and Bethune groups on single-wall carbon nanotubes in 1993 and found a "new research era" with the isolation of a monolayer of carbon atoms, also called graphene, which conducted groundbreaking experiments demonstrating outstanding phenomena such as the Klein-Tunneling and the fractional quantum hall effect. No wonder, graphene was the object of the 2010 Nobel Prize in Physics.

The "Carbon Nanostructures" book series covers the state-of-art in the research of nanocarbons and their applications. Topics related to carbon allotropes such as diamond, graphite, graphene, fullerenes, metallofullerenes, solid C60, bucky onions, foams, nanotubes and nanocones, including history, theory, synthesis, chemistry & physics, Biophysics & engineering, characterization methods, properties and applications are welcome. Within the "Carbon Nanostructures" book series, the reader will find valuable, up-to-date account of both the newer and traditional forms of carbon. This book series supports the rapid expansion of this field and is a valuable resource for students and professionals in several different areas.

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To Richard Smalley, Robert Curl and Harry Kroto

Founders of Buckminsterfullerene

Foreword

It is true that in the past few decades, discovery of new allotrope, namely, carbon nanotubes, Buckminsterfullerene, graphene oxide has created the landmark in the history of adsorption process. The rapid development of nanoscience and nanotechnology has significantly improved the adsorption mechanism. The discovery of carbon nanomaterials has been the promising adsorbents for the metal ion adsorption, effluents from the battery industries, chemical industry, pharmaceutical industries, dyes, and pesticides. A versatile and highly efficient carbon nanomaterial-based composite aids in the removal of toxic pollutants from the water. Carbon nanomaterials could replace traditional adsorbents including zeolites, activated carbon from solid wastes, silica gel, molecular sieves, activated alumina, ion-exchange resins, clays, agricultural wastes, biosorbents and miscellaneous adsorbents because of the high sorption potential, malleable surface charges, enormous pore size, large surface area, and rapid adsorption kinetics.

First part of the book deals with the fundamentals of nanomaterials, classification of carbon nanomaterials, and synthesis of carbon nanomaterials. It helps the reader to keep update the latest success and failures of nanomaterials. The literature in this field is exploding in such a manner that is extremely useful to have a concise overview. The well-documented explanation for the synthesis of carbon nanomaterials will benefit the chemist, physicist, biochemist, engineers, biologist, and another interdisciplinary scientist around the globe. The second part of the book gives the recent literatures for the adsorption and desorption of organic dyes, pesticides, micro-pollutants, heavy metals, and aromatic compounds. These studies will help the environmental scientist to learn latest literatures on the adsorption studies. The final chapter deals with the theoretical modeling of the carbon nanotubes. Finally, I recommend this book for the undergraduate, postgraduate student, experimental scientist, and computational scientist. This book is recommended for both academic and industrial researchers.

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Preface

Adsorption is one of the most important fields of research for water purification. It is also the subject of surface phenomenon which creates a layer of the adsorbate on the surface of the adsorbent. It is the important topic of physical chemistry that every student enjoys from school level to the graduate level. The target audience of this book is, namely, undergraduate students, postgraduate students of environmental engineering, chemistry, environmental science, and Ph.D. students who are active in the area of environmental remediation. This book is mainly designed for both academics and industrial researchers. The goal of the book is to explain the basic concepts of nanomaterial adsorption. We focus on basic concepts of nanomaterials and their uses as the nanoadsorbents for the water purification. The basic concepts of adsorption are well explained with suitable examples. The principal aim of the book is to reach the audience with the latest trends on adsorption for the removal of metal, micro-pollutants, food adulterants, aromatic compounds, pesticides, dyes, and oil particles. This book motivates the student to study absorption at the introductory university level to the advanced level of research.

This book gives the overview of the interdisciplinary aspects of adsorption and practical applications for the removal of hazardous chemicals from the water. We focus on the different types of adsorption isotherms, namely, Langmuir isotherm, Freundlich isotherm, BET adsorption isotherm, and others for water purification. Adsorption kinetics studies are well illustrated with different models, namely, first-order, second-order, and third-order kinetics. The readers will be able to understand the basic mathematics concepts of kinetic models and further optimize these for the complex system. The required background is the basic knowledge of chemistry, biology, mathematics, and nanoscience at the first year level of the university. This book is divided into 16 chapters. Chapters "Introduction to Nanomaterials"–"Application and Research Progress of Nanomaterials as Adsorbents in Environment Field" explain the introduction to nanomaterials, carbon nanoadsorbent, their synthesis, and surface modification. Chapters "Adsorption Isotherms and Kinetic Models" and "Adsorption and Desorption of Adulterants in the Food Industry" explain the fundamental adsorption isotherm, kinetic models, thermodynamic parameters, adsorption mechanism, and experimental adsorption techniques. Chapters "Adsorption and Desorption of Micropollutants"–"Purification of Water Using Carbon Nanomaterials" describe the adsorption and desorption of aromatic compounds, pesticides, heavy metal, micro-pollutants, food adulterant, oil particles, and dye molecules. The last two chapters deal with the theoretical modeling of carbon nanomaterials for the adsorption studies.

Madurai, India J. Tharini
Kottayam, India Sabu Thomas

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First we thank the almighty for giving this wonderful opportunity to complete this book. We express our sincere thanks for family members and friends for their support and cooperation. We thank all the authors for their wonderful contributions towards the publication of the book. We are very much indebted to all the review experts who have made very critical comments for each chapter. We express our sincere thanks to the publishers for their patience. We express our deep sense of gratitude to our co-workers and assistants. We are indebted to our mentor Dr. R. Saraswathi, Retd. Professor, Department of Materials Science, School of Chemistry, Madurai Kamaraj University for her inspiration and support.

Contents

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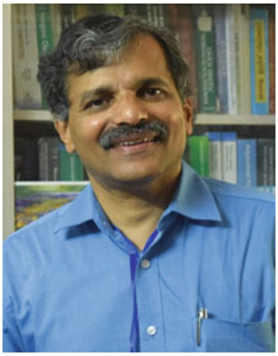

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1400 research articles in international refereed journals and has also edited and written 210 books. His H-index is 137 and total citations are more than 89,000. He has supervised 125 Ph.D. theses. He has received many international and national awards and recognitions. Under the leadership of Prof. Thomas, Mahatma Gandhi University has been transformed into a top university in India.

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Abbreviations

β-CD	β-Cyclodextrin
ADM	Adomian Decomposition Method
AFM	Atomic Force Microscope
ANN	Artificial Neural Network
AOP	Advanced Oxidation Process
ARB	Accumulative Roll Bonding
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
CN	Carbon Nanoparticles
CNs	Carbon-based Nanoadsorbents
CNTs	Carbon Nanotubes
CQDs	Carbon Quantum Dots
CVD	Chemical Vapor Deposition
DEO	Differential Evolution Optimization
DND	Detonation Nanodiamond
DWCNTs	Double-Walled Carbon Nanotubes
ECAP	Equal Channel Angular Pressing
ED	Electrodialysis
FETs	Field Effect Transistors
G-C_3N_4	Graphitic-Carbon Nitride
GA	Genetic Algorithm
GF	Graphite Flakes
GO	Graphene Oxide
GW	Graphene Wool
HPHT	High-Pressure High-Temperature
HPT	High-Pressure Torsion
LUMO	Lowest Unoccupied Molecular Orbital
MAHs	Monocyclic Aromatic Hydrocarbons
MO	Methyl Orange
MOFs	Metal–Organic Frameworks
MP	Micropollutant

MS	Mass Spectrometry
MSA	Moth Search Algorithm
MWCNT	Multiwalled Carbon Nanotubes
NDs	Nanodiamonds
NPs	Nanoparticles
NTCs	Nontubular Carbons
PAHs	Polycyclic Aromatic Hydrocarbons
PANI	Polyaniline
PET	Polyethylene Terephthalate
PPCPs	Pharmaceuticals and Personal Care Products
PS-MS	Paper Spray Mass Spectrometry
RGO	Reduced Graphene Oxide
RO	Reverse Osmosis
SEM	Scanning Electron Microscope
STM	Scanning Tunneling Microscope
SWCNT	Single-walled Carbon Nanotube
TCFs	Transparent Conductive Films
TEM	Tunneling Electron Microscope
TG	Thermogravimetric
TNT	Trinitrotoluene
VIM	Variational Iteration Technique
XRD	X-ray Diffraction

Introduction to Nanomaterials

K. K. Wang, P. V. Chai, and W. L. Ang

Abstract Nanomaterials have grown over the years globally associated to their advancement in the past decades and remarkable impact to the various applications. This chapter discussed the properties of the nanomaterials namely electrical, magnetic, mechanical, and antibacterial properties. Subsequently, the types of nanomaterials selected to be discussed in this book chapter are carbon, inorganic, organic, and composite based nanomaterials. The latter part of the book chapter shall focus on the classification of nanomaterials from zero dimensional to three dimensional and the synthesis of nanomaterials typically on bottom-up and top-downapproach.

Keywords Nanomaterials · Properties of nanomaterials · Classification of nanomaterials · Bottom-up and top-down approach

1 Introduction to Nanomaterials

The word nanomaterials can be separated into two different words which are nano and materials. The word nano in Greek means dwarf. In the current International System of Units, nano is described as a prefix whereby one nanometer equals to billionth of a meter (10^{-9}). Therefore, nanomaterials can be described as a class of materials that have singular or multiple dimensions in nanometric scale. The size of nanoparticles is set to be ranging from 1 to 100 nm.

The idea of nanotechnology is first inspired and proposed in the year of 1959 by the famous physicist Richard Feynman. During a talk with the title "There's

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Plenty of Room at the Bottom", Feynman sparked the possibilities of controlling and manipulating individual atoms or molecules. The idea came to fruition after the development of scanning tunneling microscope (STM). The STM technology allowed the researchers to catch sight of individual atoms.

1.1 Properties of Nanomaterials

Different nanomaterials exhibit different physicochemical properties. These properties have made the nanomaterials special in various applications. Examples of different properties are listed down such as electrical properties, magnetic properties, mechanical properties, and anti-bacterial properties.

1.1.1 Electrical Properties

Recently, polyaniline (PANI) based nanomaterials have attracted the interest of many researchers due to their good electrical properties despite their polymer nature. The PANI is also easy to produce and has high environmental stability [1]. The PANI is now very popular in the manufacture of various sensors, cells, and conductors [2–5]. For example, a study from Wen et al., 2018 found that the addition of 0.5 weight percentage of PANI into 60 weight percentage of silver-filled flexible conductors had greatly brought down the electrical resistivity by one-thirtieth of original. Besides, the addition of PANI had also increased the bending stability by a large margin [5]. Other than that, reduced graphene oxide (RGO) particles are also one of the nanomaterials that attract the attention of many researchers. For example, a study from Yang et al. (2017) showed that the 23 μm reduced graphene oxide with cellulose nanofiber film has an ultra-high electrical conductivity [6].

1.1.2 Magnetic Properties

Some of the nanomaterials exhibit strong magnetic properties. This unique property can allow various applications in the science and engineering industries. For example, iron oxide (Fe_2O_3) nanoparticles have been used as pollutants cleanup agent or biomedical materials due to their magnetic properties [7–9]. For example, iron oxide has been used for magnetic drug delivery in the human body [9]. On the other hand, iron oxide nanoparticles have also been used for the cleaning of marine oil spills. The cleaning of oil spills can be done using the iron oxide based nano adsorbent as the oil can be adsorbed onto the surface of the nano adsorbent. After that, the oil can be recollected using a magnet as the iron oxide based nano adsorbent has magnetic properties [7, 8]. Figure 1 shows the magnetic properties of Fe_2O_3 nanoparticles in oil remediation.

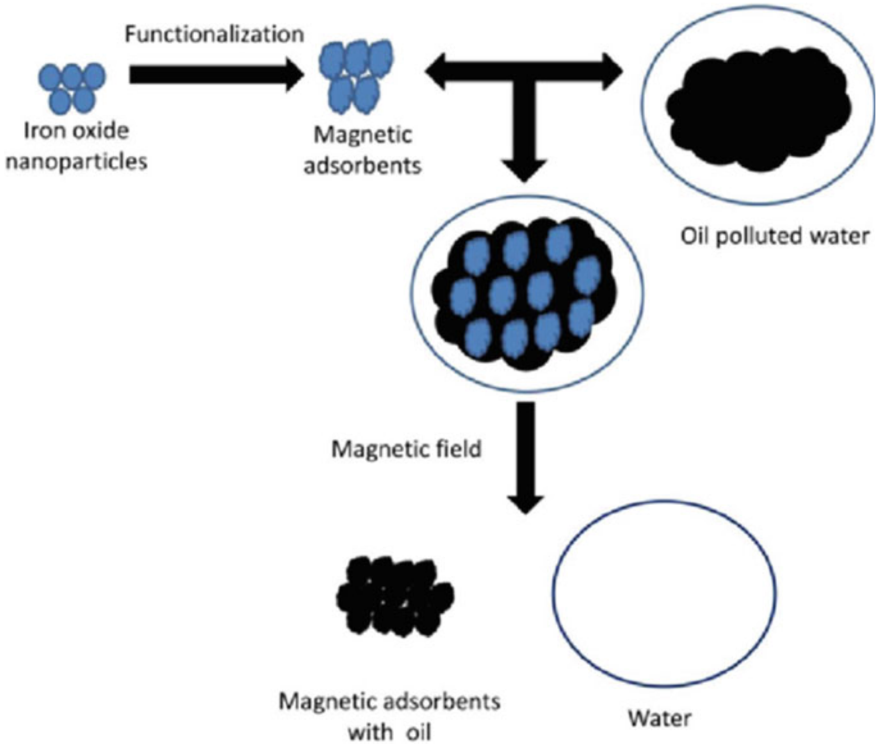


Fig. 1 Magnetic adsorbent for oil remediation [7]

1.1.3 Mechanical Properties

Carbon nanotubes (CNTs) are a type of nanomaterial that exhibits higher tensile strength than normal steel with lower density. Based on the study from Osmani et al. (2014), the tensile strength of multiwall CNT is 150.000 GPa compared to the 0.400 GPa from steel. For the density, the multiwall CNT is 2.600 g/cm^3 compared to the 7.800 g/cm^3 from steel. Lower density equals to lighter weight per unit volume [10]. This concludes that the CNTs are much stronger but lighter compared to conventional steel. Besides, the study from Hassan et al. (2022) also proved that the application of CNTs can improve the mechanical properties of concrete pavement. Based on the study, increasing weight percentage of CNTs can increase the compressive strength, tensile strength, and flexure strength of the concrete specimens after 28 days [11]. This shows that CNTs not only have high strength but are also able to increase the strength of other products such as nanofillers.

1.1.4 Anti-bacterial Properties

The anti-bacterial properties have been one of the most important properties after the COVID-19 outbreak. There are several types of nanomaterials that exhibit anti-bacterial properties. These include silver nanoparticles, and gold nanoparticles. Different kinds of nanoparticles have various possible actions towards the microbes [12]. For example, based on the study from Choi et al. (2008), the silver nanoparticles could destroy different species of Gram-positive and Gram-negative bacteria [13]. Besides, the anti-microbial properties of silver nanoparticles can also be found in medical industries as they can be found in silicone maxilla facial prostheses covered with silver nanoparticles due to the antifungal properties [14]. On the other hand, gold nanoparticles are also proven to have the anti-microbial ability. The study from Kumar et al. (2016) showed that the gold nanoparticles synthesized using auric chloride as precursor and sodium citrate as stabilizing agent are good inhibitors for the growth of water borne pathogens [15].

1.2 Types of Nanomaterials

In this section, all types of nanomaterials will be identified and introduced in detail. The nanomaterials can be listed into four types of nanomaterials namely carbon-based nanomaterials, inorganic-based nanomaterials, organic-based nanomaterials, and composite-based nanomaterials [16].

1.2.1 Carbon-Based Nanomaterials

Carbon is one of the most abundant elements on the Earth. Therefore, the attraction towards nano carbon studies has grown recently. Based on current research, carbon can be used in the production of engineering materials such as fullerenes, carbon nanotubes, and graphene [17]. Different engineering materials exhibit different strengths and applications. For example, fullerenes exhibit the lowest unoccupied molecular orbital (LUMO). This can cause the C_{60} fullerenes to reduce up to six electrons therefore stabilizes negative charges [18, 19]. Fullerenes are suitable to be used in manufacturing solar cells [18]. Figure 2 illustrates the structure of C_{60} fullerene.

Besides, the carbon nanotubes (CNTs), same as fullerenes, are formed by carbon only but have a cylindrical shape which is different compared to fullerenes. The CNTs have sparked research interests due to their high electrical conductivity, large surface area, light, and high mechanical strength characteristics. CNTs are very useful in manufacturing supercapacitors [20–22]. Furthermore, due to high mechanical strength, the CNTs can also be used in manufacturing aircraft fuselage and bullet proof vest [23, 24]. Figure 3 shows the structure of single-walled CNT.

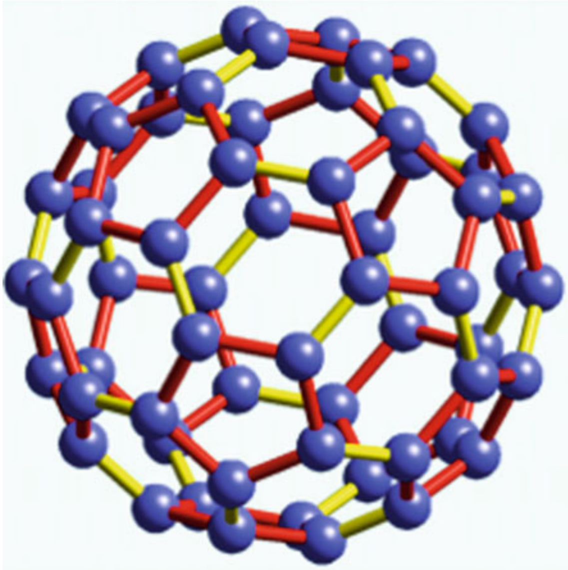


Fig. 2 Structure of C_{60} fullerene [17]

Fig. 3 Structure of single-walled CNT [25]

Graphene is arranged in two dimensions in hexagonal lattice structure formed by carbon atoms only. Like CNTs and fullerenes, graphene also exhibits high levels of electrical conductivity. It can be used in manufacturing lithium-ion batteries. Graphene can be used to tackle the issue of low power density of the current lithium-ion batteries [26]. Figure 4 shows the structure of graphene.

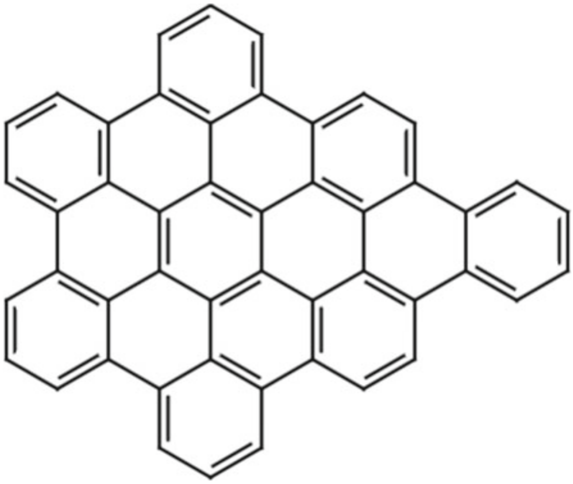


Fig. 4 Structure of graphene

1.2.2 Inorganic-Based Nanomaterials

Inorganic-based nanomaterials can be divided into two groups which are metal-based nanomaterials and metal oxide-based nanomaterials. Some examples of metal-based nanomaterials include silver, gold, and copper. On the other hand, some examples of metal oxide-based nanomaterials are copper oxide, iron oxide, and silicon dioxide. Each of them can be applied in different ways due to their unique properties. Back to Sect. 1.1, silver and gold nanoparticles can be used for antimicrobial purposes whereas iron oxide that has magnetic properties can be used as pollutants clean up agents [7, 8, 12].

1.2.3 Organic-Based Nanomaterials

Organic-based nanomaterials are the nanomaterials that are formed from organic materials excluding carbon materials. Examples of organic-based nanomaterials include dendrimers and micelle [16]. Dendrimers are synthetic polymers that are highly ordered with large number of repeating unit branches. The terminal functionalities on the surface can be anionic, neutral, or cationic [27]. Dendrimers such as glucose-modified carbosilane dendrimers can be utilized as drug delivery carriers for cancer therapy [28].

1.2.4 Composite-Based Nanomaterials

Composite-based nanomaterials are the nanomaterials that are formed from the combination of carbon-based with metal-based, metal oxide-based with organic-based, metal-based with organic-based and etcetera [16]. Nanocomposites have

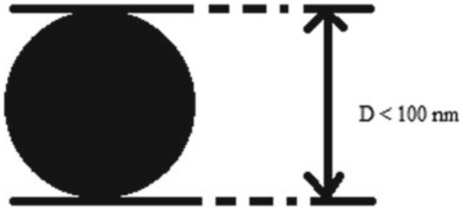


Fig. 5 Structure of nanosphere

attracted much attention as they can be employed in musculoskeletal engineering [29]. A study from Ahadian et al. (2014) utilized composites of carbon nanotubes (CNTs) with methacrylated gelatin polymer in fabricating muscle myofiber [30]. Besides, studies from Jayakumar et al. (2011) used nanocomposites of chitosan polymer coupled with TiO_2 nanoneedles or ZrO_2 in the fabrication of bone tissues [31, 32].

1.3 Classification of Nanomaterials

The nanomaterials can be categorized into several categories according to their different number of dimensions that are not in the nanometric scale which is less than 100 nm. The categories include zero-dimensional nanomaterials, one-dimensional nanomaterials, two-dimensional nanomaterials, and three-dimensional nanomaterials.

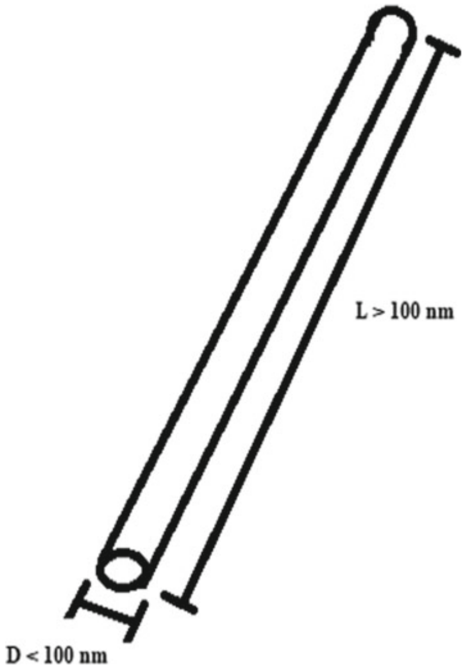
1.3.1 Zero-Dimensional Nanomaterials

The zero-dimensional nanomaterial is set to have all three dimensions including length, width, and height, within nanometric range (less than 100 nm). For example, quantum dots and nanospheres are categorized as zero-dimensional nanomaterials. Figure 5 shows an example of the structure and sizing of a nanosphere. The transmission electron microscopy (TEM) image of nanosphere can refer to the following journal [33].

1.3.2 One-Dimensional Nanomaterials

The one-dimensional nanomaterials are defined as the nanomaterials that have two dimensions in the nanometric scale whereas the other dimension is not in the nanometric scale. Examples of one-dimensional nanomaterials include nanotubes and nanowires. Figure 6 shows the structure of nanotubes and nanowires with given dimensions. Both the nanotubes and nanowires have lengths of more than 100 nm whereas the diameters are less than 100 nm.

Fig. 6 Structure of nanowires and nanotubes



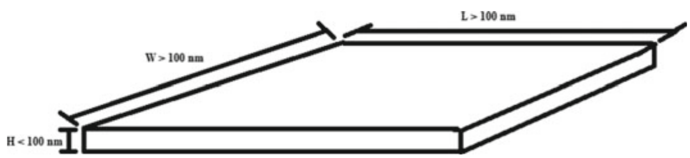


Fig. 7 Structure of nanofilm and nanoplate

1.3.3 Two-Dimensional Nanomaterials

The two-dimensional nanomaterials are a category of nanomaterials that has only one dimension in nanometric scale whereas the other two dimensions are not. The example of two-dimensional nanomaterials includes nanofilms and nanoplates. Figure 7 shows the structure of nanoplate and nanofilm with dimensions. It was seen that nanoplates have lengths and widths of more than 100 nm whereas the heights are less than 100 nm.

1.3.4 Three-Dimensional Nanomaterials

Three-dimensional nanomaterials are defined as a category of nanomaterials with no dimension either length, width, or height, is within the nanometric scale. Normally,

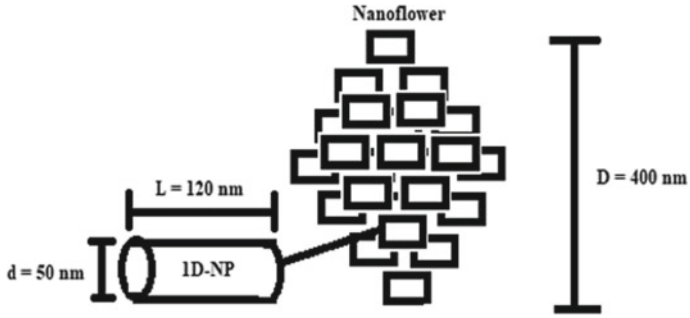


Fig. 8 Structure of nanoflower formed using one-dimensional nanotubes

this category of nanomaterial is assembled or built by zero-dimensional, one-dimensional, and two-dimensional nanomaterials. One of the examples of three-dimensional nanomaterials is nanoflowers. Figure 8 shows a drawn example of the structure of nanoflowers prepared from one-dimensional nanomaterials. From the image, it is noticeable that the nanoflower is formed from one-dimensional nanotubes with the diameters of each nanotube equal to 50 nm (less than 100 nm) and the length of each nanotube equal to 120 nm (more than 100 nm). Whereas for the whole nanoflower, all dimensions exceeded 100 nm which diameters equal to 400 nm.

1.4 Synthesis of Nanomaterials

There are two main approaches in synthesizing nanomaterials which are top-down approach and bottom-up approach. The concept behind the top-down approach is when a bulk material is broken down into smaller nano pieces. There are several methods that are under the top-down approach. These include mechanical alloying, equal channel angular pressing, high pressure torsion, and accumulative roll bonding. Besides, for bottom-up approach, the concept behind is when individual atoms are being brought together to form nanomaterials. The bottom-up approach starts building nanoparticles from either liquid or solid precursor. There are also several methods under the bottom-up approach which include co-precipitation method, sol–gel method, spray-conversion method, physical vapor deposition, and chemical vapor deposition.

1.4.1 Top-Down Method I (Mechanical Alloying)

Mechanical alloying or milling is the easiest method in producing nanomaterials. There are several types of milling methods in producing nanomaterials such as ball milling, vibratory milling, and planetary milling [34–36]. During the ball milling process, the bulk materials will be inserted into a hollow cylindrical chamber together with small balls made from zirconia, alumina, and steel. The chamber rotates horizontally, and the bulk materials will collide with the small balls using centrifugal forces. The figure of mechanical alloying of graphene can refer to the following journal [37].

1.4.2 Top-Down Method II (Equal Channel Angular Pressing)

Equal channel angular pressing (ECAP) is also a mechanical process in producing nanomaterials. During production, the nanomaterial samples are produced by pressing the needed materials through a die. When the pressing process starts, the sample passes through the die with shear deformation. The shear induces recrystallization to fine grain sizes [38]. The die contains two channels with an angle called die channel angle [39]. The pressing of the materials is done by a plunger as shown in the journal [38].

1.4.3 Top-Down Method III (High Pressure Torsion)

High pressure torsion (HPT), like ECAP, is also a severe plastic deformation method [40]. This method allows the generation of nanograins and ultrafine grains in metallic materials [41]. During the process, high pressure is exerted onto the materials by two plungers. One of the plungers is fixed and the other is rotating at a fixed speed. This exerts intense shear stress onto the material [42]. The working mechanism is demonstrated in the journal [42].

1.4.4 Top-Down Method IV (Accumulative Roll Bonding)

One of the newest severe plastic deformation methods is accumulative roll bonding (ARB). The ARB is a method to form ultrafine-grain structures in a single-phase metal [43]. The ARB process follows as a 4 mm thick sheet is rolled into 2 mm sheet with twice the original length. Then, the 2 mm sheet with twice the length is cut into two 2 mm sheets with original length. After that, the two 2 mm sheets are degreased and stacked together to make original thickness and length. Finally, the stack is then rolled again, and the cycle goes on. This method is able to allow large amount of plastic strain to the sheet without changing the dimensions. The tensile strengths can also be increased [44]. The figure of working mechanism of the ARB process can refer to the journal [45].

1.4.5 Bottom-Up Method I (Co-Precipitation Method)

Co-precipitation method is one of the easiest ways in synthesizing nanoparticles. This is done in several steps such as chemical precursor preparation, mixing of precursors, addition of precipitators (reducing agent), and purification of precipitated solids (nanoparticles) [46]. For example, the method from Massart utilized precursor's ferric chloride and ferrous chloride with the addition of ammonia solutions as precipitators, the iron nanoparticles can be obtained by centrifugation and decantation. A study from Sheng et al. (2012) also proved that the co-precipitation method can prepare Mn-Ce/TiO_2 nanocatalyst by following the similar steps [47]. The synthesis of α-Fe_2O_3 via the co-precipitation method can refer in the following journal [48].

1.4.6 Bottom-Up Method II (Sol–gel Method)

The Sol–gel method is slightly different compared to the co-precipitation method. In this method, the precursor used is molecular and usually is metal alkoxide. The precursor selected will then be dissolved in solvent of either water or alcohol followed by continuous heating and stirring to obtain gel. After that, the wet gel will further undergo drying process. Then, the final dried gel will be powdered and calcined [49]. Many researchers have been using the sol–gel methods in catalyst synthesis [50]. For example, a study from Singh et al. (2014) proved that the addition of solvent into silica source and further undergo hydrolysis, aging, and drying, the product of silica powder will be obtained as shown in the journal [51].

1.4.7 Bottom-Up Method III (Spray Conversion Method)

Spray conversion method, as known as spray pyrolysis, is a simple aerosol decomposition technique [52]. In this process, a selected precursor solution is prepared. The solution is then atomized into small droplets. These droplets are then moved towards the heated substrate surface and a thin film is generated [53]. For example, a study from Hong et al. (2008) synthesized nano sized Co_3O_4 powder by using spray conversion method. The experiment dissolved cobalt nitrate in distilled water and the solution was fed into a heated nozzle. The solution was spray dried in hot air of 250 °C [54]. The spray pyrolysis deposition is demonstrated in the following journal [52].

1.4.8 Bottom-Up Method IV (Physical Vapor Deposition)

Physical vapor deposition is a process whereby solid material is evaporated in a vacuum. This technique has been widely used in the coating industry due to the formation of thin layers of nanomaterials on a surface [55]. There are several types